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JIN, Jung Il, 1942-

COPOLYMERIZATION AND POLYMERIZATION KINETICS OF DIVINYLBENZENES.

The City University of New York, Ph.D., 1969
Chemistry, polymer

University Microfilms, Inc., Ann Arbor, Michigan

COPOLYMERIZATION AND POLYMERIZATION KINETICS OF DIVINYLBENZENES

by

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A dissertation submitted to the
Graduate Faculty in Chemistry in partial
fulfillment of the requirement for the
degree of Doctor of Philosophy,
The City University of New York.

1969

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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PREFACE

The research reported in this dissertation is divided into four closely related parts. They are :

- Part I. Copolymerization Kinetics
- Part II. Kinetics of Sulfonation of Polystyrene Crosslinked with Mixtures of Divinylbenzenes
- Part III. Polymerization Kinetics of Pure m- and p-Divinylbenzene
- Part Iv. Computer Calculation of Monomer Reactivity Ratios

Each part except Part IV contains : Introduction, Historical, Expermental, Results and Discussion, and Summary. Bibliography is given at the end of each part.

I wish to express my sincere gratitude for the guidance and help of Professor Richard H. Wiley and other members of the faculty of the Department of Chemistry of the City University of New York. I also wish to thank my parents and my wife for their support and encouragement they gave me while I was pursuing this research.

I gratefully acknowledge my indebtedness to the U. S. Atomic Energy Commission and the IBM Corporation for support of this study through Graduate Research Assistantships.

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PART I

COPOLYMERIZATION KINETICS

Introduction

Using the copolymer composition equation one can determine the two constants defined as monomer reactivity rations. Each of these constants represents the ratio of the rate constants for reactions of one type radical with its own monomer to that with the other monomer. These constants provide some insight as to the nature of the chain propagating steps of copolymerization reactions, the mechanisms involved and the copolymer composition.

Since the copolymer composition equation was developed, monomer reactivity ratios for many pairs of monomers have been determined. However, for a number of monomer pairs it has been impossible to determine the monomer reactivity ratios to the desired degree of accuracy, because there are no methods available for accurate determination of the composition of the copolymer. There are many instances when considerable variation of reactivity ratios for a particular monomer pair is obtained by different workers by ordinary analytical methods such as infrared absorption spectra, ultra violet absorption spectra, elemental analysis, and characteristic group analysis. The utilization of C^{14}-labeled monomers has proven to be of great value in determination of the copolymer composition. This method offers a means for the analysis, in principle, of any monomer pair, one of which is labeled. A convenient procedure of such an analysis has been developed using a vibrating reed electrometer and ionization chamber assay.[1,2]

The purpose of this work is to evaluate the monomer reactivity ratios for 1) the copolymerizations of methyl methacrylate with pure meta- and pure para-divinylbenzene, and 2) the copolymerizations of para-isopropylstyrene with styrene and methyl methacrylate to provide a further understanding of the nature of copolymerization characteristics of divinylbenzene isomers. Labeled monomers (methyl-C^{14} methacrylate and styrene-B-C^{14}) were used and the copolymer compositions were determined by means of their labeled monomer contents using a vibrating reed electrometer and an ionization chamber. This research also provides an additional insight into the nature of the structure of polystyrene crosslinked through copolymerization with divinylbenzene isomers.

Historical

In this section the previous research on copolymerization kinetics is reviewed briefly to provide the background for the experimental studies and discussions that follow. The topics covered, which are treated in more detail in many treatises on polymer chemistry, are: the derivation of the coplymer composition equation, the experimental evaluation of the equation, the application of the equation to the divinylbenzene system, the use of labeled monomers, the significance of the magnititude of the r_1 and r_2 values, the Q and e system, application of molecular orbital theory, application of the Hammett equation, and the statistical distribution of a monomer unit in coplymer chain.

Monomers such as styrene are converted to polymer of high molecular weight by either a free radical or an ionic mechanism (which can be either cationic or anionic). These processes exhibit the characteristics of typical chain reactions. In this thesis we shall be concerned chiefly with copolymerization by the free radical mechanism.

Free radical addition polymerization, which can be initiated by light, heat, or peroxide, is considered to proceed at least by three basic steps: initiation (introduction of one or more free radicals into the system), propagation (attack of a free radical upon the double bond of a monomer), and termination (destruction of the terminal radical on a growing chain). Each of these steps will be described somewhat in detail in the Part III "Polymerization Kinetics of pure meta- and para-Divinylbenzene."

When two different polymerizable monomers are mixed in the presence of an initiator the resulting macromolecules in general contain monomer units of both types of monomers, since the growing chain radicals can be attacked by either type of monomer. Such a reaction is called copolymerization, and the resulting polymer is a copolymer.

Bayer[3] purposedly carried out the first copolymerization of isoprene with butadiene around 1911. For a number of years the study of copolymerization kinetics lagged behind that of the properties of copolymers.

A. Copolymer Composition Equation.

In 1936 Dostal[4] made the first attempt to investigate the mechanism of copolymerization under the assumption that the rate of addition of monomer to a growing chain free radical depends only on the nature of the terminal group on the radical chain and is independent of the length or overall composition of the polymer chain. However, Dostal made no attempt to test his assumption experimentally.

After several unsuccessful approaches, the first trial to treat copolymerization kinetics in a systematic way was made by Wall[5] in 1941. Wall made an important advance by suggesting that the relative rates of addition of monomers to growing chain free radicals might be dependent only on the nature of the monomers being added and on their relative concentrations. These assumptions led him to the following equation:

$$\frac{m_1}{m_2} = \frac{k_1}{k_2}\,\frac{M_1}{M_2} \qquad (1)$$

where M_1/M_2 is the ratio of the concentration of the two monomers in the feed, m_1/m_2 is the ratio of the concentrations of the added monomers in the resulting copolymer, and k_1/k_2 is the relative rate of addition of the two individual monomers M_1 and M_2 to the growing chain radical. This simple equation is found to hold for many free radical copolymerizations and for most ionic copolymerizations even to the present day. The above equation says that chain endings have no effect on the rate of addition of the two monomers.

However, it was soon discovered that this simple equation did not apply to a number of copolymerization systems.

Almost simultaneously Mayo and Lewis[6], Alfrey and Goldfinger[7], and Wall[8] independently derived copolymerization equations that took into account the effects of the last added unit on the rates of addition of the two individual monomers, and assumed that the steady state applied to each radical type separately. The four simultaneous, competing chain propagation reactions in binary copolymerization are:

$$-M_1\cdot + M_1 \xrightarrow{k_{11}} -M_1\cdot \qquad (2)$$

$$-M_1\cdot + M_2 \xrightarrow{k_{12}} -M_2\cdot \qquad (3)$$

$$-M_2\cdot + M_1 \xrightarrow{k_{21}} -M_1\cdot \qquad (4)$$

$$-M_2\cdot + M_2 \xrightarrow{k_{22}} -M_2\cdot \qquad (5)$$

where $-M_1\cdot$ and $-M_2\cdot$ represent chains ending in monomer unit M_1 and M_2 respectively. The k's are the characteristic propagation rate constants for each of these propagation reactions. Accordingly, the rates of disappearance of M_1 and M_2 by incorporation in the copolymers are given by:

$$-\ d(M_1)/dt = k_{11}\ (M_1\cdot)\ (M_1) + k_{21}\ (M_2\cdot)\ (M_1) \qquad (6)$$

$$-\ d(M_2)/dt = k_{22}\ (M_2\cdot)\ (M_2) + k_{12}\ (M_1\cdot)\ (M_2) \qquad (6')$$

Also, since we are dealing with radicals as low-concentration intermediates, and since chains are long so that the major path by which radicals $M_1\cdot$ and $M_2\cdot$ are formed and destroyed is by interconversion of one into the other, we may write the steady-state expression

$$d(M_1\cdot)/dt = d(M_2\cdot)/dt = k_{21}(M_2\cdot)\ (M_1) - k_{12}(M_1\cdot)\ (M_2) = 0 \qquad (7)$$

By defining $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$, and combining Eqs. (6), (6'), and (7), it can be shown that the composition of the copolymer being formed at any instant is given by

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{(M_2)} \cdot \frac{r_1(M_1) + (M_2)}{(M_1) + r_2(M_2)} \qquad (8)$$

Equation (8) relates the composition of the copolymer being formed at any instant to the monomer concentrations (M_1) and (M_2) in the feed by means of two parameters r_1 and r_2. Here r_1 and r_2 are the monomer reactivity ratios characteristic of the particular monomer pair. The ratio of the rates of addition of the two monomers is also the ratio of the molar concentrations of the two monomers in the resulting copolymer. If we denote this ration by m_1/m_2, we may now rewrite the above differential form of the copolymer composition equation in the form:

$$\frac{m_1}{m_2} = \frac{(M_1)}{(M_2)} \cdot \frac{r_1 \ (M_1) + (M_2)}{r_2 \ \ (M_2) + (M_1)} \qquad (9)$$

It must be emphasized that this form of the equation is valid only for the composition of the initial copolymer formed at monomer concentrations (M_1) and (M_2). However, Eq. (8) in the differential form is valid at any conversion for relating the instantaneously forming copolymer with the instantaneous monomer composition.

The relative reactivity ratios, r_1 and r_2, which appear in Eq. (9) can be computed from the composition of the copolymer formed in a series of mixtures containing different percentages of the two monomers when the per cent of the monomer polymerized (yield or conversion) is kept low, eg., less than 10 per cent. At this low conversion, when the reactivities of the two monomers are not vastly different, the concentrations of the monomers in the polymerizing mixture are substantially constant, and may be assumed to be equal to the initial concentrations. The composition of the polymers must be measured accurately to obtain reliable values of r_1 and r_2 — poor analytical data account for many of the inconsistencies in reported r-values.

B. Experimental Evaluation of the Monomer Reactivity Ratios.

There are several different methods for computing the values of r_1 and r_2. Equation (9) can be rewritten as:

$$r_2 = \frac{(M_1)}{(M_2)} \left[\frac{m_2}{m_1} \left(1 + r_1 \frac{(M_1)}{(M_2)} \right) - 1 \right] \qquad (10)$$

This equation shows r_2 as a linear function of r_1 and each experiment with a given feed gives a straight line; the intersection of several of these allows the evaluation of r_1 and r_2. Figure 1 gives a typical plot for such a determination for the copolymerization of styrene and methyl methacrylate[10]. If experimental errors are high, the lines may not intersect in a single point: the region within which the intersection occur gives information about the precision of the experimental results.

Another method was developed by Fineman and Ross[9]. Substituting F for $(M_1)/(M_2)$ and f for m_1/m_2 into Eq. (9) gives the following results:

$$f = F \frac{r_1 F + 1}{F + r_2} \qquad (11)$$

The equation is then rearranged to give:

$$(f - 1)/F = r_1 - r_2 \, (f/F^2) \qquad (12)$$

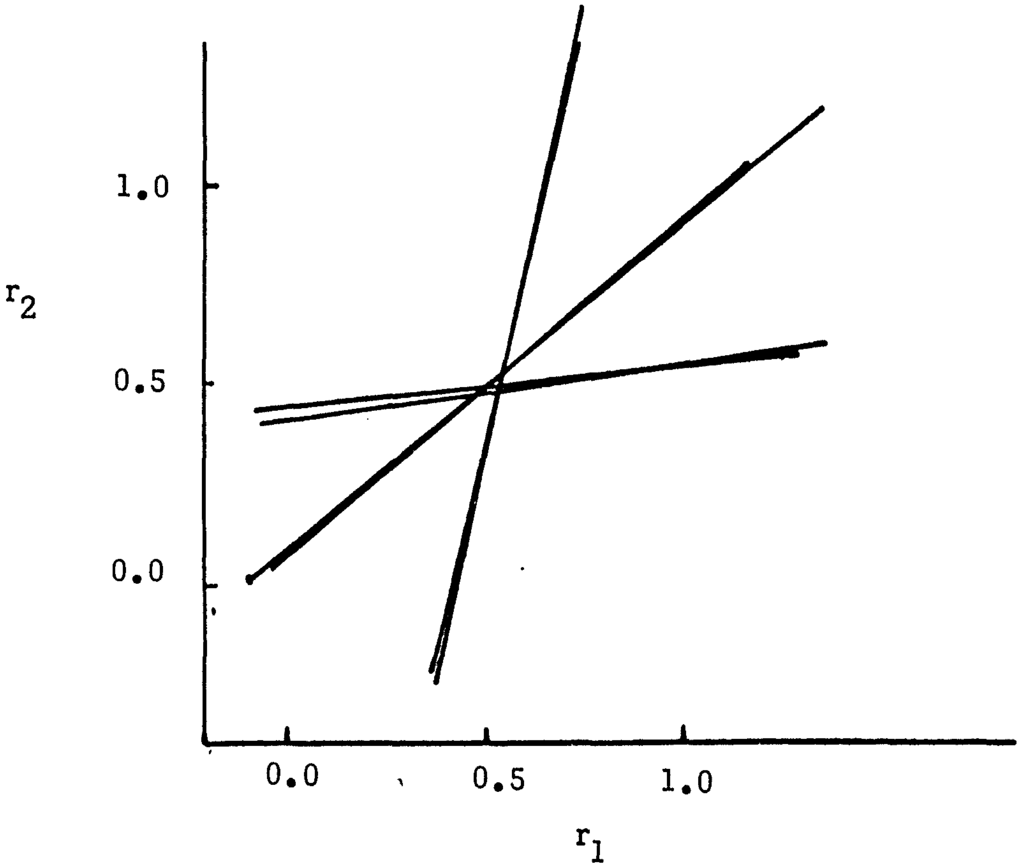

Figure 1. Intersect Plot for Copolymerization of Styrene ($r_1=0.53$) and Methyl Methacrylate ($r_2 = 0.49$) at 60°C.

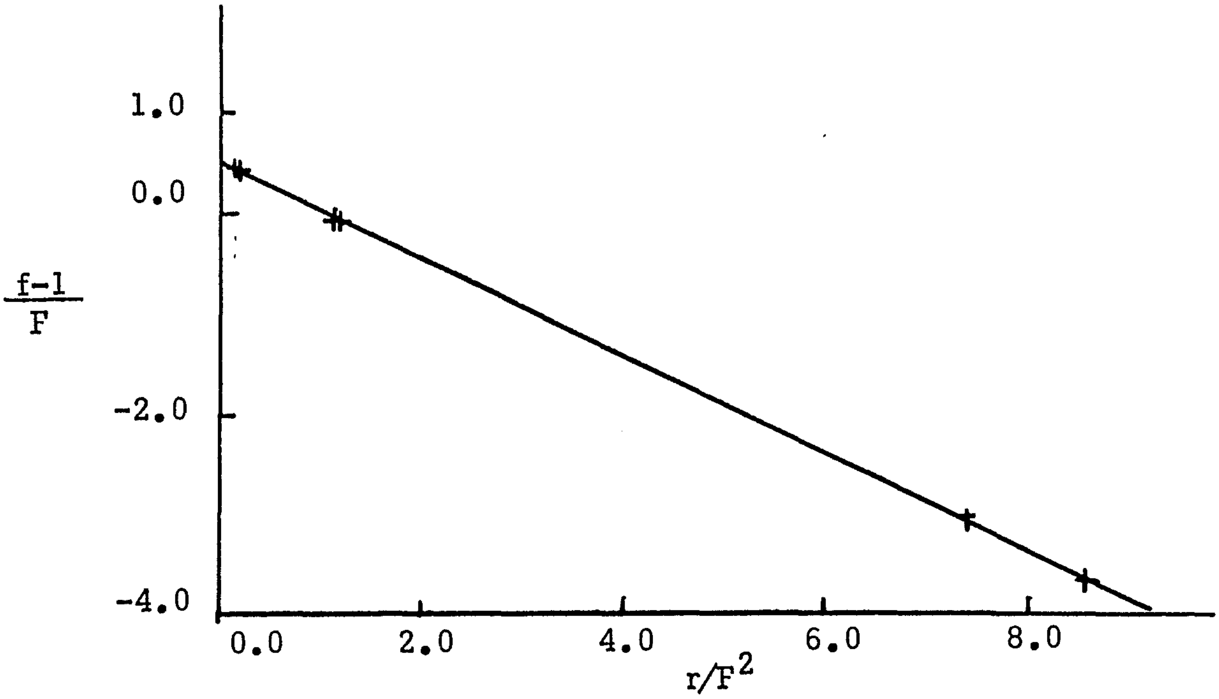

Figure 2. Fineman-Ross Plot for Copolymerization of Styrene ($r_1 =0.52$) and Methyl Methacrylate ($r_2 =0.49$) at 60°C.

Equation (12) states that a plot of $(f - 1)/F$ against f/F^2 is linear, and that the slope of the plot equals $-r_2$ and the intercept equals r_1. A least squares analysis can be carried out to determine the line of the best fit through the experimental points. The use of Eq. (12) to calculate the relative reactivity ratios is illustrated in Figure 2 for the copolymerization of styrene and methyl methylacrylate.[10]

A third method of analyzing the data is the direct curve fitting on polymer-monomer composition plots. This is a less precise method, since the composition curve is rather insensitive to small changes in r_1 and r_2.

If the conversions are so high that an appreciable drift in monomer concentration occurs, corrections have to be made. One way of doing this is as follows. The chemical analysis of the copolymer gives the average composition, rather than the composition of the initial copolymer. This average copolymer composition is now plotted against the average monomer composition during the reaction, rather than against the initial monomer composition. This correction appears to be fairly satisfactory for small drifts in composition, but certainly can not account for large drifts. A more elaborate method has been developed by Mayo and Lewis.[6] They obtained the following integrated copolymer composition equation:

$$r_2 = \frac{\log \dfrac{M_2^o}{M_2} - \dfrac{1}{P} \log \dfrac{1 - P \dfrac{M_1}{M_2}}{1 - P \dfrac{M_1^o}{M_2^o}}}{\log \dfrac{M_1^o}{M_1} + \log \dfrac{1 - P \dfrac{M_1}{M_2}}{1 - P \dfrac{M_1^o}{M_2^o}}}$$

where $P = (1 - r_1)/(1 - r_2)$, M_1^o and M_2^o are the initial molar concentrations of the two monomers, and M_1 and M_2 are their concentrations at the time when copolymerization is stopped and the sample is withdrawn. The r_1 and r_2 can then be evaluated graphically or through use of a computer[11] from composition-conversion data. However, if it is desired to calculate the change in copolymer composition with conversion for a system in which r_1 and r_2 are known, the most convenient method is a numerical or graphical one developed by Skeist.[12]

$$\ln \frac{(M_1) + (M_2)}{(M_1^o) + (M_2^o)} = \int_{M_1^o}^{M_1} \frac{dM_1}{x_1 - M_1}$$

In this equation x_1 represents the instantaneous mole fraction of monomer M_1 in the copolymer which is formed when the mole fraction of monomer one is M_1 (monomer one, M_1, is assumed to be the more reactive of the two monomers.). The ratio, $((M_1) + (M_2))/((M_1^o) + (M_2^o))$, is the ratio of the total number of moles of mixed monomers, which remain unreacted to the total number of moles of mixed monomers which were present initially. The symbol (M) refers to number of moles and the symbol M refers to mole fraction.

Copolymerization equations for systems of more than two monomers have been derived,[13] and several experimental studies of copolymerizations involving three monomers[14] have been reported. Six reactivity ratios are required for treatment of the composition in a three component systems.

C. Application of the Copolymer Composition Equation to Divinyl Systems.

Up to now the discussion has been only about monomers containing one vinyl group or those unsaturated compounds which generally react to add only one monomer. The copolymer equation was revised by Alfrey and coworkers[15] for the vinyl-divinyl copolymerization, in which one of the monomers is a symmetrical divinyl compound. The equation is:

$$\frac{d(M_1)}{d(M_2)} = \frac{(M_1)}{2(M_2)} \cdot \frac{r_1\,(M_1) + 2(M_2)}{2r_2\,(M_2) + (M_1)} \qquad (13)$$

where (M_1) and (M_2) represent the molar concentrations of the monovinyl and divinyl compound in the feed, and $d(M_1)$ and $d(M_2)$ the molar concentrations of the monovinyl and divinyl monomer respectively in the instantaneous copolymer. At low conversion the above equation can be rewritten as follows:

$$\frac{m_1}{m_2} = \frac{(M_1)}{2(M_2)} \cdot \frac{r_1\ (M_1)\ +\ 2(M_2)}{2r_2\ (M_2) + (M_1)} \qquad (14)$$

or

$$r_2 = \frac{(M_1)}{2(M_2)} \left\{ \frac{m_2}{m_1} \left(1 + r_1 \cdot \frac{(M_1)}{2(M_2)} \right) - 1 \right\} \qquad (15)$$

In the use of this equation there was a question as to whether the proper value to be used for m_2 is one-half that of the analytically determined per cent of divinyl monomer in the copolymer, as previously suggested by Alfrey et al.,[15] or the whole value.

Wiley and coworkers[16, 17, 18] have determined the reactivity ratios of the three divinylbenzene isomers and ethylene glycol dimethacrylate copolymerized with styrene using equation (15). They concluded that the above equation could be used to evaluate the monomer reactivity ratios of independent symmetrical divinyl monomers only when the mole percent of divinyl monomer in the copolymer was used for m_2, but not $m_2/2$. However, they always lacked a definitive solution of the copolymerization equation for the styrene-para-divinybenzene system.

The experimental techniques used in the determination of reactivity ratios in peroxide initiated copolymerization are usually relatively simple. The method used in the present work, for all of the monomer pairs, consist of sealing weighed amounts of the two monomers in an evacuated tube with the desired amount of benzoyl peroxide. The polymerizations are carried out in a constant-temperature bath and the reactions are stopped before 10 per cent conversion is reached. The copolymer is isolated from the reaction mixture by precipitation of the polymers with a nonsolvent. The polymers are redissolved or swollen in a proper solvent and reprecipitated with a nonsolvent. This procedure is repeated several times until the polymer is free from monomers, and then the polymer is dried in a vacuum oven. A freeze-drying technique can be used to isolate the polymer in a dried form. By weighing the dried polymer, the yield is obtained. The compositions of copolymers are then analyzed chemically or physically, and the r_1 and r_2 values are computed.

The composition of copolymer has been determined by standard elementary analysis,[19, 20] characteristic group analysis, refractive index measurement,[21] U.V. absorption spectra,[22] and I.R. absorption spectra.[23] The above mentioned analystical methods are not sufficiently accurate to provide reactivity ratios of the degree of reliability that might be desired in many cases. Pairs of isomeric monomers such as m- and p- chlorobenzene or methyl crotonate and methyl methacrylate give copolymers which show no variation in elemental composition with change in monomer ratio. The nitrogen content of polyacrylonitrile[15] is consistently found to be lower than expected and corrections have to be made. Gilbert and Williams[24] reported that I.R. analysis of isoprene—butadiene copolymers was not satisfactory where the concentration of isoprene was more than 50 per cent.

D. Use of Labeled Monomers.

A possible solution to this problem is the utilization of labeled monomers for determination of the copolymer composition. The most useful procedures for the determination of the radioactivity of polymer samples prepared from labeled monomers are probably those based on combustion of the polymer to carbon dioxide, which is collected in an ionization chamber, and assayed in a vibrating reed electrometer.[10] The combustion technique offers advantages in rapidity and precision in the assay but involves destruction of the sample and requires quantitative combustion of the polymer.

E. Significance of the Values of r_1 and r_2.

Since the rate constants for initiation and termination do not appear in the copolymer composition equation, the composition of the copolymer is independent of over-all reaction rate and initiator concentration. Moreover, the reactivity ratios are unaffected in most cases by the presence of inhibitors, chain transfer agents, or solvent. Even in heterogeneous systems they remain unchanged unless the availability of the monomers is altered by their distribution between phases. A change from a free radical to an ionic mechanism, however, changes r_1 and r_2 remarkedly. When the values of r_1 and r_2 are available, it enables us to look into the relative reactivity of the radicals--usually the order of reactivity of the radicals is the reverse of that for the monomers, hence the nature of the propagation step and the structure of the copolymer.

Wall[8] paid attention to the close analogy between the copolymer-monomer mixture composition relationships and vapor-liquid equilibria in binary systems. He introduced the term ideal copolymerization for the case $r_1.r_2 = 1$, in recognition of the analogy to vapor-liquid equilibria for ideal liquid mixtures. When $r_1 > 1$, the polymer is richer in M_1 than in the monomer feed. For $r_1 < 1$, the opposite holds. It is also apparent that the end group on the growing chain has no influence on the rate of addition, and the two types of units are arranged at random along the chain in relative amounts determined by the composition of the feed and the relative reactivities of the two monomers. The copolymer equation reduces to $dM_1/dM_2 = r_1.M_1/M_2$.

If $r_1r_2 > 1$, the tendency for radicals of a given kind to regenerate themselves by the addition of a like unit exceeds their tendency for alternation. Such a copolymer would contain sequences of like units in greater abundance than in a random copolymer of the same composition, and this tendency favoring sequences should be greater the larger the product r_1r_2. Wiley and coworkers[18] found that the r_1r_2 product is greater than 1 in styrene-para-divinyl-benzene copolymerization and rationalized it in terms of block-polymerization. If $r_1 = r_2 = 0$, each radical prefers to react exclusively with the other monomer and the monomers alternate regularly along the chain regardless of the composition of the monomer feed. The copolymer equation simplifies to $dM_1/dM_2 = 1$. The last possibility, with both r_1 and r_2 greater than unity, would exist if each radical preferred to add its own monomer: in the extreme, the two monomers would simultaneously homopolymerize. Very few cases are known so far. Most observed copolymerizations lie between the ideal and the alternating systems, i.e., $0 < r_1 r_2 < 1$. There is at best but few established instances of free radical polymerization in which the product $r_1 r_2$ is significantly greater than unity.

F. The Q and e Scheme.

Mayo and Walling[25] suggested the existence of a semiquantitative relationship between alternation and the polar properties of the monomers involved. The manner in which such polar effects bring about changes in the rates of radical addition reactions has received a good deal of discussion which parallels closely similar consideration of the detailed mechanism by which electron supply and withdrawal influences the rates of strictly polar reactions.

In addition to such polar effects, it has been suggested[19] that, at least in strongly alternating systems, the energy of the transition state may be lowered by the participation of resonance structures in which electron transfer has occurred between radical and olefin. In an attempt to explain the alternating copolymer of styrene and maleic anhydride Bartlett and Nozaki[26] analyzed a charge-transfer complex which, they claimed, was the reactive intermediate. This work was later supported by Barb.[27] Complexes of series of substituted styrenes and maleic anhydride, and their corresponding alternating copolymers were studied by Walling and his coworkers.[19] These researchers concluded that the complexes were determining the nature of the polymeric products of free-radical initiations. Recently, charge-transfer complexes in solutions of comonomers such as divinyl ether and maleic anhydride[28] have been identified by use of U.V. spectroscopy. Of course, steric effects also contribute to the tendency of some monomer to alternate.

An interesting quantitative attempt to relate the concepts of polar effects, together with that of over-all reactivity associated with resonance stabilization has been made by Alfrey and Price.[29] They expressed the rate constant for the reaction of a $M_1\cdot$ radical with M_2 monomer in the form:

$$k_{12} = P_1Q_2 \cdot \exp(-e_1e_2) \qquad (16)$$

where P_1 is the general reactivity of the radical $M_1\cdot$, Q_2 is a quantity related to the reactivity and the resonance stablization of the monomer M_2, and e_1 and e_2 are considered to be proportional to the residual electrostatic charges in the respective reacting groups and related to the charges on $M_1\cdot$ and M_2 respectively by the relation:

$$e_1 = C_1(rDkT)^{-1/2} \qquad (17)$$

where C_1 is the actual charge on $M_1\cdot$, r the separation of the charges in the activated complex, D the "effective" dielectric constant, k the Boltzmann constant, the T the absolute temperature. If it is further assumed that the same e_j applies both to the monomer M_j and to the radical $M_j\cdot$, the rate constant for the reaction of $M_1\cdot$ with M_1 becomes

$$k_{11} = P_1 Q_1 \cdot \exp(-e_1{}^2) \qquad (18)$$

From the definitions of the monomer reactivity ratios and Eqs. (16) and (18), it follows that

$$r_1 = (Q_1/Q_2) \exp \left\{-e_1(e_1-e_2)\right\} \qquad (19)$$

$$r_2 = (Q_2/Q_1) \exp \left\{-e_2(e_2-e_1)\right\} \qquad (20)$$

and

$$r_1 . r_2 = \exp \left\{-(e_1-e_2)^2\right\} \qquad (21)$$

Originally, Q and e were chosen for styrene as 1 and -1, respectively. Subsequently, Price has changed this base to 1.0 and -0.8 as giving a series of Q values for monomers in better accord with his experiments. Hence, assigning two parameters, a Q and an e, to each of a set of comonomers, it is possible to calculate reactivity ratios r_1 and r_2 for any pair. In consideration of the huge number of monomer pairs which may be selected from large number of monomers the advantages of such a scheme over copolymerization experiments on each pair are obvious.

However, the above derivation has been criticized on theoretical grounds. In the first place, there is no a priori justification for the assumption that the alternating effect arises solely from electrostatic interaction between fixed charges and for assuming equal charges for monomer and derived radical. If this is the case, the alternating effect should depend on the reaction medium, ie., on its dielectric constant. This has not been found to be the case.[25] The second is that Eqs. (19) and (20) do not uniquely define Q and e for any monomer. Rather, they must be arbitrarily chosen for one monomer and the remainder of the system built up on this base as mentioned before. Furthermore, the steric factors are not accommodated in the Q-e scheme.

G. Application of Molecular Orbital Theory.

More recently attempts have been made to formulate a rigorous theoretical basis for predicting monomer reactivity in copolymerization. Evans et al.[30] calculated the activation energies of the various radical-monomer addition reactions using Molecular Orbital Theory under the assumption that for a series of similar monomers the entropy of activation is approximately equal, and they concluded that high monomer reactivity correlates with a substantial gain in resonace stabilization upon addition of monomer to radical. Further they made the suggestion that the Q value of a monomer can be identified with the quantity exp $\{(R_A-R_M)/RT\}$, where R_M and R_A are the resonace energies of monomer and radical adduct, respectively. In another approach Hayashi et al.[31, 32] have calculated the pi conjucation energy in radical-monomer systems by using a LCAO molecular orbital technique and showed that the monomer reactivity ratios agreed well with reported values. The pi energies of several vinyl compounds have been determined by Fueno et al.,[33] and correlations were shown between the beta carbon localization energies and methyl affinities of vinyl compounds. These workers suggest that there is a relationship between P and Q and the localization energies of radical and monomer, and that the e_1e_2 product is probably related to the resonance stabilization energy in the transition state between monomer and radical adduct. Recently Levinson[34] has improved the approach of Hayashi, and included resonace and polar factors in his approach. He showed the parallelism between the e value and the electron affinity of a monomer and between the Q value and the localization energy. Even though the above calculation methods of monomer reactivity ratios give quite satisfactory results, it may be noted that these methods differ by a factor of 2 to 3.

H. Application of the Hammett Equation.

Hammett[35] found that, for many polar reactions, the ratio of the rate or equilibrium constant for a meta or para substituted benzene derivative to that of the unsubstituted derivative could be given as the product of two parameters, rho, which is specific for the reaction, and sigma, specific for the substituent, and this can be expressed as follows:

$$\log (K/K_0) = \rho\sigma \qquad (22)$$

In order to examine this relationship for a radical reaction, Walling, Mayo et al.[19] have studied a correlation between the σ- value of a substituted styrene and the reactivity with the styrene type of free radical. It was found that the plot of the logarithms of the relative reactivities against the Hammett σ- values for the particular substituents fitted to a straight line with an approximate slope of 0.51. However, styrenes with electron-supplying groups, especially para-dimethylamino and para-methoxy groups, showed abnormally enhanced reactivities and deviated considerably from the line. The same scheme was extended for the reactions of the substituted styrenes with the methyl methacrylate radical and the plots of log $(1/r_1)$ versus Hammett's σ-values fell on a reasonably good straight line (slope of 0.33) with the exception of para-methyl-, para-dimethylamino-, and para-methoxystyrene.

Recently Wiley et al.[36] redetermined the monomer reactivity ratios of the styrene-para-dimethylaminostyrene, styrene-para-methoxystyrene, styrene-meta-methylstyrene, and styrene-para-methylstyrene pairs using radioactivity assay for copolymer analysis. They found that a plot of log reactivity ratios against the sigma values for the ionization of substituted benzoic acid gives a plot with two linear regions of different slope. Below 0.0 sigma (electron donor substituents) the slope is zero. From this observation they concluded that electrostatic effects operate differently in determining the reactivity of styrene radicals with electron donor substituents than they do in determining the reactivity of styrene radicals with electron attracting substituents.

I. Statistical Distribution of a Monomer Unit in Copolymer.

Sakaguchi[37] has derived the following relationships for ascertaining the sequential distribution of syndiotactic and isotactic units in a polymer:

$$F_n = \frac{f_{iso}^{\,n}}{(1+r_1)^2}\left(\frac{r_1}{1+r_1}\right)^{n-1} \qquad (23)$$

$$G_m = f_{iso}\left(1+\frac{m-1}{1+r_1}\right)\left(\frac{r_1}{1+r_1}\right)^{m-1} \qquad (24)$$

where F_n is the fraction of polymer chains in blocks of isotactic units n long, f_{iso} is the total fraction of isotactic structure in the polymer. G_m is the fraction of polymer chains existing in blocks of isotactic units equal to m and longer than m, and r_1 is a pseudo-reactivity ratio for the isotactic units. A similar expression exists for syndiotactic units. By appropriate manipultation Eqs. (23) and (24) were altered by Berger[38] so as to apply for copolymers in general and thus be compatible with the copolymer equation.

$$(25) \qquad F_n = \frac{F_1 \cdot n}{\left\{1+(M_1/M_2)\,r_1\right\}^2}\left(\frac{(M_1/M_2)\;r_1}{1+(M_1/M_2)\,r_1}\right)^{n-1}$$

(26)

$$G_m = F_1 \left(1 + \frac{m - 1}{1 + (M_1/M_2)\ r_1}\right) \times \left(\frac{(M_1/M_2)\ r_1}{1 + (M_1/M_2)\ r_1}\right)^{n-1}$$

where M_1, and M_2 are mole or mole fractions of monomers in the feed and F_1 the mole fraction of M_1 in the growing chain or copolymer formed. F_n now means the fraction of polymer existing in blocks of monomer M_1 units n long. G_m is the fraction of polymer existing in M_1 units of m and longer. There are corresponding equations for M_2. Equation (25) tells us that if r_1 is constant, F_n is proportional to the mole fraction of monomer M_1 in the growing chain.

Wiley and coworkers have studied the polymerization and coplymerization characteristics of divinylbenzene isomers in some detail. For the ortho-divinylbenzene and styrene copolymerization system, noncrosslinked copolymers were obtained, based on their solubility.[17] They appeared to have approximately one double-bond per divinylbenzene unit, based on the infrared absorption characteristics. This particular behavior of ortho-divinylbenzene indicates that the two vinyl groups therein are nonplanar, as is consistent with NMR data[39] for the isomers, and that one of vinyl groups does not copolymerize. For the meta isomer copolymerization with styrene the monomer reactivity ratio values obtained at different conversion levels are different.[18] At low conversions r_1 (styrene) is lower than r_2 (meta-divinylbenzene); at high conversions r_2 is lower than r_1. The latter fact was rationalized by the increased participation of the second of the divinyl units in the high-conversion copolymer. In the para-divinylbenzene case, no well-defined monomer reactivity ratios could be obtained in its copolymerization with styrene, and the product of the best selected r_1 and r_2 values was greater than unity.[18, 40] They explained this fact in terms of block-polymerization tendencies, and this was proved by several other experiments, for example, rates studies of sulfonation of polystyrene crosslinked with meta- and para-divinylbenzenes,[41] pyrolytic degradation kinetic studies of copolymers of styrene with meta- and para-divinylbenzenes,[42] and mass spectroscopic characterization of the divinylbenzene-styrene copolymers.[43]

Experimental

Standard C^{14}-labeled Monomers

Methyl-C^{14} methacrylate was supplied by Tracerlab, Inc. with a specific activity of 0.34 millicurie/millimole. The sample contained 293.9 milligrams (0.314 ml.) with a total activity of 1.0 millicurie and was stabilized with hydroquinone. This sample was diluted with 450 volumes of freshly distilled unlabeled methyl methacrylate (Eastman Org. Chemicals), n_D^{20} 1.4135 (Literature value,[44] 1.4136), and was stored under nitrogen at -10°C with a small quantity of 2,6-di-tert-butyl-para-cresol as a stabilizer until used. This diluted sample was used for the copolymerizations with meta- and para-divinylbenzenes.

Dilutions were carried out under nitrogen atmosphere in a polyethylene bag and a well ventilated hood. The calculated amount of unlabeled methyl methacrylate (141 ml.) was added to a 500 ml. brown bottle, the sealed glass tube containing C^{14}-labeled methyl methacrylate was rinsed with unlabeled methyl methacrylate, and placed in the dilution bottle which was being flushed with nitrogen. A heavy glass rod, which was rinsed with unlabled methyl methacrylate, was introduced into the bottle touching the sealed tube. The rod was tapped gently with a hammer breaking the tube containing the C^{14}-labeled methyl methacrylate. The diluted methyl-C^{14} methacrylate, thus obtained, was stabilized with the cresol used before and the sample was stored under nitrogen atmosphere in a deep freeze at $-10^{o}C$. This diluted sample had a specific activity of about 7.6×10^{-1} microcurie per millimole. The second diluted labeled methyl methacrylate was obtained by diluting 54 ml. of the first diluted methyl-C^{14} methacrylate prepared above to 60 ml. with unlabeled methyl methacrylate to give about 6.84×10^{-1} microcurie per millimole and stored under the same condition as used for the first sample. This second sample was used for the copolymerizations of methyl methacrylate and para-isopropylstyrene. The prepared samples were allowed to set two or three days to reach equilibrium before using. All labeled monomers were kept under nitrogen atmosphere and their containers were opened only at room temperature.

Styrene-B-C^{14}, prepared and supplied by Tracerlab, Inc. with a specific activity of 0.17 millicuri/millimole, contained 612.7 mg. and had total activity of 1.0 millicurie. This sample was stabilized with picric acid. A quantity of unlabeled styrene supplied by Baker Chemical Co. was purified by vacuum distillation in which the middle fraction, n_D^{20} 1.5467 (Literature value,[45] 1.5465) was collected and used for the dilution of labeled monomer. Styrene-B-C^{14} (0.665 ml.) was diluted with 210 volumes (140 ml.) of freshly distilled unlabeled styrene. This diluted styrene-B-C^{14} had about the specific activity of 5.2×10^{-1} microcurie/millimole. This dilution was carried out in the same manner as with C^{14}-labeled methyl methacrylate and stored under the same condition used for diluted labeled methyl methacrylate. The sample was used for the copolymerizations of styrene and para-isopropylstyrene.

Divinylbenzenes

meta-Divinylbenzene was prepared and supplied by Centre de Recherches du Groupe Petrofina, Bruxelles with purity of 95+ % and was stabilized with 0.25 % tert-butylcatechol. The major impurity was found to be meta-ethylvinylbenzene by gas chromatographic analysis. This sample was purified using apreparative vapor fractometer (Perkin-Elmer Model 154) and Bentone* column. The composition of the column support and the preparation of the fractionation column were described in detail earlier,[46] and the exact same procedures were followed in this experiment. As a result of several preliminary experiments, it was decided to use a temperature of 150°C and a helium carrier gas pressure of 15 psi, as the retention time of meta-divinylbenzene seemed quite reasonable with good resolution between meta-divinylbenzene and the impurity (ethylvinylbenzene) peaks. Under these conditions 2 ml. of impure meta-divinylbenzene solution in benzene (2:3) was injected and the meta-divinylbenzene part was collected. The meta-divinylbenzene thus obtained was 99.5+% pure by gas chromatographic analysis using a Perkin-Elmer R column (polypropylene glycol on chromosorb-W) and flame ionization detector (Figure 3). The purity was calculated by taking a small shoulder at

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*An organo-clay whose composition is described as dimethyl dioctadecyl ammonium bentonite.

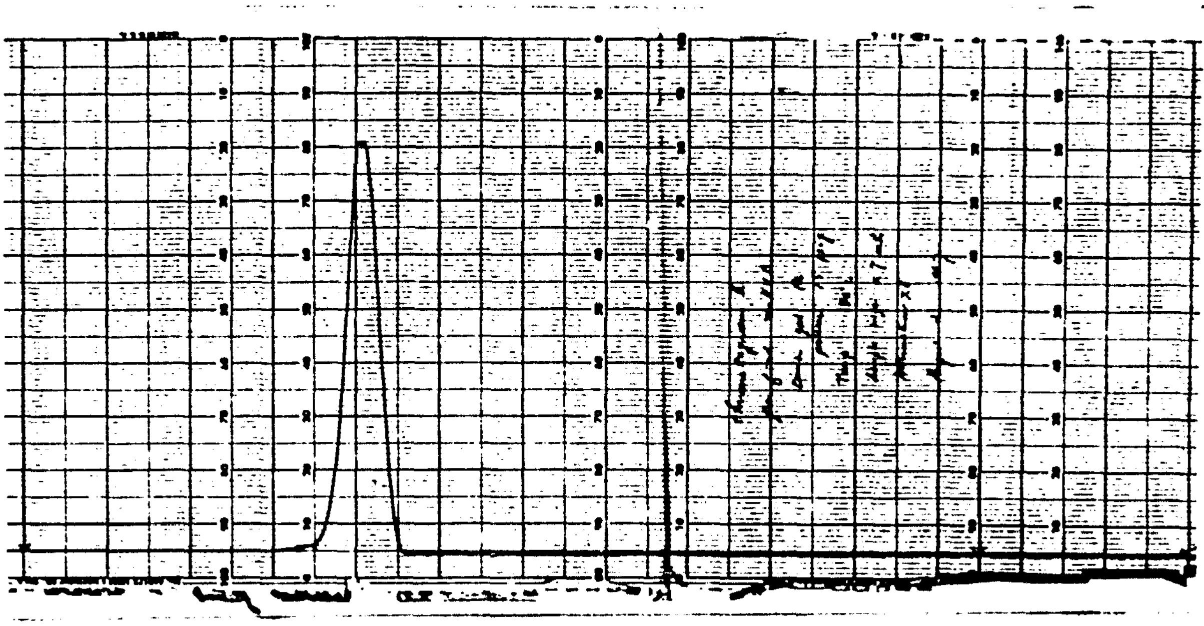


Figure 3. Gas - chromatographic Analysis of m-Divinylbenzene.

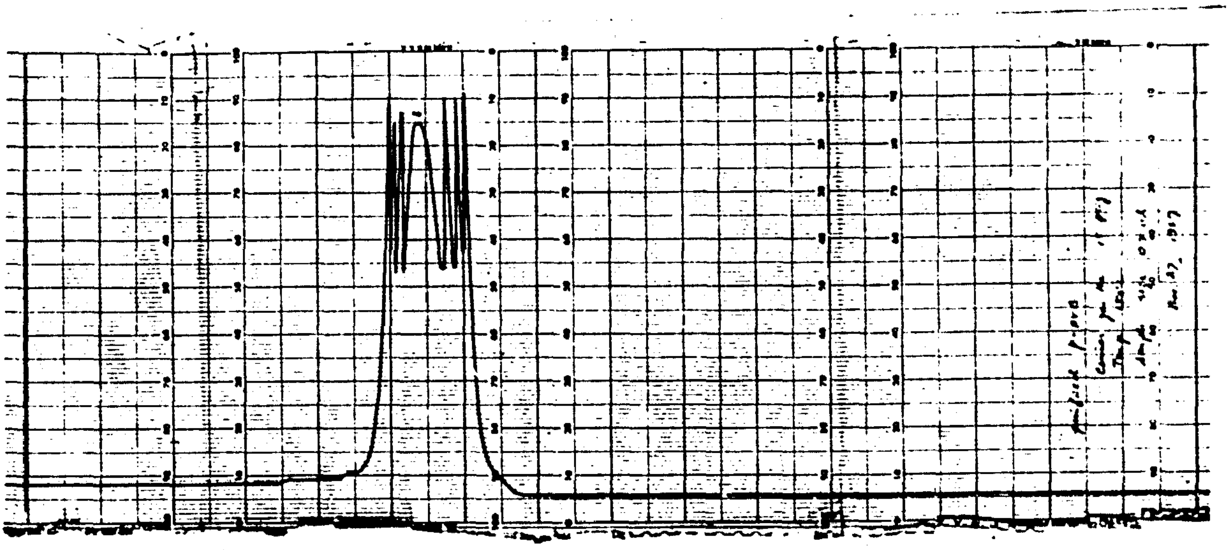


Figure 4. Gas-chromatographic Analysis of p-Divinylbenzene.

the tail part of m-divinylbenzene peak as that from a possible impurity (p-divinylbenzene). This material was stored under nitrogen at -10°C with a small quantity of the stabilizer 2,6-di-tert-butyl-para-cresol until used.

para-Divinylbenzene was supplied by Cosden Chemical Co. with the purity of about 92 %. This para-divinylbenzene was dissolved in equal part of benzene and 2 ml. of this solution was injected on the column. The above mentioned Bentone column and column temperature of 140°C and a helium carrier gas pressure of 5 psi were used. The purified sample had about 98.7 % of para-divinylbenzene by gas chromatographic analysis with flame ionization detector. The para-divinylbenzene thus obtained was dissolved in an equal amount of benzene and purified once more by the procedure mentioned above. The detailed procedures were described by Venkatachalam.[46] Gas chromatographic analysis showed that this sample was 99.5 + % pure by Perkin-Elmer R column and flame ionization detector (Figure 4). The purity of p-divinylbenzene was calculated by taking two small shoulders, one at the beginning of the p-divinylbenzene peak and the other at the tail part of the peak, as those from impurities. The per cent values were determined as fraction of the sum of the products of peak widths at half height times the peak heights.

para-Isopropylstyrene

para-Isopropylstyrene was synthesized by decarboxylation of para-isopropylcinnamic acid prepared from para-isopropylbenzaldehyde and malonic acid via the Doebner condensation reaction. The procedures are as follows:

1) Preparation of para-Isopropylcinnamic Acid; A mixture of 62.44 g. (0.6 mole) of malonic acid (Eastman Org. Chemicals), 74.1 g. (0.5 mole) or para-isopropylbenzaldehyde (Eastman Org. Chem.), 100 ml. of ethanol, and 12.5 ml. of pyridine (Fisher Scientific Co.) was heated on a steam-bath overnight. The pasty mass was broken up, and 200 ml. of 1 N hydrochloric acid was added. Mixing well, the precipitates were filtered off and washed with cold n-heptane.. The product obtained was recrystallized from ethanol. The yield was 49.3 g. (0.26 mole; 52%) and the melting point was 157.5 - 159°C (Literature value,[48] 157 - 159°). Neutralization equivalent of this acid was found to be 188.6 (calculated value for $C_{12}H_{14}O_2$ is 190).

2) Decarboxylation of para-Isopropylcinnamic Acid; Sixty-five grams (0.34 mole) of the above acid was dissolved in 220 ml. of quinoline (Baker Analyzed reagent) and 7 g. of copper acetate (Baker Analyzed reagent) was added. The solution was added dropwise to a 250 ml. three neck flask which contained 7 g. of purified copper powder (Baker Chemical Co.), 25 ml. of quinoline. The flask was fitted with a stirrer and a distillation assembly, and preheated to 270°C on the wood metal bath. A small quantity of inhibitor (2,6-di-tert-butyl-p-cresol) was added to the reaction flask and to the receiver.

The entire operation was carried out under a steady flow of nitrogen. After all the acid mixture was added, another 25 ml. of quinoline was added and the distillation was stopped. An equal volume of cold 20% sulfuric acid was added to the distillate, to which small pieces of ice had been added, and the mixture was shaken thoroughly. The upper layer containing para-isopropylstyrene was separated and washed twice with 3 N. sodium hydroxide and twice with distilled water. Additional product could be obtained from the quinoline layer by extracting with chloroform. The washed crude product was dried over sodium sulfate and was kept at - 10°C under nitrogen atmosphere. The dried para-isopropylstyrene was vacuum distilled under nitrogen. The vapor chromatographic analysis with Perkin-Elmer flame ionization detector and an R column showed the material to be 100% pure. The yield was 45.2 g. (0.31 mole: 91%, calculated as para-isopropylcinnamic acid).

Initiator

In all polymerizations and copolymerizations solid benzoyl peroxide was used as the initiator. Benzoyl peroxide supplied by Fisher Scientific Co. was purified by methanol precipitation from concentrated chloroform solution. It was very carefully dried under vacuum.

Preparation of Standard C^{14}-labeled Polymers

Standard polymethyl-C^{14} methacrylates were prepared in the same manner as will be described later in the next section, "Copolymer Preparation."

After distillation of 1.50602 g. of the first dilution of methyl-C^{14} methacrylate (specific activity of about 7.60×10^{-1} microcurie/millimole) into a reaction cell, 0.2 weight per cent of solid benzoyl peroxide was added. The cell was degassed, sealed under vacuum, and placed in a 70°C constant temperature bath for about 30 minutes. The polymer was purified four times as will be described later, freeze dried, and dried to a constant weight for 48 hours in a vacuum oven at 40°C and 1 mm. pressure. The polymer sample was removed from the oven for weighing after 24 hours and every 8 hours after. It was found that the weight recorded after 48 hours drying was the same that recorded after 32 and 40 hours within ± 0.00002g. This polymer was used as a standard for the analyses of the copolymers of methyl methacrylate and meta- and para-divinylbenzene.

The second polymethyl-C^{14} methacrylate standard, which was used as standard for the analyses of the methyl methacrylate-para-isopropylstyrene copolymers, was prepared by using 1.91245 g. of the second dilution of methyl-C^{14} methacrylate monomer and 0.1 per cent by weight of solid benzoyl peroxide. Polymerization was carried out at 70°C in constant temperature bath for 62 minutes. The purification and freeze drying procedures will be described later in the next section "Copolymer Preparation." The polymer was dried to a constant weight for 48 hours in a vacuum oven at 40°C and 1 mm. pressure.

Previously diluted styrene-B-C^{14} was vacuum distilled into a reaction cell by the procedure which will also be found in the next "Copolymer Preparation" section. Polymerization was carried out in a 70°C constant temperature bath for 64 minutes by using 1.38520 g. of diluted styrene-B-C^{14} and 0.1 per cent by weight of solid benzoyl peroxide as initiator. This polystyrene-B-C^{14} standard was used as a standard for the analyses of styrene-para-isopropylstyrene copolymers.

Copolymer Preparation

All work performed with the C^{14}-labeled monomers was carried out in a well-ventilated hood. The general procedures for copolymer preparations will be described; variations for certain copolymer preparations will be explained under the particular copolymer heading. A stainless steel tray, with 1.5 inches depth, 20.5 inches width, and 32.5 inches length, was covered with thin aluminum foil and used to work on. The covered tray was lined with blotting paper. The paper and the aluminum foil were replaced frequently. Handling, cleaning of contaminated glassware, and disposal of waste were carried out according to the directions given by Overman and Clark[47] on radiological safety. All of the polymerization and copolymerization reactions were carried out in a heavy-walled Pyrex tubes similar to

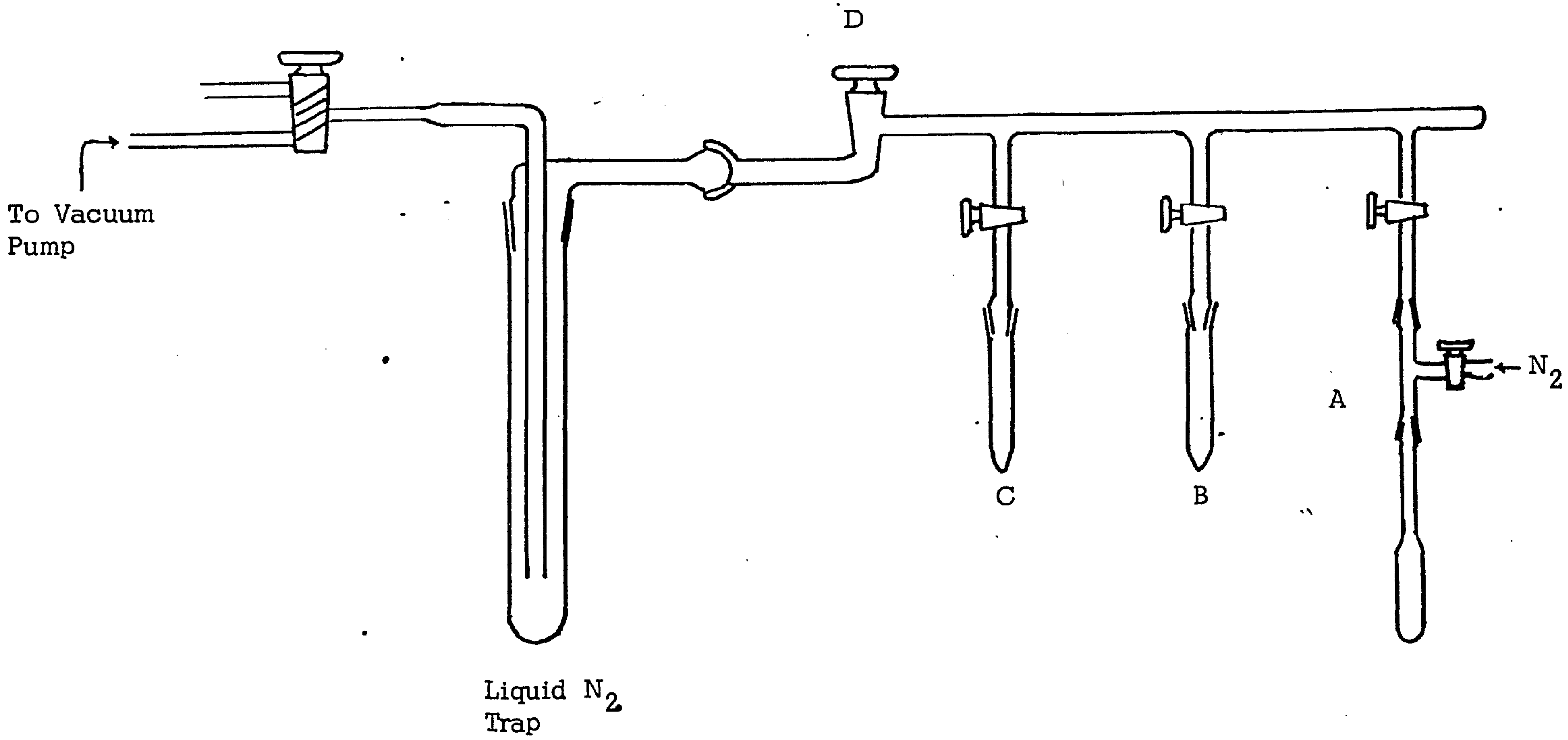


Figure 5. Vacuum Line for Distillation of Monomers into Reaction Cells.

those suggested by Alfrey et al..[15] Small rubber stoppers were used to stopper the cells. The reaction cell was connected to a vacuum system as shown in Figure 5. This vacuum system was used to distill volatile monomers directly into polymerization cells at room temperature just prior to polymerizations. Less volatile monomers (divinylbenzenes) were vacuum distilled in a microdistillation apparatus under nitrogen just prior to polymerization and transferred into the reaction cells with a long dropper under a blanket of nitrogen.

The C^{14}-labeled monomer, which was diluted as described earlier under the section "Standard C^{14}-labeled Monomer," was placed in a 15 ml. graduated centrifuge tube at B and the other monomer in a similar tube at C as shown in Figure 5. All monomers were stored under nitrogen and the vacuum system was flushed with nitrogen prior to attaching the centrifuge tubes containing monomers. Each monomer was degassed by the following procedure: the stopcock to the monomer tube was closed; and the contents were frozen either in liquid nitrogen or in a dry ice-acetone mixture. The remainder of the vacuum line was evacuated and the stopcock leading to the monomer tube was opened for about five minutes while keeping the monomer frozen. Closing the stopcock the frozen monomer was allowed to melt at room temperature one or two minutes; this process could be hastened by immersing the cell in a beaker of water at room temperature. The monomer was then refrozen, degassed, and remelted. The process was repeated at least four times. After degassing the stopcocks at B and C were kept closed. A weighed reaction cell was connected to the vacuum line at A. After evacuating for 15 minutes, the reaction cell was immersed in either liquid nitrogen or dry ice-acetone mixture. Stopcock D was closed and stopcock C was opened slowly, in order to avoid bumping, until distillation started. After the proper amount of monomer was distilled into the reaction cell, stopcocks A and C were closed and D was opened. After the contents of the reaction cell were allowed to melt at room temperature, the reaction cell was filled with nitrogen, and then removed from the vacuum line and stoppered. The vacuum grease on the ground glass joint of the reaction cell was removed with a piece of tissue paper dampened with benzene. After weighing the reaction cell was greased again and connected to the vacuum line at A under a continuous nitrogen stream.

Approximately the required amount of the second monomer was distilled into the reaction cell through the stopcock B, and weighed as was described before for the first monomer. The appropriate amount of solid benzoyl peroxide was added into the reaction cell. After reconnection of the reaction cell to the vacuum line, stopcock A and nitrogen inlet were closed. The contents of the cell were frozen in liquid nitrogen or dry ice-acetone mixture, stopcocks D and A were reopened. After evacuating the reaction cell for five minutes, stopcock A was closed, and the contents were allowed to melt at room temperature. The contents were refrozen. This degassing process was repeated three times. The contents in the reaction cell were frozen and the stopcock A was opened. The reaction cell was sealed about 2 inches below the ground glass joint under vacuum by using a small flame from a torch while stopcock A was closed.

The contents of the cells were polymerized to less than ten per cent conversions (exact conversions are given in Tables 6-10) in a constant temperature bath maintained at 70°C. Trial runs with non-labeled monomers were carried out in order to determine the lengths of time needed to obtain conversions of less than 10 per cent. After polymerization the cell was removed from the bath and quickly frozen in a dry ice-acetone mixture or in liquid nitrogen. The cell was then etched with a file on the neck and was broken open. The contents were carefully transferred to a 15 ml. cetrifuge tube which had been weighed. The polymerization cell was rinsed three times with approximately 0.5 ml. of benzene each time and the rinses were added to the cintrifuge tube. About 10 ml. of methanol was added to the centrifuge tube to precipitate the polymer or copolymer formed, and the contents of the tube were thoroughly mixed by a pointed stainless steel spatula. After centrifuging the tube at approximately 4000 r.p.m. on an International Clinical Centrifuge for ten to twenty minutes, the supernatant liquid was decanted into a special container for radioactive waste and disposed of at a later time. The precipitated polymer or copolymer was redissolved in a minimum amount of benzene (approximately one to two milliliters). The crosslinked copolymers from the copolymerizations with divinylbenzenes could not be dissolved, but were swollen in benzene. It was then reprecipitated with methanol as before and centrifuged. This process was repeated four to five times to remove all unreacted monomers. After final decantation the contents of the centrifuge tube were redissolved or suspended in about one to two milliliters of benzene. The tube was then rolled in a nearly horizontal position on a bed of fine dry ice allowing a relatively uniform distribution of the frozen contents on the wall of the centrifuge tube. After freezing the contents thoroughly and covering the tube mouth with filter paper the tube was placed in a vacuum dessicator and a vacuum was applied immediately. The filter paper cover was used to prevent the loss which might occur from bumping during evacuation of the dessicator. A 0.1 mm. vacuum was applied to the dessicator for at least four hours to remove the benzene leaving the copolymer in an essentially dried form. The tube was then dried to a constant weight in a vacuum oven at 40°C and 1 mm. pressure. The tube was cooled to room temperature, weighed, and the copolymer weight was determined. The yield was determined by dividing the weight of the copolymer produced by the total weight of the two monomers used. Determination of reactivity ratios was accomplished by preparing at least five duplicate samples of the monomer pairs with different monomer feed composition.

Copolymerization Reactions

1) Methyl Methacrylate and m-Divinylbenzene

meta-Divinylbenzene was prepared as mentioned earlier. A quantity of meta-divinylbenzene was washed three times with 1 N. KOH and with distilled water, dried over calcium chloride, and vacuum distilled in a microdistillation apparatus. The middle fraction, b.p. 34°C/1 mm., n_D^{24} 1.5755 (Literature values,[16, 49] 34°C/1mm. and n_D^{25} 1.5754), was used for the preparation of seven copolymers of meta-divinylbenzene and the first standard methyl-C^{14} methacrylate. meta-Divinylbenzene was placed in the reaction cells with a Pasteur pipette under a blanket of nitrogen and was degassed. Methyl methacrylate was distilled into the reaction cell by using the vacuum line as described under "Copolymer Preparation" section. Solid benzoyl peroxide (0.2% by weight of the monomers) was used as the intiator. The monomer mixtures were degassed, sealed under vacuum, and polymerized at 70°C for 30 to 100 minutes giving 3 to 6.5% of copolymer. The copolymers were isolated and dried as described before. Analyses of copolymers were carried out (as weill be described later under the section "Analysis and Determination of Activity of Standard C^{14}-labeled Polymers) by using the vibrating reed electrometer-ionization chamber radioactivity assay technique. Data and results are shown in Table 6.

2) Methyl Methacrylate and p-Divinylbenzene

para-Divinylbenzene which had been prepared as described earlier was washed, dried, and distilled twice in a manner similar to that used for meta-divinylbenzene. The middle fraction, m.p.

29.7°C, n_D^{35} 1.5855 (Literature values,[16, 49] 29.5-30°C and 1.5857), in the second distillation was placed in the reaction cells with a Pasteur pipette under a nitrogen blanket. Six copolymers of methyl methacrylate and para-divinylbenzene were prepared by using the first standard methyl-C^{14} methacrylate. Polymerization was carried out at 70°C with 0.1% of solid benzoyl peroxide by weight of monomers as the initiator for 10 to 55 minutes giving copolymer yields of 1 to 3%. Purification and drying methods of the copolymers were described previously. Crosslinked copolymers were swollen, but not dissolved in benzene. The swollen copolymers were precipitated with methanol. The process was repeated at least five times. Analysis was carried out in the same manner as will be described in the next section. Data and results are shown in Table 7.

3) Styrene and p-Isopropylstyrene

Five copolymers of styrene and para-isopropylstyrene, n_D^{20} 1.5290; b.p. 85°/12mm (Literature values,[50] n_D^{24} 1.5190 and 45°/1.3 mm), were prepared using the synthesized para-isopropylstyrene mentioned earlier. The vacuum line was used for the preparation of the monomer mixture as described in "Copolymer Preparation" section. The polymerization was carried out at 70°C with 0.1% of solid benzoyl peroxide by weight as the initiator and required 30 to 86 minutes to give the conversions given in Table 8. Analytical data, which were obtained in the same manner as will be described later in the section

"Analysis and Determination of Activity of Standard C^{14}-labeled Polymers," are included in the same Table 8.

4) Methyl Methacrylate and p-Isopropylstyrene

Six copolymers of methyl methacrylate and para-isopropylstyrene were made by using the second standard methyl-C^{14} methacrylate monomer. Solid benzoyl peroxide (0.1% by weight of monomers) was used as the initiator. Polymerization was carried out at 70°C and required 56 to 62 minutes to give the conversions of 2.5 to 4% copolymer. The procedures for the preparation of monomer mixture and analysis of copolymer formed were the same as the styrene-para-isorpopylstyrene copolymerization system. The results and data are shown in Table 10.

Analysis and Determination of Activity of Standard C^{14}-labeled Polymers

Two samples of the first polymethyl-C^{14} methacrylate standard were analyzed for the radioactivity by the ionization chamber-vibrating reed electrometer radioactivity assay technique.[1, 2] The samples of the polymer were burned in a micro carbon-hydrogen combustion train similar to the one described by Niederl and Niederl.[51] An Applied Physics Corporation Cary Model 31 vibrating reed electrometer was used with a Honeywell Electronic 15 strip chart chromatography recorder. The combustion train consists of a well cleaned combustion tube with fillings of platinum wire, cupric oxide, lead peroxide, and silver wire. The procedure for filling the combustion tube as described in detail by Niederl and Niederl was employed in this experiment.

Water formed during the combustion process was removed by an absorption tube containing magnesium perchlorate (Anhydrone; flakes 3 to 5 mm. long) which had been inserted between the capillary ending of the combustion train and the flow meter. The ionization chamber was connected to the flowmeter, as shown in Figure 6, to collect the gases produced from combustion of the polymer containing C^{14}-labeled monomer.

Two samples of the first polymethyl-C^{14} methacrylate standard for combustion were weighed on a microbalance. Porcelain microcombustion boats approximately 4mm. deep, 5mm. wide, and 17mm. long were used for weighing and burning the polymers. The boats were always handled with stainless steel forceps used only for this purpose. In order to avoid moisture pick up and to get more accurate weights of polymers, the inside of the balance was kept dry with desiccant placed in the balance box. The boat was weighed after putting a piece of aluminum foil under the boat on the balance pan. After weighing the boat was filled with dried polymer. The boat, while being filled with polymer sample, was placed in a clean plastic bag on the stainless steel tray (which was covered with aluminum foil) to prevent small flakes of polymer from being blown away. Copolymer

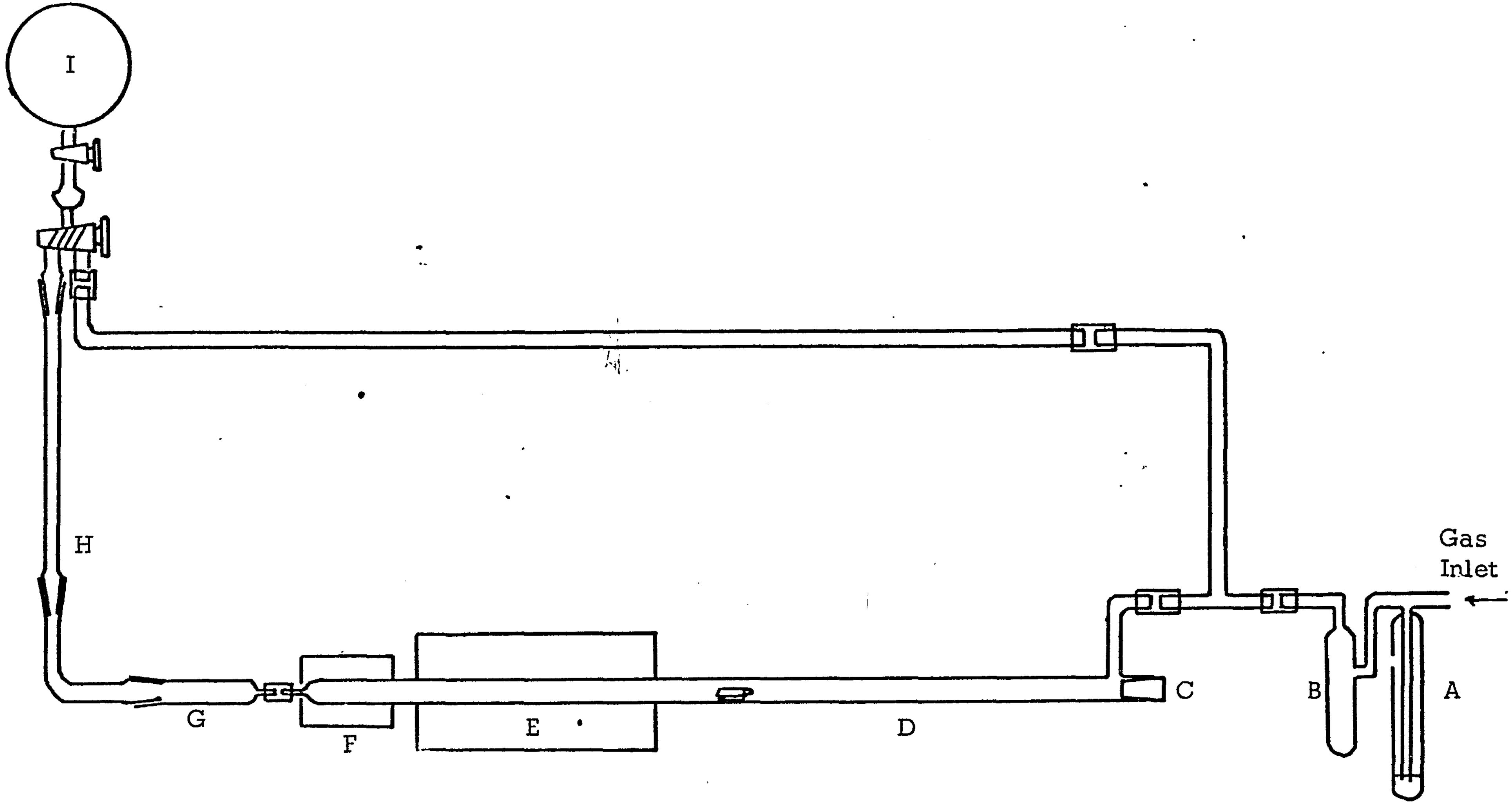


Figure 6. Combustion Train: A Pressure release valve; B Oil trap; C Rubber stopper; D Quartz combustion tube; E Furnace; F Heating mortar; G Water absorption tube; H Gas flowmeter; I Ionization chamber.

was carefully transferred from the centrifuge tube into the boat and packed with the stainless steel spatula. After each use the spatula was cleaned with dry tissue paper then with tissue paper moistened with benzene and placed in a special disposal container in the hood used for radioactive work. Tissue paper used for spatula cleaning was placed in the plastic bag which was then closed at the top and held secure with a rubber band. The bag was placed in a container for the radioactive wastes to be disposed of later. The boat with polymer was again placed on the balance pan which had been covered with thin aluminum foil and was allowed to reach equilibrium for fifteen minutes before weighing. Combustion samples ranged from approximately 4 to 12 mg. in weight.

A combustion furnace temperature of 700°C was used. The heating mortar had a preset temperature of 175 to 180°C. Medical oxygen containing 5% carbon dioxide was used as a combustion gas. The gas flow rate through the combustion system was indicated by a flowmeter. As the furnace was heating to operating temperature the flowmeter was set about 0.1 to 0.2 units to allow combustion gas to flow slowly through the combustion train. This was done to prevent impurities and moisture from entering the combustion train. A Cary-Tolbert stainless steel spherical ionization chamber having a 500 ml. capacity was used throughout this work. After evacuating the ionization chamber for 15 to 20 minutes, it was placed in position at the end of the combustion assembly as shown in Figure 6. The boat containing the weighed polymer sample was placed in the combustion tube after removing the rubber stopper by using a glass rod to push the boat to within 5 cm. of the furnace. After replacing the stopper, the combustion gas flow rate was increased, and the needle valve in the ionization chamber was opened slowly in such a way as to attain a gas flow rate of about 15 ml. per minute as indicated by a flowmeter reading of about 3.5 units.

Combustion was started by placing a hissing Bunsen burner about 10 cm. from the end of the combustion tube and gently heating the polymer with a small flame of a microburner in order to decompose it. This was done carefully to avoid overheating which would cause the sample to explode leading to spattering, excess back pressure, and possible loss of radioactive carbon dioxide. Decomposition usually required about 10 minutes. Once the decomposition of the sample was completed, the microburner was removed, and the Bunsen burner was used to carry out the combustion to completion. During a period of 5 minutes the Bunsen burner was gradually moved from its original position to a position under the boat where it was left for an additional five minutes. Then another five minutes was used to gradually move the burner from the boat to the furnace.

The same procedure was repeated with the Bunsen burner but using 1.5, 2, and 1.5 minutes respectively in going from the original position to one just under the boat; under the boat; and from the boat to the furnace. The Bunsen burner was then removed, the combustion gas was allowed to flush the combustion train until the flowmeter dropped to zero. A total of 40 to 50 minutes was required to complete the entire decomposition and conbustion process. It was necessary, during the combustion process, to reset the flowmeter by slightly opening the needle valve to compensate for the decrease in gas flow rate caused by the decrease in vacuum in the ionization chamber. When not in use the combustion train was cooled gradually by the flowing combustion gas and then shut off from the atmosphere before turning off the gas.

The ionization chamber was carefully placed on the vibrating reed electrometer head. Three hand screws on the side of the electrometer head were used to hold the chamber tightly in place. The positive terminal of two 90 volt batteries wired in series was connected to the electrometer head and the negative terminal was attached to the ionization chamber. The electrometer head was provided with a manually operated turret switch with six positions. The switch had a ground position, an open position, and 4 other positions in which condensers or resistors could be connected in series with the feed back line of the electrometer circuit. The condensers were designed for use where large amounts of radioactivity would be encountered. Resistors were designed for radioactivity determination by the high resistance leak method. Throughout this study the open position was used, because it was found that the levels of radioactivity were not sufficient to warrant use of condensers or resistors in this work.

Radioactivity was determined by the rate of charge method. The electrometer and the recorder were allowed to remain on continuously. When not used the electrometer was left on the ground position at 30 volts. After setting the voltage selector on the appropriate scale, the turret switch was placed on the open position and the recorder pen was allowed to travel from the 10 division to the 90 division as shown in Figure 7. The electrometer was manually discharged by turning the turret switch to the ground position causing the recorder pen to return to zero. The procedure was repeated by switching to the open position. The average time of one recording ranged approximately from 3 to 15 minutes, and the recording was repeated five to seven times. After removal of the ionization chamber the dust cover was replaced on the electrometer head and the chamber was evacuated for at least 15 minutes before being used again. Checks by determining backgrounds after evacuation showed ten minutes were sufficient to remove all of the radioactive carbon dioxide. The radioactive carbon dioxide was removed from the ionization chamber by evacuation through an absorption "U" tube containing Ascarite. At least two analyses of each polymer were made and the analytical values were found to be within 1.6% of the mean of the two analyses as can be seen in Tables 1 to 10.

A fairly uniform background could be obtained by evacuating and filling the ionization chamber with combustion gas just prior to use.

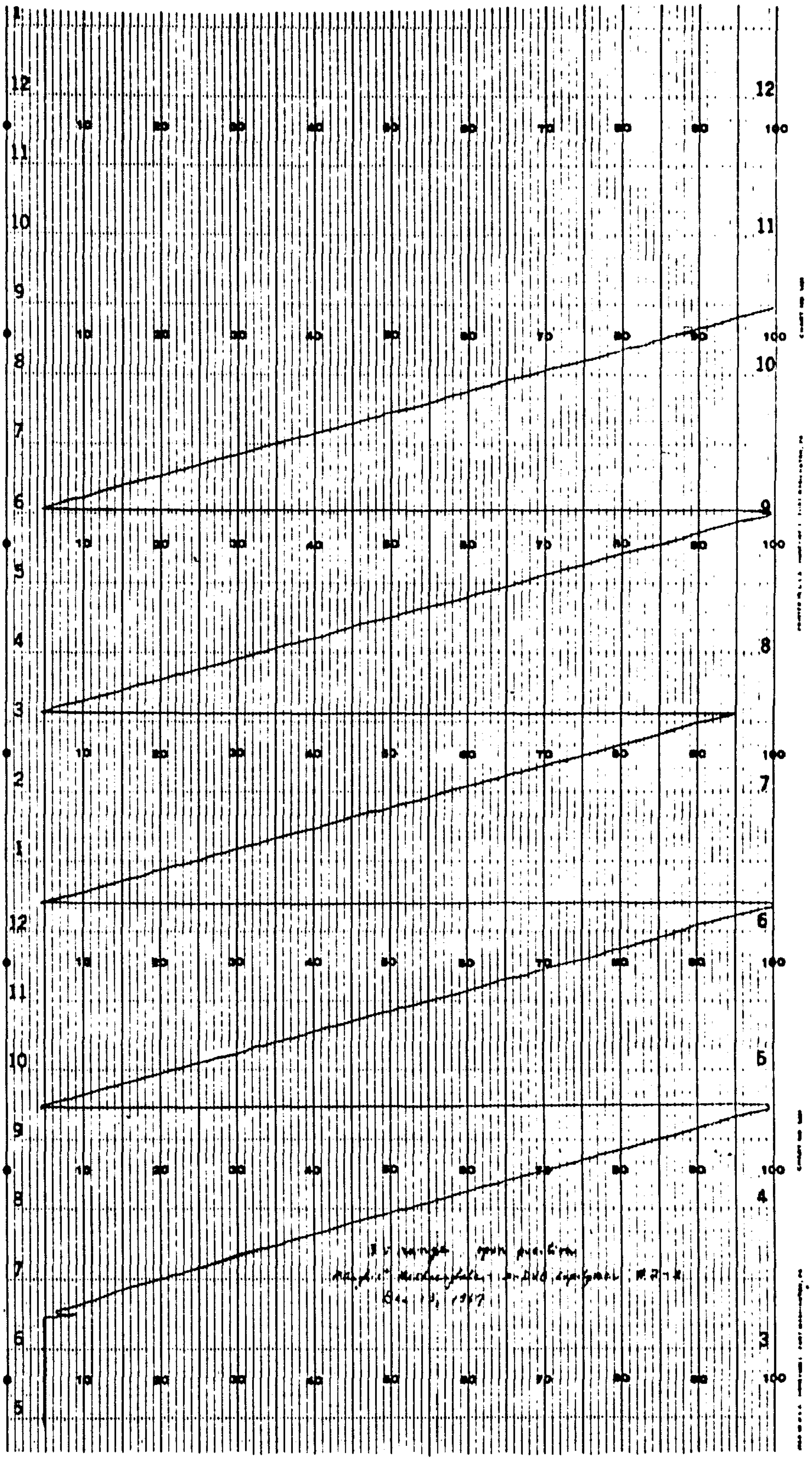


Figure 7. Chart Paper Showing a Recording of the Radioactivity of a Typical Copolymer Sample. (Recorder Range, 3v)

Background was always determined using the 30 millivolt scale until at least five uniform recordings were obtained. Figure 8 shows a typical background determination. When not in use the ionization chamber was kept filled with combustion gas.

Table 1.

Analysis of First Standard Polymethyl-C^{14} Methacrylate
(Background, 0.1420mv/sec; charge, 8000 mv.)

No.	Sample Wt. mg.	Time, sec.	Specific Charge rate, mv./sec./mg.
1	5.27	450.95	3.3393
2	7.99	298.54	3.3361

Average specific charge rate and standard value, 3.3377±0.0016.

Analytical data for the first standard polymethyl-C^{14} methacrylate is shown in Table 1. The background count is the average of 7 readings and 2 determinations. The average chart advancements in inches, were multiplied by 120 to obtain time in seconds. One inch of vertical distance represented a travel time of two minutes. The values for the sample calculation, shown below for the radioactivity of the first polymethyl-C^{14} methacrylate standard are taken from Table 1. The charge in millivolt is divided by time in seconds, then background count is substracted, and the result is divided by the sample weight in milligrams giving a value in millivolts per second per milligram, which is the specific charge rate. The calculation of the background will be shown later in the section "Sample Calculations for the Determination of Monomer Reactivity Ratios."

$$\frac{\left(\frac{8000}{450.95} - 0.1420\right)\ \text{mv/sec}}{5.27\ \text{mg}} = 3.3393\ \text{m./sec./mg.}$$

A second sample of the same polymethyl-C^{14} methacrylate standard was analyzed and then averaged as shown in Table 1. This standard value is used for the analysis of copolymers of methyl methacrylate and meta- and para-divinylbenzene.

Specific activity of the second standard polymethyl-C^{14} methacrylate was analyzed by the same method as the first standard. The analytical data and results are shown in Table 2.

Table 2.

Analysis of Second Standard Polymethyl-C^{14} Methacrylate
(Background, 0.18895 mv./sec.; Charge, 8000 mv.)

No.	Sample Wt. mg.	Time, sec.	Specific Charge rate, mv./sec./mg.
1	6.77	380.26	3.0797
2	7.89	330.00	3.0486

Average specific charge rate and standard value, 3.0642 ± 0.0045.

The time given for both samples is the average rate of charge time for eight readings at 8000 millivolts. The standard value of this polymer was used for the analysis of methyl methacrylate-para-isopropylstyrene copolymers.

Table 3.

Analysis of Standard Polystyrene-B-C^{14}
(Background, 0.18895 mv./sec.; Charge, 240 mv.)

No.	Sample Wt., mg.	Time, sec.	Specific Charge rate, mv./sec./mg.
1	6.97	318.90	0.080866
2	8.13	284.33	0.080583

Average specific charge rate and standard value, $8.0725\text{x}10^{-2} \pm 0.0011$.

Two samples of the standard polystyrene-B-C^{14} were analyzed to determine the specific activity. The spherical ionization chamber was used and analysis was carried out by the same manner as described above for polymethyl-C^{14} methacrylate standards. Data and results are shown in Table 3. The time given for both samples is the average rate of charge time for seven readings at 240 millivolts. The standard value of this labeled polymer was used for the analysis of styrene-para-isopropylstyrene copolymers.

Copolymer Radioactivity Assay

The copolymers prepared for this work were analyzed for radioactivity by a method similar to the one used for the standard C^{14}-labeled polymers as described in the previous section. The vibrating reed electrometer was used with a recorder and radioactivity was determined by using the open position of the turret switch. Duplicate analyses were made for each sample and each analysis was obtained from 5 to 7 counting determinations. All the details of the analysis for the radioactivity of the copolymer samples were exactly the same as described in the previous section and the analytical data and results are included in Tables 6 - 10.

Sample Calculations for Determination of Monomer Reactivity Ratios

Figure 8 shows a typical recording of background using a 500 ml. spherical ionization chamber. Table 4 shows data from the recording. The 30 millivolt electrometer setting was used with the turret switch in an open position. The vertical distances traveled by the recorder pen from the 10 division to the 90 division are presented in Table 4.

Table 4.

Typical Background Radioactivity (Charge, 24 mv.)

No.	1	2	3	4	5	6	7	Average
Chart inches	1.36	1.38	1.51	1.34	1.33	1.44	1.48	1.406

The average of the chart inches for this run was multiplied by 120 to obtain time in second. The charge in millivolts is then divided by the time in second to get the background in millivolts per second. From zero to 100 on the chart paper is 30 millivolts using the 30 millivolt electrometer scale setting, therefore the charge in millivolts from 10 to 90 is 24 millivolts. The actual calculation is:

$$\frac{24 \text{ mv.}}{1.406 \text{ inches} \times 120 \text{ sec./inch}} = 0.1423 \text{ mv./sec.}$$

One more determination of background obtained by the similar method to the one described above gave 0.1417 mv./sec.. Hence the average value of the background is 0.1420 millivolts per second.

A typical copolymer analysis which was obtained from the second analysis of the copolymer number 2 (Table 6) of methyl methacrylate/meta-divinylbenzene copolymerizations is presented in Table 5 and Figure 7.

Table 5.

Typical Copolymer Analysis for Radioactivity (Charge, 2400 mv.)

No.	1	2	3	4	5	Average
Chart inches	2.41	2.40	2.41	2.37	2.42	2.402

The average chart inches is multiplied by 120 seconds per inch obtaining the time required to build up a charge of 2400 millivolts; then the charge in millivolts is divided by the seconds and background is subtrated:

$$\frac{2400 \text{ mv.}}{2.402 \text{ inches} \times 120 \text{ sec./inch}} - 0.1420 \text{ mv./sec.} = 8.1844 \text{ mv./sec.}$$

The charge rate of this sample is 8.1844 millivolts per second. This value is divided by the sample weight in milligrams which gives the specific charge rate of this sample.

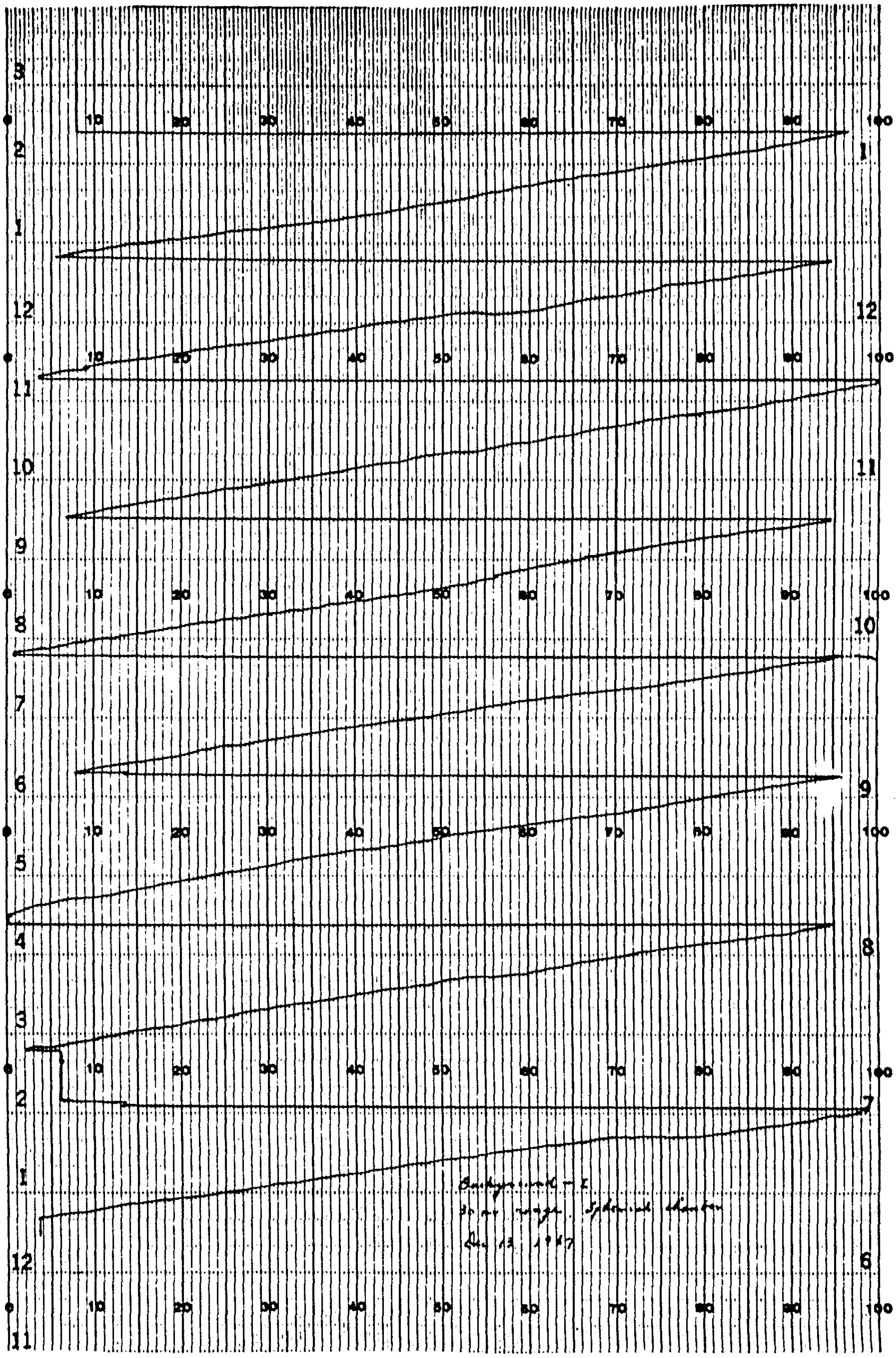


Figure 8. Chart Paper Showing a Recording of Typical Background Radioactivity. (Recorder Range, 30 mv.)

$$\frac{8.1844 \text{ mv./sec.}}{8.14 \text{ mg.}} = 1.0054 \text{ mv./sec./mg.}$$

Another sample of this copolymer was analyzed using 9.03 mg. as shown in Table 6. The specific charge rate obtained for this sample was 0.9919 mv./sec./mg.. The average of these two analyses is 0.9987 mv./sec./mg..

The specific charge rate of the copolymer is then divided by the specific charge rate of the first polymethyl-C^{14} methacrylate standard and multiplied by 100 to obtain the per cent of methyl methacrylate in the copolymer.

$$\frac{0.9987 \text{ mv./sec./mg.}}{3.3377 \text{ mv./sec./mg.}} \times 100 = 29.92\%$$

Hence the per cent of meta-divinylbenzene is 70.08.

From Table 6 it can be seen that the monomer feed used to prepare copolymer number 2 was composed of 0.6947 g. of methyl-C^{14} methacrylate and 0.8621 g. of meta-divinylbenzene. The molar ratio of the two monomers in the feed, M_1/M_2, is found by dividing the number of moles of methyl methacrylate by the number of moles of meta-divinylbenzene. However, when we use divinylbenzene as a comonomer, we have to use $M_1/2M_2$ instead of M_1/M_2 as mentioned in the "Historical" section.

$$\frac{M_1}{2M_2} = \frac{\dfrac{0.6947\ \text{g.}}{100.12\ \text{g./mole}}}{2 \times \dfrac{0.8621\ \text{g.}}{130.19\ \text{g./mole}}} = 0.5239$$

The molar ratio of meta-divinylbenzene to methyl methacrylate in the copolymer formed is obtained as shown below:

$$\frac{m_2}{m_1} = \frac{\dfrac{70.08\ (\text{\% of m-divinylbenzene})}{130.19\ (\text{molecular wt. of m-divinylbenzene})}}{\dfrac{29.92\ (\text{\% of methyl methacrylate})}{100.12\ (\text{molecular wt. of methyl methacrylate})}}$$

$= 1.801$

These two qualitities, M_1/M_2 and m_2/m_1, are used to evaluate r_1 and r_2 values using the copolymer composition equation where r_2 is expressed as a linear function of r_1.

$$r_2 = \frac{M_1}{2M_2}\left[\frac{m_2}{m_1}\left(1 \quad r_1 \frac{M_1}{2M_2}\right) - 1\right]$$

Assigning two values, for example, zero and one for r_1, two values for r_2 can be obtained. Each two values of r_1 and r_2 will represent a line on the final graphical solution of the copolymer equation. Assigning value of zero for r_1 we get $r_2 = 0.5239 \{ 1.801 (1 + 0) -1 \} = 0.4196$; assigning r_1 a value of one, $r_2 = 0.5239 \{ 1.801 (1 + 0.5239) - 1\} = 0.9140$.

Values of r_1 and r_2 were obtained by the above procedure from the six other copolymers of methyl methacrylate/meta-divinylbenzene.

Plotting the values of r_2 versus r_1 seven lines were obtained as shown in Figure 9, the intersection of which gives the monomer reactivity ratios for methyl methacrylate (r_1) and meta-divinylbenzene (r_2).

The Fineman-Ross method for the determination of the reactivity ratios involves the use of the following expression for the above copolymerization equation:

$$\frac{f - 1}{F} = r_1 - \frac{f}{F^2} \times r_2$$

where $f = m_1/m_2$ and $F = M_1/M_2$.

For the monovinyl-divinyl copolymerizations, F is modified to $M_1/2M_2$. The values of $(f - 1)/F$ and f/F^2 are determined for each copolymer and $(f - 1)/F$ is plotted versus f/F^2. The best line is drawn through these points by the method of least squares. The intercept on the $(f - 1)/F$ axis is r_1 and the negative slope of the line is r_2. A Fineman - Ross plot for the methyl methacrylate - meta-divinylbenzene copolymerizations is shown in Figure 10.

Results and Discussions

The solutions of the differential copolymer equation were obtained by the intersect method and by the Fineman-Ross method,[9] and are shown on the following pages. All the analyses of copolymer compositions were carried out by using a C^{14}-labeled comonomer in preparations of copolymers and using the vibrating reed electrometer and ionization chamber method for the determination of copolymer radioactivities. The only one intersect plot, which is for the copolymerization of methyl methacrylate and para-divinylbenzene, does not give a satisfactory solution for the copolymer composition equation. Reasons will be given later. Duplicate analyses were carried out for each copolymer sample and average values of the analyses were used in the evaluation of the monomer reactivity ratios.

Copolymerization of Methyl Methacrylate and m-Divinylbenzene

According to the classification of divinyl monomers made by Alfrey, Bohrer and Mark,[15] m-divinylbenzene is an example of a symmetrical independent divinyl monomer where the two vinyl groups have approximately equal reactivities. And it has been shown empirically that the revised copolymer composition equation for the copolymerizations of monovinyl and divinyl monomers should be used to describe copolymer compositions for the copolymerization of styrene and meta-divinylbenzene.

The values of monomer reactivity ratios for the copolymerization of methyl methacrylate (M_1) and meta-divinylbenzene (M_2), which were obtained by the intersection method and by the Fineman-Ross method and are represented in Figures 9 and 10, are $r_1=0.41$, and $r_2=0.61$. The least squares analysis was used for the linear plot. These values are in accord with previously observed values for the copolymerization of styrene and methyl methacrylate. The reported values[52] of monomer reactivity ratios for the methyl methacrylate-styrene copolymerization, where a C^{14}-labeled monomer and vibrating reed electrometer-ionization chamber assay technique were used, as in this experiment, are r_1 (methyl methacrylate) = 0.46 and r_2 (styrene)= 0.52. The reactivity ratios obtained for this copolymerization system using chemical analysis[19] are also r_1 (methyl methacrylate) = 0.46 and r_2 (styrene) = 0.52.

The Q and e values of meta-divinylbenzene calculated by the Alfrey-Price equations with these values are $Q = 1.1$ and $e = -0.8$. These values are very close to those of styrene ($Q = 1.0$ and $e = -0.8$) and are in the same range as those for meta-methylstyrene ($Q = 0.95$, $e = -0.8$)[15] and para-methylstyrene ($Q = 1.05$, $e = -0.9$).[15] The previously reported values[18] of the monomer reactivity ratios for the copolymerization of styrene and meta-divinylbenzene are quite close to unity. These values are in accord with the estimates based on Huckel MO calculation of $r_1 \cong r_2 \cong 1$.

All the above results indicate that the vinyl groups of meta-divinylbenzene have reactivities almost equal to those of the styrene

Table 6. Copolymerization of Methyl Methacrylate(M_1) with m-Divinylbenzene

	Monomer Feed							Copolymer Composition		
No.	M_1, g.	M_2, g.	Molar ratio $M_1/2M_2$	Conv. %	Sample wt., mg.	Charge time, sec.[a]	Charge mv.	Spec. chg. rate mv./sec./mg.[c]	m_1 wt. %[b]	Molar ratio m_2/m_1
1.	0.3166	1.1105	0.1854	5.62	10.68	403.20	2400	0.5440	16.28	3.956
					6.40	663.84	2400	0.5427		
2.	0.6947	0.8621	0.5239	6.62	9.03	263.75	2400	0.9919	29.92	1.801
					8.14	288.24	2400	1.0054		
3.	0.8349	0.8055	0.6739	5.98	6.46	324.96	2400	1.1212	33.77	1.509
					9.21	226.94	2400	1.1328		
4.	1.0375	0.6630	1.0174	5.47	4.84	360.16	2400	1.3474	40.21	1.144
					6.57	268.92	2400	1.3368		
5.	1.2325	0.5242	1.5286	5.29	9.04	541.87	8000	1.6174	48.18	0.8272
					9.62	515.44	8000	1.5986		
6.	1.3177	0.4873	1.7581	4.22	5.81	241.20	2400	1.6881	50.30	0.7599
					9.35	507.90	2400	1.6694		
7.	1.7693	0.2003	5.7434	3.10	3.92	257.88	2400	2.3379	70.02	0.3291
					4.58	223.50	2400	2.3360		

[a] Average of 5-7 readings.

[b] Average of two determinations.

[c] Deviation: average, ± 0.4 %; maximum, ± 0.7 %.
Background, 0.1420 mv./sec..

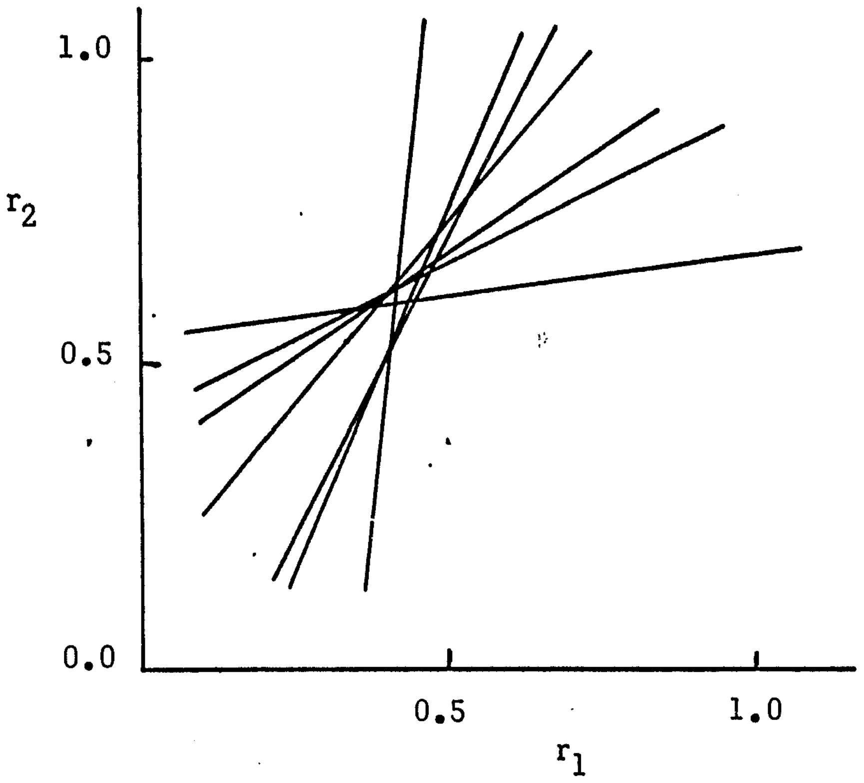
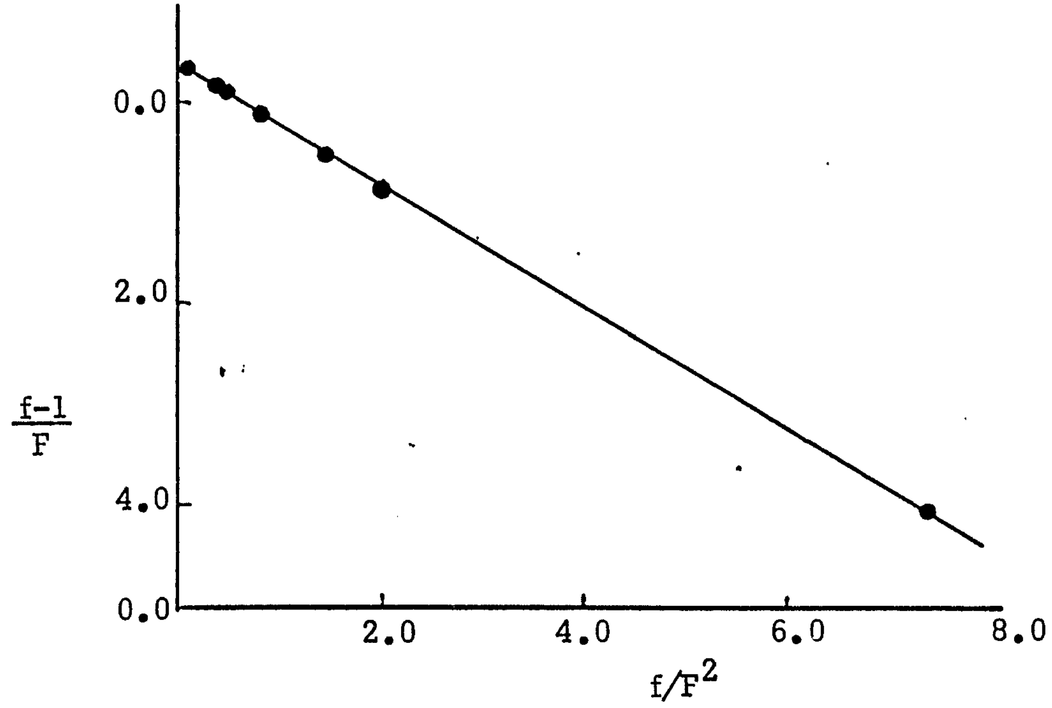


Figure 9. Intersect plot for Copolymerization of Methyl Methacrylate ($r_1 = 0.41$) and m-Divinylbenzene ($r_2 = 0.61$) at 70°C.



Figre 10. Fineman-Ross plot for Copolymerization of Methyl Methacrylate (r_1=0.41) and m-Divinylbenzene (r_2= 0.61).

vinyl groups, and that in the styrene-meta-divinylbenzene copolymer the meta-divinylbenzene unit is dispersed rather uniformly throughout the copolymer chain. And the fact that the data for the copolymerizations of meta-divinylbenzene with typical monovinyl monomers (styrene and methyl methacrylate) give fairly precise solutions of the revised copolymerization equation confirms the fact that meta-divinylbenzene is a good example of symmetrical independent divinyl monomer. Moreover there is little likelihood of any considerable conjugation between the two vinyl groups in meta-divinylbenzene. However, it must be noted that when a divinylbenzene molecule is incorporated into a copolymer chain through one of its two vinyl groups, the reactivity of the second unreated vinyl group will be reduced considerably by a shielding effect of the benzene nuclei of the nearby styrene or meta-divinylbenzene monomer unit in the copolymer chain.

Copolymerization of Methyl Methacrylate and p-Divinylbenzene

para-Divinylbenzene is quite different from the meta isomer by virtue of the direct conjugation between the two vinyl groups in positions para to one another. As mentioned above, the behavior of the meta compound can be adequately represented by the revised copolymer composition equation for monovinyl-divinyl copolymerizations, but the behavior of para-divinylbenzene is not so predictable and indicates that the degree of homogeniety of the copolymer formed is much less than that of meta-divinylbenzene copolymer. When pure para-divinylbenzene was copolymerized with C^{14}-labeled methyl methacrylate and the copolymers were analyzed by the technique described herein, it was found that neither the ordinary copolymer composition equation nor the revised equation could suitably express the monomer reactivity ratios for this copolymerization system. Table 7 gives the data and results and Figures 11 and 12 show the intersection and the Fineman-Ross plots for the solutions of the copolymer composition equation. The revised copolymer composition equation was used for the sake of consistency. The intersect plot does not give a satisfactory solution for the equation and deviations from the linear plot are considerable. The intersect plot resembles that for the styrene-para-divinylbenzene copolymerization. If all of the experimental data, given in Table 7, and Figures 11 and 12, are used, values of r_1(methyl methacrylate) = 0.10 and r_2(p-divinylbenzene) =0.93 are obtained by the least squares analysis of the Fineman-Ross plot (solid line in Figure 12). These results were obtained from data which include two copolymerizations, those with 9.4 mole % (No. 1) and 87.3 mole % (No. 6) of para-divinylbenzene, which deviate from the data from the other runs. If these two are omitted from the analysis of the data, values of r_1= 0.62 and r_2=1.30 are obtained from the linear plot (dotted line in Figure 12). These values are in only fair accord with those from styrene-para-divinylbenzene copolymerizations (r_1(styrene) = 0.77, r_2(p-divinylbenzene) = 2.08).[18]

One can give serveral different reasons why the copolymerizations with para-divinylbenzene do not give well-defined solutions of the

Table 7. Copolymerization of Methyl Methacrylate(M_1) with p-Divinylbenzene

	Monomer Feed							Copolymer Composition		
No.	M_1, g.	M_2, g.	Molar ratio $M_1/2M_2$	Conv. %	Sample wt., mg.	Charge time, sec.[a]	Charge mv.	Spec. chg. rate mv./sec./mg.[c]	m_1 wt. %[b]	Molar ratio m_2/m_1
1.	1.1034	0.1489	4.8182	2.81	4.35	349.38	2400	1.5465	46.53	0.8838
					8.25	184.50	2400	1.5375		
2.	0.9553	0.4386	1.4161	2.77	6.35	239.71	2400	1.5115	45.59	0.9177
					7.26	213.05	2400	1.5321		
3.	0.7322	0.7384	0.6447	3.07	4.45	212.27	800	0.8149	24.57	2.361
					6.07	465.96	2400	0.8251		
4.	0.5120	0.8102	0.4109	2.85	5.76	207.59	800	0.6444	19.24	3.229
					5.91	203.95	800	0.6397		
5.	0.4454	0.9954	0.2910	2.95	4.00	393.25	800	0.4731	14.40	4.572
					5.73	272.26	800	0.4880		
6.	0.1451	1.2929	0.0729	1.04	8.71	473.21	800	0.1778	5.363	13.57
					7.63	527.40	800	0.1802		

[a] Average of 5-8 readings.

[b] Average of two determinations.

[c] Deviation: average, ± 0.7 %; maximum, ± 1.55 %.
Background, 0.1420 mv./sec..

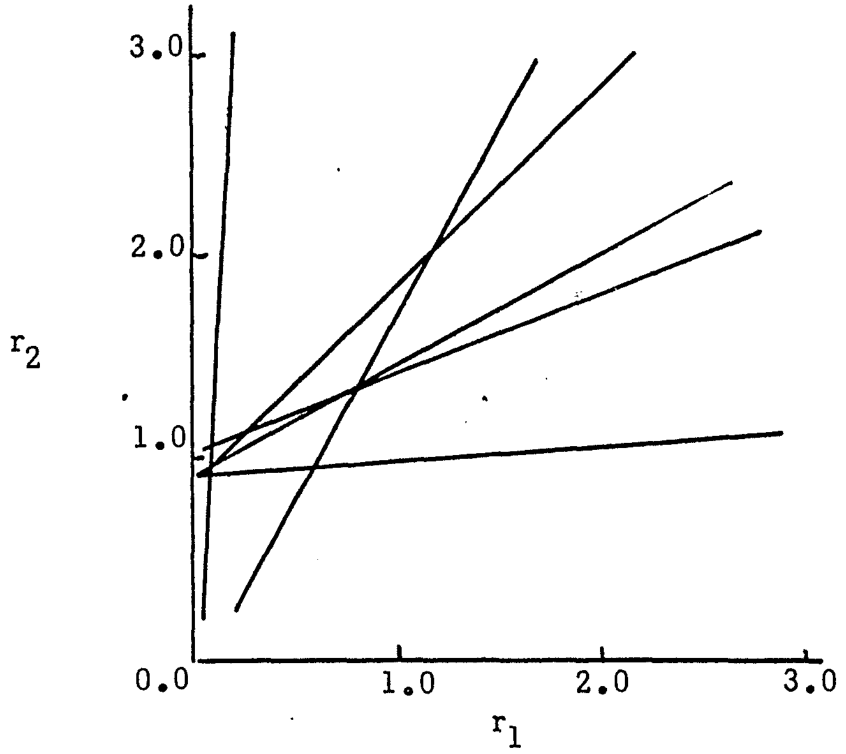


Figure 11. Intersect plot for Copolymerization of Methyl Methacrylate (r_1=0.62) and p-Divinylbenzene (r_2 =1.3) at 70°C.

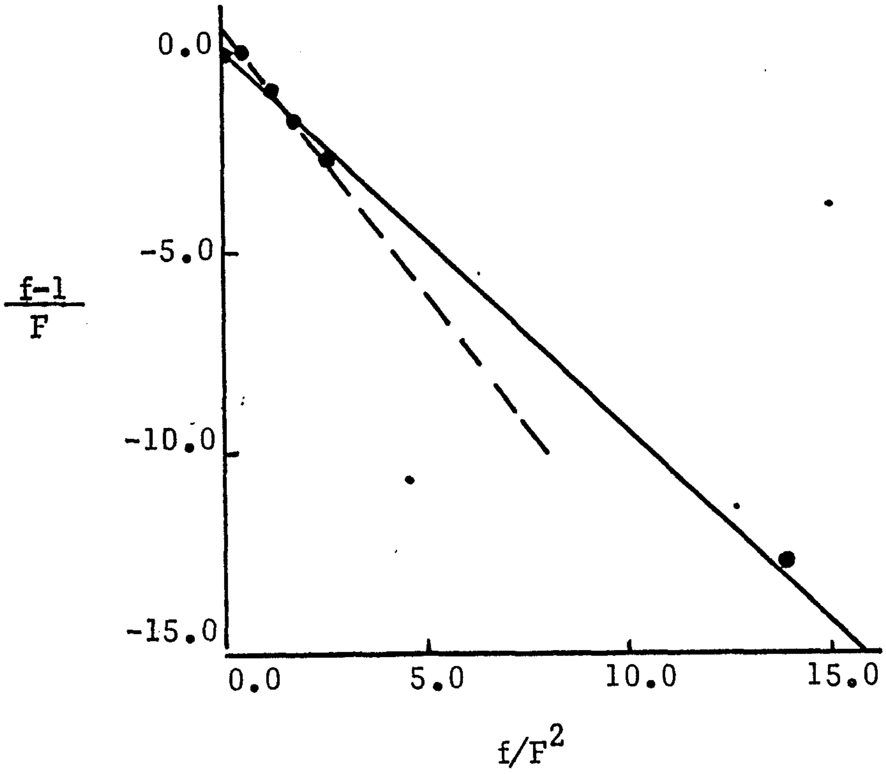
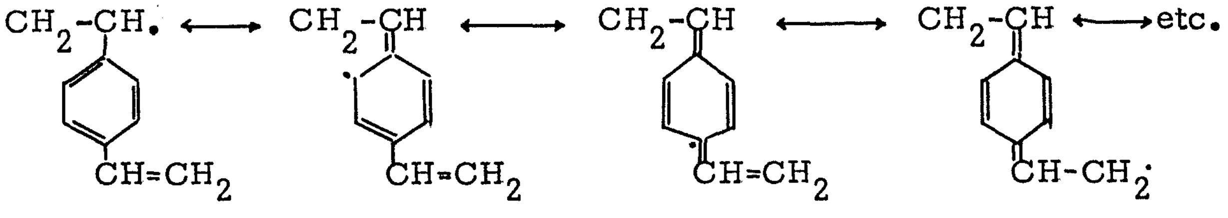


Figure 12. Fineman-Ross plot for Copolymerization of Methyl Methacrylate (r_1 = 0.62) and p-Divinylbenzne (r_2=1.3).

copolymer composition equation. It is certain that the deviation from linearity and the area of intersection in the intersect plots is too large to believe that this phenomenon is due merely to experimental error.

A logical explanation of these results can be postulated by considering the structural characteristic of para-divinylbenzene. It is a well-known fact that a monomer exhibits a strong reactivity toward any free radical when the resulting adduct is highly stabilized by resonance. Because of the direct conjugation between the two vinyl groups through the benzene ring, para-divinylbenzene would offer additional resonance stabilization in the resulting adduct and would show greater reactivity in copolymerization reactions than a monomer without such a conjugation, e. g., styrene.



Since methyl methacrylate is known to be less reactive than styrene, when methyl methacrylate and p-divinylbenzene compete with a free radical, para-divinylbenzene will be more reactive than methyl methacrylate and will preferentially polymerize with itself. This will result in a greater value of monomer reactivity for para-divinylbenzene than for methyl methacrylate. This supposition is supported by the fact that the values of r_1 are, no matter how the data are treated, rather low and the values for r_2 are rather high.

If the divinylbenzene does react predominantly with itself, it is possible to have much clustering of the divinylbenzene units in the copolymer chain because the pendant vinyl groups in the copolymer chain will tend to favor their undergoing a chain reaction. Storey[53] recently studied the initial rates and gel points for the copolymerization of styrene and para-divinylbenzene, and his results imply that intrachain crosslinking to produce microgels is an important reaction even at low crosslinker (p-divinylbenzene) levels and is the dominant reaction at moderate to high levels even before gelation.

On the other hand, it must be noted that the reactivity of a pendant vinyl group of the divinylbenzene unit in the copolymer chain cannot be the same as the reactivity of a vinyl group in the unreacted divinylbenzene monomer. Therefore, as soon as para-divinylbenzene is incorporated into a copolymer chain through a reaction of one of its two vinyl groups, the mixture becomes a three component copolymerization system consisting of methyl methacrylate, para-divinylbenzene, and para-isopropylstyrene-like unit. In a three component copolymerization there are nine possible reactions and a total of six monomer reactivity ratios to be considered. In the above three component system, however, one has no way to evaluate the molar concentration of p-alkylstyrene component, although there should exist some sort of relationship between it and para-divinylbenzene. Also the ratios involving the divinyl monomer or radical cannot be estimated in this complicated system since the divinylbenzene : alkylstyrene relationship is subject to constant fluctuation. It is therefore very difficult to describe the methyl methacrylate-para-divinylbenzene copolymerization even by a usual copolymer composition equation for three components.

Copolymerization of p-Isopropylstyrene and Styrene

As mentioned before in the copolymerizations of methyl methacrylate or styrene and para-divinylbenzene, satisfactory solutions for the copolymer composition equation could not be obtained, and this has been explained by the possible participation of the second vinyl group of para-divinylbenzene unit in the copolymerization reactions even in the early (low conversions) stages. In order to verify this supposition para-isopropylstyrene, which is similar to the unit which would be formed from having one vinyl group of the divinylbenzene incorporated into the copolymer chain, was taken as a model compound and studies of its copolymerization kinetics with styrene were undertaken.

Braun and Keppler[54] determined the monomer reactivity ratios for the copolymerization of styrene and p-isopropylstyrene using infrared absorption measurement. The values obtained are r_1 (styrene) = 1.11 and r_2 (p-isopropylstyrene) = 0.54. Comparing these values with those of styrene and other para-substituted styrenes copolymerizations it can be seen that this r_2 value is unexpectedly low. One cannot

Table 8. Copolymerization of Styrene(M_1) with p-Isopropylstyrene

	Monomer Feed							Copolymer Composition		
No.	M_1, g.	M_2, g.	Molar ratio M_1/M_2	Conv. %	Sample wt., mg.	Charge time, sec.[a]	Charge mv.	Spec. chg. rate mv./sec./mg.[c]	m_1 wt. %[b]	Molar ratio m_2/m_1
1.	1.92604	0.78410	3.4488	3.31	6.36	472.91	240	0.059939	74.85	0.2392
					12.84	264.20	240	0.060913		
2.	0.97545	0.40772	3.3591	5.74	9.53	350.52	240	0.059637	73.88	0.2518
					12.23	276.37	240	0.060679		
3.	0.67733	0.64609	1.4719	5.37	7.92	500.63	240	0.044584	55.02	0.5823
					6.40	586.20	240	0.044238		
4.	0.79158	1.92366	0.57777	4.94	13.62	498.74	240	0.026058	32.66	1.4685
					9.84	617.44	240	0.026667		
5.	0.26807	1.07953	0.34865	2.08	10.70	762.00	240	0.017632	22.04	2.5197
					7.26	311.79	80	0.017946		

[a] Average of 5-10 readings.

[b] Average of two determinations.

[c] Deviation: average, ± 0.8 %; maximum, ± 1.2 %.
Background, 0.12629 mv./sec..

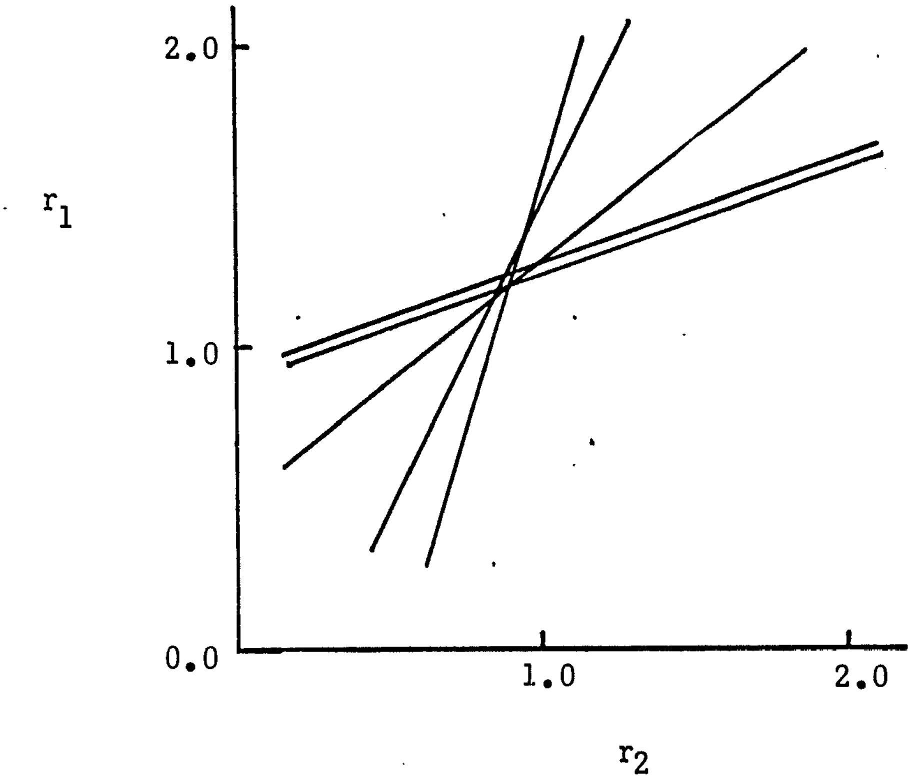


Figure 13. Intersect plot for Copolymerization of Styrene ($r_1 = 1.22$) and p-Isopropylstyrene ($r_2 = 0.89$) at 70°C.

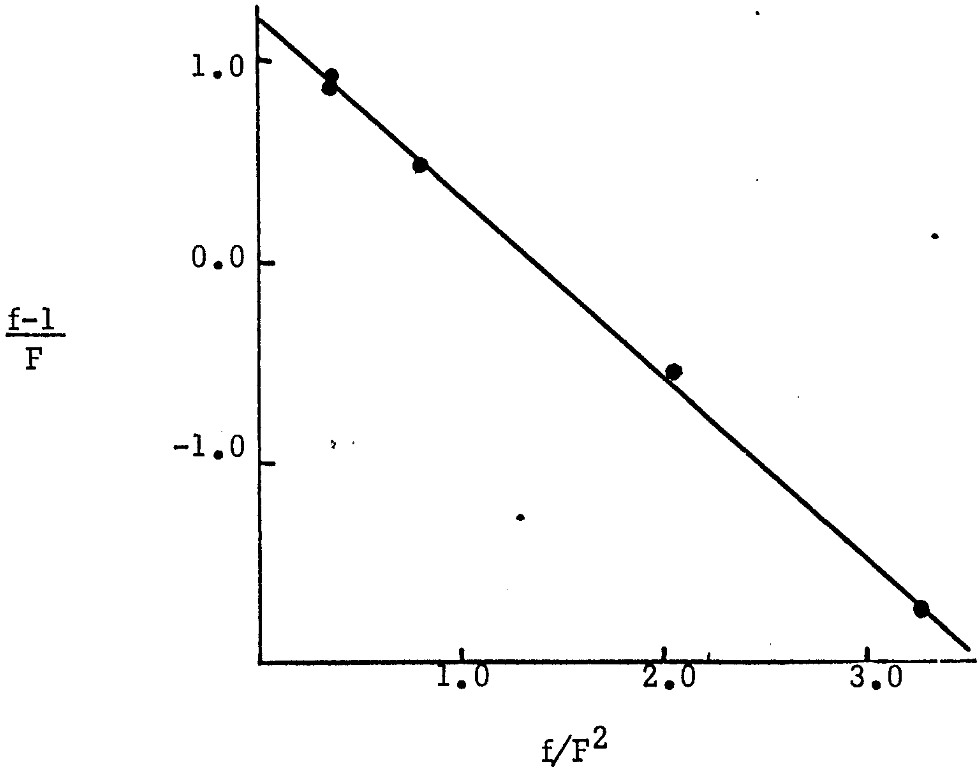


Figure 14. Fineman-Ross plot for Copolymerization of Styrene ($r_1 = 1.22$) and p-Isopropylstyrene ($r_2 = 0.89$) at 70°C.

justify the prediction of the possible early participation of the pedant vinyl group (p-isopropylstyrene-like unit in the methyl methacrylate or styrene and para-divinylbenzene copolymerization systems) into the chain reaction with such a low r_2 value (p-isopropylstyrene). The monomer reactivity ratios for this copolymerization system were re-evaluated to get more reasonable values. The experimental results from styrene-p-isopropylstyrene copolymerizations are given in Table 8 and the r_1 and r_2 plots from the copolymer composition equations are shown in intersect and linear plots in Figures 13 and 14, respectively. The least squares analysis of the Fineman-Ross plot gives the values of r_1 (styrene)= 1.22 and r_2(p-isopropylstyrene) = 0.89. The r_1r_2 product is slightly greater than one (1.09). This value of the r_1r_2 product is in contradiction to an empirical generalization that the reactivity ratios product r_1r_2 is almost always, but with a few exceptions, equal to or less than unity. It appears, however, from the obtained values that a situation exists for this copolymerization system where r_1 is slightly greater than unity and r_2 is slightly less than unity. These results together with those from the copolymerization of styrene and p-divinylbenzene establish that p-isopropylstyrene is somewhat, but not considerably, less reactive to the styryl radical than styrene. And styrene, in turn, is much less reactive to this radical than p-divinylbenzene. Since, as we have seen above, p-isopropylstyrene and styrene do not have so great a difference in their reactivities, this may be considered to suggest that the styrene-p-divinylbenzene copolymerization system

Table 9.

Monomer Reactivity Ratios Calculated by Using Integrated Copolymer Composition Equation

Run No.[a]	r_1	r_2	Run No.	r_1	r_2
12.	1.278	0.998	34.	1.291	0.999
13.	1.269	0.975	35.	1.290	0.999
14.	1.279	0.999	41.	1.501	0.998
15.	1.279	0.999	42.	1.497	0.999
21.	1.244	0.998	43.	1.498	0.998
23.	1.244	0.999	45.	1.437	0.968
24.	1.245	0.999	51.	1.538	0.998
25.	1.244	0.999	52.	1.538	0.998
31.	1.269	0.975	53.	1.539	0.998
32.	1.289	0.999	54.	1.534	0.997
			Average	1.36	0.99

[a] For example, run number 45 means that experiment 4 was taken as the first member of the pair and experiment 5 was used as the second member of the input data.

should be regarded as a three component copolymerization system. This is a conclusion consistent with that suggested earlier.

Using the computer program described by Montgomery and Fry,[55] the monomer reactivity ratios for this copolymerization system were calculated using the integrated form of the copolymer composition equation. The results are given in Table 9. The monomer charge ratios, copolymer compositions, and conversion data for all twenty combinations (1 with 2 being a different pair from 2 with 1, etc.) of pairs of experiments in Table 8 were used in the Fortran II program as input data. Values of $r_1 = 1.37$ and $r_2 = 0.99$ were obtained as averages of results for all twenty pairs. Of these, experiments 4 and 5 (used as the first member of the pairs) gave much higher values of r_1 (1.44-1.54) than those (r_1 1.24-1.29) from experiments 1, 2, and 3 (taken as first members of the pairs). Although numbers 4 and 5 are for the low styrene composition experiments, there is no basis for excluding them from the averages for this reason. It was noted by Montgomery and Fry that the r_1 values they obtained for vinyl acetate-vinyl chloride reactivity ratios were higher than those from differential analysis.

Copolymerization of Methyl Methacrylate and p-Isopropylstyrene

Since the monomer reactivity ratios for the copolymerizations of methyl methacrylate and m-divinylbenzene, and methyl methacrylate and p-divinylbenzene have been obtained, the monomer reactivity ratios for the copolymerization of methyl methacrylate and p-isopropylstyrene have been determined in order to see the structural characteristics of these copolymers and to compare one to another. The experimental results from the copolymerization of methyl methacrylate and p-isopropylstyrene are given in Table 10 and the values of the monomer reactivity ratios for this system, which were obtained by intersection and linear plots, are shown in Figures 15 and 16. The values of the monomer reactivity ratios obtained by the least squares analysis of the Fineman-Ross plot are r_1 (methyl methacrylate) = 0.44 and r_2(p-isopropylstyrene) = 0.39. The Q and e values for p-isopropylstyrene calculated by Alfrey-Price equations using the above monomer reactivity ratio values are $Q = 1.1$ and $e = -0.9$. These values are in the same range as those for p-methylstyrene ($Q = 1.05$, $e = -0.9$).[15] These results together with those for the copolymerization of methyl methacrylate and p-divinylbenzene indicate that both of p-divinylbenzene and p-isopropylstyrene are more reactive toward the methyl methacrylate radical than methyl methacrylate. The results clearly suggest that the pendant vinyl groups (p-isopropylstyrene-like units) in the copolymer chain of methyl methacrylate and p-divinylbenzene will take part in the subsequent chain reactions even in the early stages of the reaction and that a copolymer with much local clustering of p-divinylbenzene units will be produced as in the copolymerization of styrene and p-divinylbenzene.

Table 10. Copolymerization of Methyl Methacrylate(M_1) with p-Isopropylstyrene

	Monomer Feed							Copolymer Composition		
No.	M_1, g.	M_2, g.	Molar ratio M_1/M_2	Conv. %	Sample wt., mg.	Charge time, sec[a]	Charge mv.	Spec. chg. rate mv./sec./mg[c]	m_1 wt. %[b]	Molar ratio m_2/m_1
1.[d]	1.98845	0.78977	3.6773	3.51	7.93	543.99	8000	1.8307	60.43	0.4483
					12.93	327.84	8000	1.8726		
2.[d]	1.98845	0.78977	3.6773	3.35	9.82	435.36	8000	1.8520	60.44	0.4483
					8.71	490.28	8000	1.8517		
3.	0.72210	0.64345	1.6391	2.60	7.42	218.68	2400	1.4536	47.67	0.7516
					4.62	344.35	2400	1.4677		
4.	0.60373	0.70438	1.2518	2.99	7.21	246.07	2400	1.3266	44.00	0.8715
					6.32	271.31	2400	1.3698		
5.	0.45655	0.93177	0.71564	3.28	5.87	353.40	2400	1.1247	36.74	1.1789
					8.25	253.04	2400	1.1267		
6.	0.31075	0.95468	0.47541	2.97	5.96	409.08	2400	0.95268	31.09	1.5172
					6.83	358.37	2400	0.95287		

[a] Average of 4-8 readings.

[b] Average of two determinations

[c] Deviation: average, ± 0.55 %; maximum, ± 1.6 %. Background, 0.18895 mv./sec..

[d] A monomer mixture was divided into two portions.

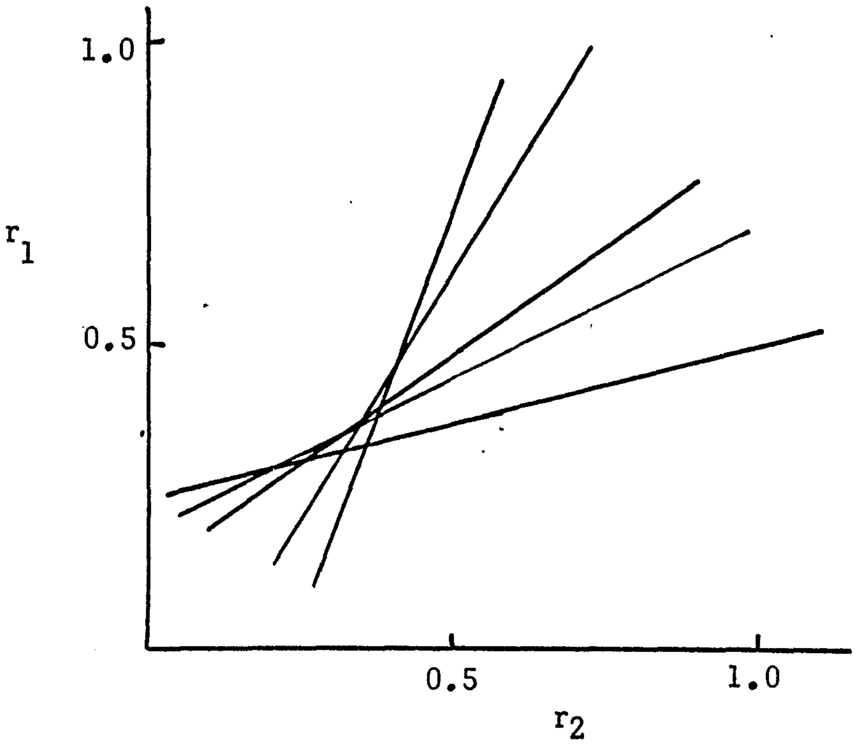


Figure 15. Intersect plot for Copolymerization of Methyl Methacrylate (r_1=0.42) and p-Isopropylstyrene (r_2 = 0.38) at 70°C.

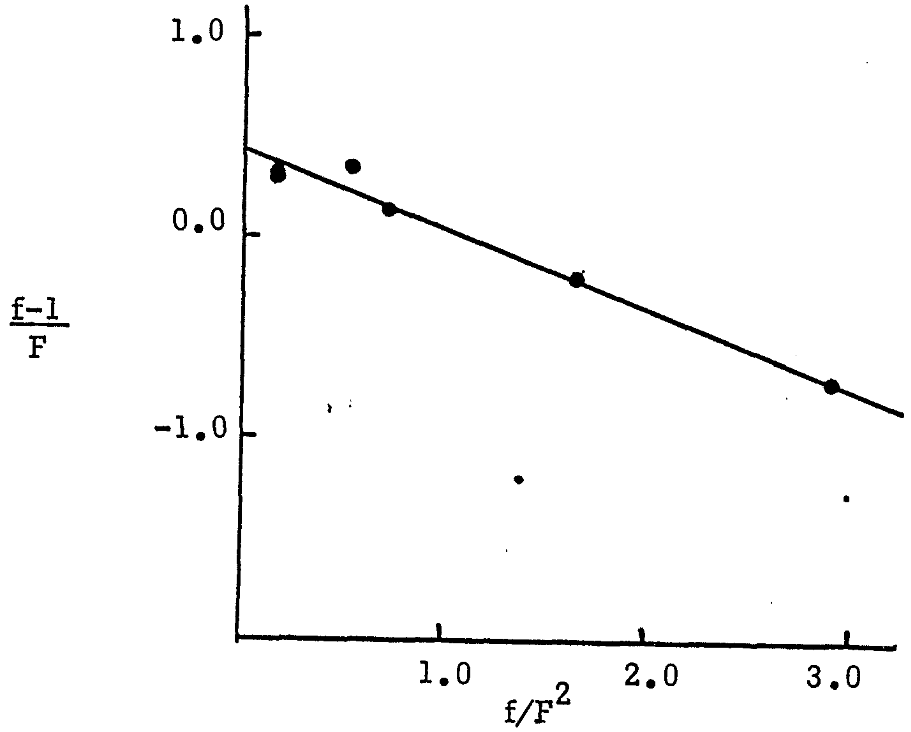


Figure 16. Fineman-Ross plot for Copolymerization of Methyl Methacrylate (r_1 = 0.44) and p-Isopropylstyrene (r_2=0.39).

Using the monomer reactivity ratios for the copolymerizations of p-divinylbenzene, m-divinylbenzene, and p-isopropylstyrene with methyl methacrylate one can compare the structural differences of the copolymers formed from each copolymerization by statistical considerations. As mentioned earlier in the "Historical" section the fraction of the copolymer existing in blocks of n-monomer units long can be calculated using equation (25). Such calculations for the monomer M_2's (p-divinylbenzene, m-divinylbenzene, and p-isopropylstyrene) were carried out for the above three copolymers using the observed monomer reactivity ratios and are represented in Figure 17. The number on each line denotes the experiment number used for these calculations, which is the same as the number represented in the Table for each copolymerization. For the methyl methacrylate-p-divinylbenzene system the values of $r_1 = 0.62$ and $r_2=1.30$ were used for this calculation. This figure shows that, as the number of units of monomer 2 in a row, n, increases, the fraction of methyl methacrylate - p-divinylbenzene copolymer existing in n long blocks of monomer 2 (p-divinylbenzene) decreases much more slowly than that of methyl methacrylate-m-divinylbenzene copolymer existing in n long blocks of monomer 2(m-divinylbenzene) does. The fraction of methyl methacrylate-m-divinylbenzene copolymer existing in n blocks of monomer 2 (m-divinylbenzene), in turn, decreases more slowly as n increases than that of methyl methacrylate-p-isopropylstyrene copolymer existing in n long blocks of monomer 2 (p-isopropyl-

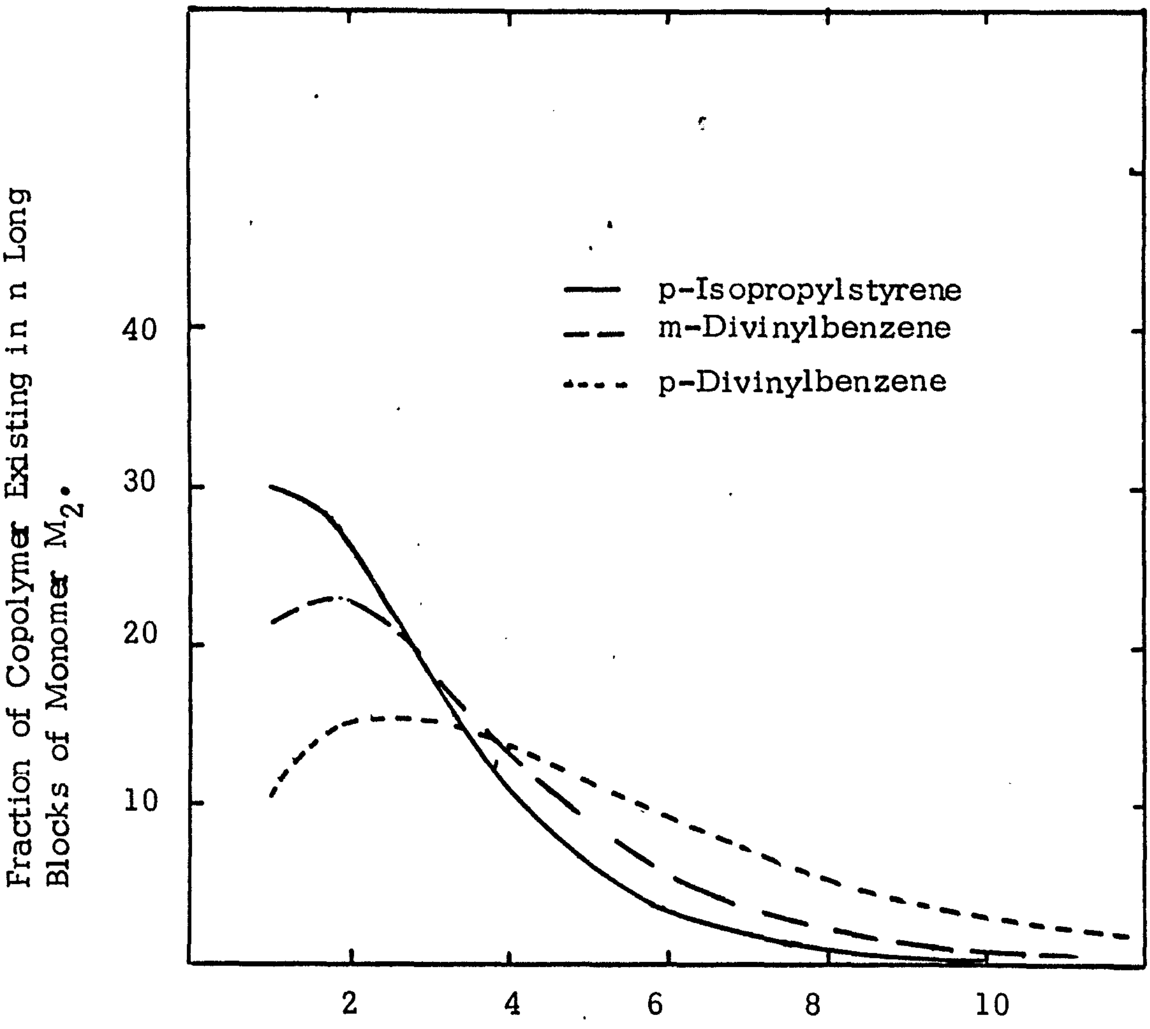


Figure 17. Fraction of Copolymer Existing in n Long Blocks of Monomer M_2.

styrene) does. In other words, one has the greatest probability to have longer blocks of M_2 (p-divinylbenzene) in methyl methacrylate-p-divinylbenzene copolymer and the least in methyl methacrylate-p-isopropylstyrene copolymer.

It must be noted that the monomer feed compositions, M_2/M_1, used for these calculations are slightly different from one another, and the magnititude of this value is smallest for the copolymerization with p-divinylbenzene and largest for the copolymerization with p-isopropylstyrene. If the same M_2/M_1 values were used for this comparison, the differences between these three copolymers would be more favorable for the conclusion drawn above--i.e., a greater fraction of p-divinylbenzene copolymer, but a smaller fraction of p-isopropylstyrene copolymer would be predicted to have longer blocks of M_2 (p-divinylbenzene or p-isopropylstyrene).

In addition, one can compute the mean length of the sequences of each monomer and the sequence-length distribution of each monomer in the copolymer formed from the monomer feed composition and the monomer reactivity ratios using the equations of Miller and Nielson.[56] These equations are:

$$\bar{n}_i = \frac{r_i M_i + M_j}{M_j}$$

$$W(n_i) = \left(\frac{r_i M_i}{r_i M_i + M_j}\right)^{n_i - 1} \frac{M_j}{r_i M_i + M_j}$$

where $\bar{n}_i$ is the mean length of the sequences of monomer i, M_i and M_j are the initial molar concentrations of monomers i and j respectively, r_i is the monomer reactivity ratio for monomer i, $W(n_i)$ is the probability that a sequence of monomer i contains exactly n_i units of monomer i.

The results of such calculations for the three copolymerizations are shown in Figures 18 and 19. Figure 18 indicates how the mean length of the sequence of M_2 changes as the mole fraction of M_2 in the feed increases and shows that the mean length of the sequence of p-divinylbenzene in the methyl methacrylate-p-divinylbenzene copolymer increases fastest and that of p-isopropylstyrene in the methyl methacrylate-p-isopropylstyrene copolymer increases most slowly. For any arbitrarily chosen mole fraction of M_2 in feed (e.g. 0.6) the mean length of the sequence of p-divinylbenzene is always longest (approximately 3) and that of p-isopropylstyrene is always shortest (about 1.5) in their copolymers with methyl methacrylate. And the mean length of m-divinylbenzene is always in-between those for the other two copolymers, e.g., approximately 2 when the mole fraction of meta-divinylbenzene in the feed is 0.6.

Figure 19 shows what fraction of M_2 (para-divinylbenzene, m-divinylbenzene, or p-isopropylstyrene) in the copolymer has the sequence length of n. The data from the three copolymerizations, which were used for the calculations for Figure 17, were used for

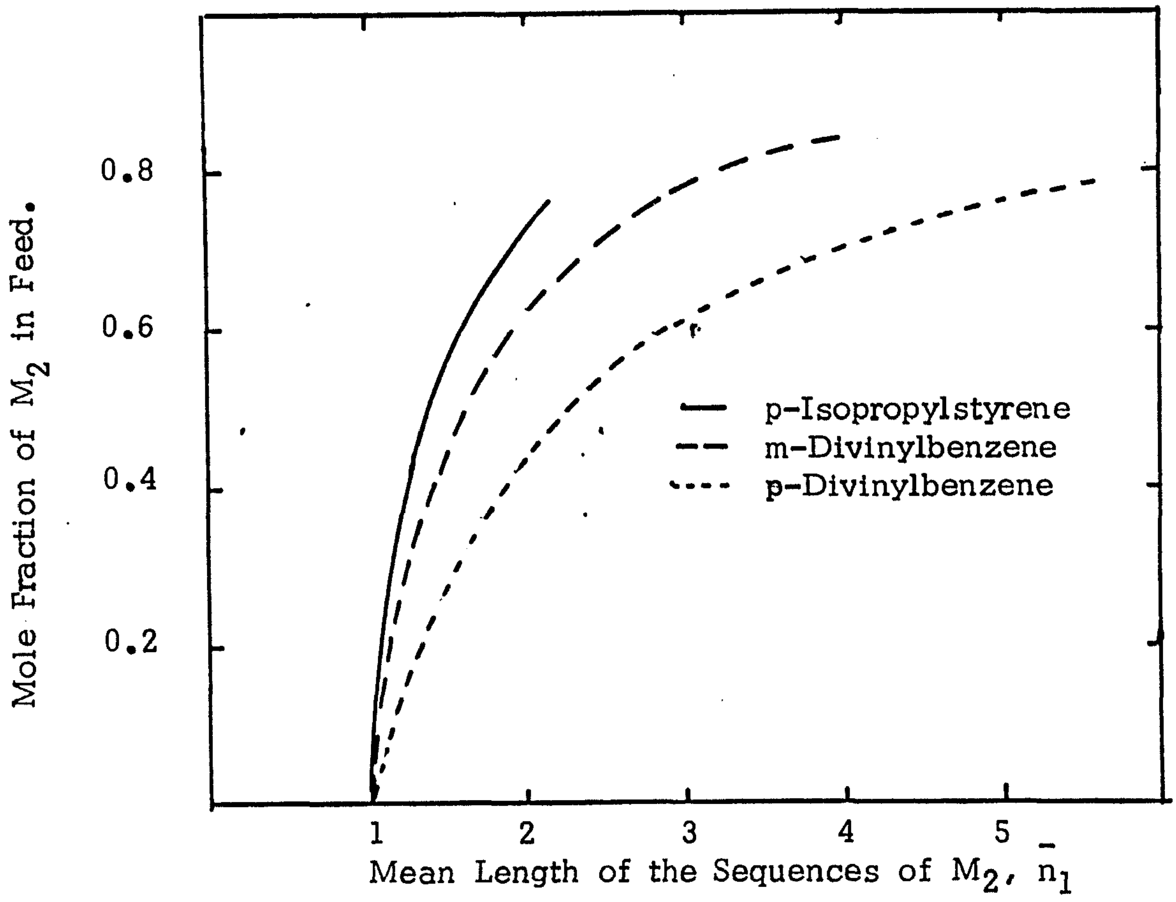


Figure 18. Dependence of Mean Length of the Sequence of M_2 on its Mole Fraction in Feed.

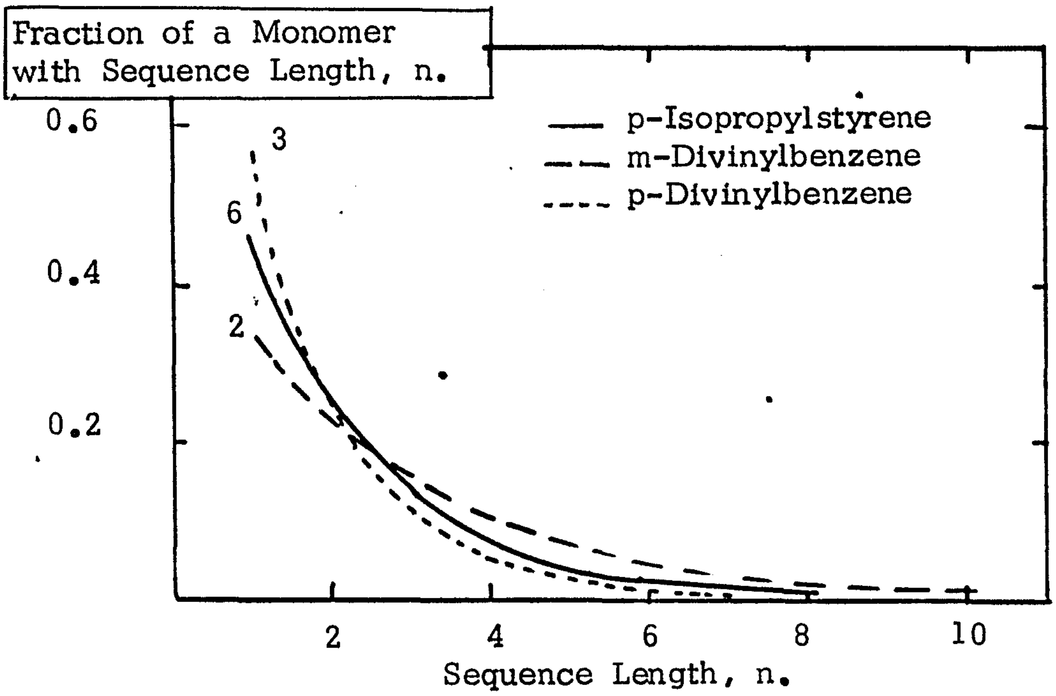


Figure 19. Sequence Length Distribution in Copolymers.

this representation. This Figure also shows that a higher fraction of p-divinylbenzene in its copolymer with methyl methacrylate has longer sequence length than that of meta-divinylbenzene in its copolymer with methyl methacrylate does, and that the latter, in turn, has longer sequence length than that of p-isopropylstyrene in its copolymer with methyl methacrylate.

All of these statistical considerations are considered to support the conclusions that the copolymerization of methyl methacrylate and p-divinylbenzene produces the copolymer with most clustering of the divinylbenzene, and that methyl methacrylate-p-isopropylstyrene copolymerization gives the most alternating copolymer. It is also indicated that there is more clustering of the divinyl units in the para than in the meta-divinylbenzene copolymers. This is consistent with various previously reported physical data[41,42] characterizing the two types of polystyrene crosslinked with meta- and para-divinylbenzene and with recently reported mass spectrometric analyses of the copolymers.[43]

Summary

The monomer reactivity ratios for four monomer pairs involving methyl methacrylate and divinylbenzene monomers have been determined using the vibrating reed electrometer-ionization chamber technique..

By the use of the revised copolymer composition equation for divinyl monomers, it has been confirmed that m-divinylbenzene functions essentially as a symmetrical independent divinyl monomer, for which the reactivity ratios are not greatly different from those for the methyl methacrylate: styrene system. The obtained values of r_1=0.41 and r_2 = 0.61 also suggest that this divinyl monomer produces rather homogeneous crosslinkings.

Results obtained for the copolymerization of methyl methacrylate and p-divinylbenzene have substantiated the fact that the behavior of the latter compound is rather unpredictable, leading to a nonhomogeneous copolymer in which the crosslinkages do not show a uniform distribution. No satisfactory values of the reactivity ratios for this monomer pair could be obtained, although it appears that the values of r_1 = 0.62 and r_2 = 1.30 are reasonable ones. The copolymerization of styrene and p-isopropylstyrene gave monomer reactivity ratios of r_1 = 1.22 and r_2 = 0.89. These values indicate that p-isopropylstyrene, which is a similar unit to that formed from having one vinyl group of p-divinylbenzene reacted, is slightly less reactive than styrene, and indicate that the styrene-p-divinylbenzene copolymerization system

should be regarded as a three component copolymerization system as suggested earlier.

The monomer reactivity ratios obtained for the copolymerization of methyl methacrylate and p-isopropylstyrene are $r_1 = 0.44$ and $r_2 = 0.39$. These values suggest the possible participation of the pendant vinyl group of the p-divinylbenzene copolymer in the subsequent chain reactions even in the early stages of the copolymerization.

Structural differences between the three methyl methacrylate copolymers were studied by statistical considerations using the obtained reactivity ratio values for the above mentioned three copolymerizations. The results show that there is the greatest probability for longer blocks of monomers (least alternating structure) in p-divinylbenzene copolymer and the least (most alternating structure) in p-isopropylstyrene copolymer, The conclusions are consistent with the predictions by the magnititudes of the product r_1r_2 for the alternating tendencies of the copolymers.

Bibliography

1. B. M. Tolbert, U.S. Atomic Energy Commission Report, UCRL-3499, 1956.
2. R. H. Wiley and B. Davis, J. Polymer Sci., 46, 423 (1960).
3. O. Bayer, British Patent, 27,361 (1917).
4. H. Dostal, Monatsh., 69, 424 (1936).
5. F. T. Wall, J. Am. Chem. Soc., 63, 1862 (1941).
6. F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc., 66, 1594 (1944).
7. T. Alfrey, Jr., and G. Goldfinger, J. Chem. Phys. 12, 205 (1944).
8. F. T. Wall, J. Am. Chem. Soc., 66, 2050 (1950).
9. M. Fineman and S. D. Ross, J. Polymer Sci., 5, 269 (1950).
10. B. Davis, Ph. D. Thesis, University of Louisville, Louisville, Kentucky, 1962, Page 124.
11. D. R. Montgomery and C. E. Fry, J. Polymer Sci., C25, 59 (1968).
12. I. Skeist, J. Am. Chem. Soc., 68, 1781 (1946).
13. T. Alfrey, Jr. and G. Goldfinger, J. Chem. Phys., 12 322 (1944).
14. C. Walling and E. R. Briggs, J. Am. Chem. Soc., 67, 1774 (1945).
15. T. Alfrey, Jr., J. J. Bohrer, and H. Mark, Copolymerization, Interscience Publishers, Inc., New York, 1952.

16. R. H. Wiley and E. E. Sale, J. Polymer Sci., 42, 491 (1960).

17. R. H. Wiley and B. Davis, Polymer Letters, 1, 463 (1963).

18. R. H. Wiley, W. K. Mathews, and K. F. O'Driscoll, J. Macromol. Sci. (Chem.), A1(3), 503 (1967).

19. C. Walling, E. R. Briggs, K. B. Wolfstim, and F. R. Mayo, J. Am. Chem. Soc., 70, 1537 (1948).

20. G. G. Carmeron, D. H. Grant, N. Grassie, J. E. Lamb, and I. C. McNeill, J. Polymer Sci., 36, 173 (1959).

21. K. R. Hennery-Logan and R. V. V. Nichols, in F. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

22. R. Simha and L. A. Wall, J. Research Natl. Bur. Standards, 41, 521 (1948).

23. C. M. Marvel, G. E. Inskeep, R. Deaning, D. Hein, P. V. Smith, J. D. Young, A. E. Juve, C. H. Schroeder, and M. M. Godd, Ind. Eng. Chem., 40, 2371 (1948).

24. R. D. Gilbert and H. L. Williams, Can. J. Chem., 30, 4114 (1952).

25. F. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

26. P. D. Bartlett and K. Nozaki, J. Am. Chem. Soc., 68, 1495 (1946).

27. W. Barb, Trans. Faraday Soc., 49, 143 (1953).

28. G. B. Butler and K. C. Joyce, J. Polymer Sci., C22, 45 (1968).

29. T. Alfrey, Jr. and C. C. Price, J. Polymer Sci., 2, 101 (1947).

30. M. G. Evans, J. Gergely, and E. C. Seaman, J. Polymer Sci., 3, 866 (1948).

31. K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura, and K. Fukui, J. Polymer Sci., 14, 312 (1954),

32. K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura, and K. Fukui, J. Polymer Sci., 20, 537 (1956).

33. T. Fueno, T. Tsuruta, and J. Furukawa, J. Polymer Sci., 40, 487, 499 (1959).

34. G. S. Levinson, J. Polymer Sci., 60, 43 (1962).

35. L. P. Hammett, Physical Organic Chemistry, Chapter 7, McGraw-Hill Book Co., New York, 1940.

36. R. H. Wiley, L. K. Heidemann, and B. Davis, Polymer Letters, 1, 521 (1963).

37. Y. Sakaguchi, Kobunshi Kagaku, 17, 333 (1960).

38. M. Berger, J. Polymer Sci., A1, 1601 (1963).

39. R. H. Wiley, T. H. Crawford, and N. F. Bray, Polymer Letters, 3, 99 (1965).

40. R. H. Wiley and T. O. Ahn, J. Polymer Sci., A6, 1293 (1968).

41. R. H. Wiley and T. K. Venkatachalam, J. Polmer Sci., A3, 1063 (1965); A4, 1892 (1966).

42. R. H. Wiley and F. E. Martin, J. Macromol. Sci. (Chem.) A1, 635 (1967).

43. R. H. Wiley and L. H. Smithson, Jr., J. Macromol. Sci. (Chem.), A2, 589 (1968).

44. R. H. Wiley and E. E. Sale, J. Polymer Sci., 42, 479 (1960).

45. R. H. Boundy and R. F. Boyer, Styrene, Page 57, Reinhold Publishing Corp., New York, 1952.

46. T. K. Venkatachalam, Ph. D. Thesis, University of Louisville, 1965.

47. R. T. Overman and H. M. Clark, Radioisotope Techniques, McGraw-Hill, New York, 1960.

48. Belstein, 9, 629.

49. R. H. Wiley et al, J. Phys. Chem., 68, 1776 (1964).

50. J. D. Matlack, S. N. Chinai, R. A. Guzzi, and O. W. Levi, J. Polymer Sci., 49 533 (1961).

51. J. B. Niederl and V. V. Niederl, Organic Quantitative Microanalysis, John Wiley & Sons, Inc., New York, 1948.

52. R. H. Wiley and B. Davis, J. Polymer Sci., 62, S132 (1962).

53. B. T. Storey J. Polymer Sci., A3, 265 (1965).

54. P. Braun and H. G. Keppler, Macromol. Chem., 78, 100 (1964).

55. D. E. Montgomery and D. C. Fry, J. Polymer Sci., C25, 59, (1968).

56. R. L. Miller and L. E. Nielson, J. Polymer Sci., 46, 303, (1960).

PART II

KINETICS OF SULFORATION OF POLYSTYRENE CROSS-LINKED WITH MIXTURES OF DIVINYLBENZENES

Introduction

One of the most widely used crosslinking reagents for the preparation of crosslinked copolymers is divinylbenzene. Various sulfonated polystyrenes crosslinked with divinylbenzene have been used as cation exchange resins. In order to investigate the structure of these resins kinetic studies for the copolymerization reactions of divinylbenzene isomers, measurements of swelling ratios[1] and sulfonation velocities of the crosslinked bead copolymers,[2] mass spectral study of the bead copolymers,[3] and studies on the degradation velocities of copolymers[4] and sulfonated bead copolymers[5] have been carried out in this laboratory earlier.

In earlier studies it was found that the polystyrene beads crosslinked with 2 : 1 mixture of meta- and para-divinylbenzene show an enhanced sulfonation rate as compared to those of the copolymer beads crosslinked with pure para-, and pure meta-, and commercial divinylbenzene.

To delineate the precise relation between the sulfonation velocity and meta to para ratio of these divinylbenzenes, quantitative comparisons were made of the rates of sulfonation of a series of bead copolymers prepared from styrene and divinylbenzene in which the meta to para ratio of the two isomers was varied over the entire range.

In addition, a new method for the preparation of more concentrated para-divinylbenzene from commercial divinylbenzene, which consists of several monovinyl and divinylbenzenes along with other compounds, is described.

Historical

In this section a short historical review of synthetic ion exchange resin chemistry and of earlier related experimental studies are described to provide a background for the experimental studies and discussions in the later sections.

An ion exchange resin is a high molecular weight polymer containing chains of atoms tied together by crosslinking chemical structures. Such resins also have ionic groupings as integral parts of the polymer structure and these exchange either cations or anions on contact with an electrolyte solution.

Ion exchange resins are essentially highly insoluble electrolytes consisting of an enormous nondiffusible ions and many simple diffusible (or exchangeable) counter-ions. Cation exchange resins and anion exchange resins are defined as polymers containing anionic groups and cationic groups, respectively, with equivalent amount of exchangeable ions of opposite charge.

The cation exchange resins usually contain phenolic, carboxylic, sulfuric, or phosphoric acid groups as non-diffusible ionic groups; the anionic exchange resins contain quaternary ammonium, sulfonium, or phosphonium basic groups as non-diffusible groups; and amphoteric exchangers contain both types of ionic groups as non-diffusible ones.

Although ion-exchange phenomena have been used throughout human history, the phenomenon was not recognized until Thompson[6] and Way[7] in England investigated the fate of ammonia in soils. They noted that when fertilizer was applied to soils, the ammonia was absorbed by the soil in exchange for the potassium and calcium already present on the soil particles. In 1876 Lemberg[8] found that it was possible to transform the mineral leucite ($K_2O \cdot Al_2O_3 \cdot 4SiO_2$) into analcite ($Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$) by leaching the mineral with a solution of sodium chloride, and that the transformation could be reversed by treating the analcite with a solution of potassium chloride. The research done by Way and Lemberg stimulated many soil scientists and geochemists. However, it was not until the beginning of the twentieth century that ion exchange was used for industrial water softening. Gans[9] employed both natural and synthetic aluminum silicate for industrial water softening and also for treating sugar solutions. However, the limitations of siliceous ion exchangers became more and more evident as commercial exploitations of these substances were attempted.

In 1935 Adams and Holmes[10] observed that certain synthetic resins were capable of exchanging ions. They further illustrated that stable and high-capacity cation exchangers could be synthesized as a sulfonic acid resin, and that the polyamine-type resins exhibited anion exchange properties. The utility of these resins was rapidly recognized by many chemists, with the result that a large number of new and unique uses were found for ion exchange and many attempts were made to modify and improve these resins.

For resins to be useful in an ion exchange process, it must be sufficiently hydrophilic to permit diffusion of ions through the structure at a finite and usable rate and be sufficiently crosslinked to have but a negligible solubility in water or other solvents.

Other important practical requirements are: 1)the resin must contain a sufficient number of accessible ionic exchange groups, 2) the structure of the resin must be chemically stable so as not to undergo degradation during use, and 3) the swollen resin should be denser than water.

There are two synthetic methods to introduce the ionizable groups (cationic or anionic) into the monomers of the ion exchange resins. The first method is to form a polymer unit first and then to introduce the ionic groups into the polymer structure. The second method consists of introduction of the ionic groups into the monomer first and then subsequent polymerization of these ionic group containing monomers.

Ion exchange resins have been made by both the condensation and addition polymerization methods. The phenol-formaldehyde resin is a typical example of a condensation type of polymers used for ion exchange resins and polystyrene crosslinked with divinylbenzene is the most commonly used addition type polymer.

The pioneering work of Adams and Holmes was followed by the stimulating discoveries of D'Alelio[11] who synthesized the extremely stable and versatile ion exchange resins derived from styrene and acrylics. D'Alelio took the first patent on the synthesis of high capacity nuclear sulfonic acid cation exchange resins by the sulfonation with sulfuric acid of the copolymers prepared from a mixture of styrene and divinylbenzene. It is necessary to mention that the divinylbenzene used in all the preparations of the resins was commercial material, which is a mixture of different components. As mentioned above, two methods can be used in the preparation of sulfonated copolymer from styrene and divinylbenzene. One is the copolymerization with one of comonomers containing sulfonic acid groups, usually para-divinylbenzenesulfonic acid. The other method is to sulfonate the copolymer prepared from a mixture of styrene and divinylbenzene and this was followed in the present work.

Wiley and coworkers[2] recently found that the polystyrene beads crosslinked with pure para-divinylbenzene sulfonated faster than did those crosslinked with pure meta-divinylbenzene. They explained this phenomenon on the basis of the network structure of the copolymers and concluded that the copolymerization of styrene with para-divinylbenzene gives a structure with a tightly crosslinked nucleus to which long chains of polystyrene are attached, and the copolymerization of styrene with meta-divinylbenzene give a structure in which the crosslinks are more widely distributed than in the styrene-para-divinylbenzene copolymer. In addition, the copolymer beads prepared from styrene and a mixture of 2:1 meta- and para-divinylbenzene showed markedly enhanced rates of sulfonation. They[1] also correlated the swelling ratios of the copolymer beads with the possible net-work structures thereof.

The fact that over a period of approximately thirty years the utilization of ion exchange resins for separations, recoveries, deionizations, catalyses, as well as for water softening on an industrial scale, has become a reality illustrates the importance of these resins and is indicative of the future usefulness that may be expected of them.

Experimental

Monomers

Styrene was supplied by Baker Chemical Co. and was stabilized with tert-butylpyrocatechol. This was washed four times with 1 N. sodium hydroxide solution and four times with distilled water. The washed styrene was dried over calcium chloride under a nitrogen atmosphere and vacuum distilled over a potassium hydroxide pellet in which only the middle fraction, n_D^{20} 1.5467 (Literature value,[12] 1.5465), was collected and used for the preparation of the copolymer beads.

The meta-divinylbenzene used for this work was prepared by the preparative gas chromatographic method in the manner described in the first part of this thesis.[13] A quantity of prepared meta-divinylbenzene which had been stabilized with a small amount of inhibitor under nitrogen and kept at - 10°C was washed three times with 1 N. sodium hydroxide solution and with distilled water, dried over calcium chloride, and vacuum distilled over one or two pellets of potassium hydroxide to insure the complete removal of inhibitor from the monomer. Only the middle traction, b.p. 34°C/ 1mm., n_D^{24} 1.5755 (Literature values,[1, 14] 34°C/1mm., and 1.5754), was collected and used for the preparation of the copolymer beads.

para-Divinylbenzene was isolated from commercial divinylbenzene, which is a complex mixture of meta- and para-ethylvinylbenzene, meta- and para-divinylbenzene, with traces of naphthalene and indene,, by complexing with cuprous chloride.[15, 16, 17] The procedures are as follows:

One hundred grams of commercial divinylbenzene (supplied by Dow Chemical Co. with para-divinylbenzene content of 20.5%) was placed in a 400 ml. beaker and was cooled to between 0 and 5°C. A 30 g. portion of anhydrous cuprous chloride (Baker Analyzed Reagent) was added slowly with continuous stirring. As the slurry became viscous small quantities of toluene were added (total about 50 ml.) to render the slurry mobile. After stirring for 30 minutes the yellow solid complex was collected on a Buchner funnel with suction. The solid was reslurried with 100 ml. of toluene cooled to between 0 and 5°C and was again collected. The toluene washing was repeated twice more. Finally the solid was suspended in 100 ml. of toluene and was decomposed by heating to 80°C. The grey slurry was filtered hot and the cake of cuprous chloride was washed with hot toluene. The toluene was separated from the combined filtrate and washings by fractionation under vacuum. Before fractionation of toluene a small quantity of di-tert-butyl-para-cresol was added to the mixture of filtrate and washings. The residue was then vacuum distilled to give 12 to 13 g. (60 to 65% yield) of para-divinylbenzene. With 10 g. of commercial divinylbenzene, twice complexed, the yield was 40 to 50%. The para-divinylbenzene thus obtained was found to be 80 to 90% pure in a series of three check runs. For further purification, this para-divinylbenzene was partially crystallized by cooling to 5°C, and the unfrozen liquid was decanted. The remaining solid crystals (5.8 g. from 13.2 g.) were 96.5% pure.

Further purification by one preparative gas chromatographic separation on a Bentone column, a method used for the preparation of pure para-divinylbenzene in the previous work,[13] gave material of 99.5+% purity in 40% yield. If the uncrystallized 80 to 90% purity material is chromatographed directly, it must have been passed through the column at least twice to get a purity of 99+% with considerably less favorable yield. The purity of the samples was calculated from the relative peak areas of the analytical chromatograms which were obtained by using a Perkin-Elmer vapor fractometer, Model 154D with an R (Poly(propylene glycol) on Chromosorb-W) column and a flame ionization detector. para-Divinylbenzene prepared by the above method was vacuum distilled under nitrogen over potassium hydroxide pellets and the material used for this work had m.p. 30°C, n_D^{35} 1.5856 (Literature values,[1,14] 29.5 - 30°C and 1.5857) and was found to be 99.5+% pure by gas chromatographic analysis.

Initiator

Solid benzoyl peroxide was used as the initiator throughout this work and was purified by precipitation from a concentrated chloroform solution. Benzoyl peroxide was supplied by Fisher Scientific Co.. Purified benzoyl peroxide was dried under vacuum very carefully at room temperature.

Dispersion Agent

Carboxymethyl cellulose ether sodium salt, supplied by Matheson Coleman & Bell (99.5 % pure in dry base; premium refined grade), was used as such without further treatment.

Preparation of Copolymer Beads

One gram of carboxymethyl cellulose ether sodium salt was dissolved in 250 ml. of distilled water with vigorous stirring. This dispersion solution was introduced into a 500 ml., 3-neck round bottomed flash half immersed in an oil bath maintained at 80^{o}C. The flask was fitted with a nitrogen inlet, an air condenser, and a "V" shaped stirrer. The solution was stirred under a nitrogen blanket with a stirrer which was powered by a Thyratron controlled motor running at a constant speed of about 300 r.p.m. until the solution attained thermal equilibrium with the bath.

After stopping the stirring, the mixture of monomer and solid benzoyl peroxide (0.1% by weight of monomer mixture) was added to the suspension solution. The stirring was then resumed and the copolymerizations were allowed to proceed for twenty hours. At the end of this time the milky emulsion was transferred to a 2 liter beaker and one liter of distilled water was added to this mixture. This was thoroughly mixed. Next, the emulsion was decanted and the beads were washed several times with distilled water to wash off all the dispersion agent and remove imperfect beads. The wet beads were then sieved through a set of 10, 20, 30, and 40 mesh standard screens under a constant flow of distilled water. These beads on the screens were washed with distilled water three or four times. Then the beads were dried at 80°C for 40 minutes on the specific screens. The dried beads were transferred from the sieves after cooling and bottled separately according to their mesh sizes. The copolymerizations were carried out by using 8 mole % of the cross-linking agent, a mixture of meta- and para-divinylbenzene, in which the meta/para ratio of the two isomers was varied over a range from 4 to 22%. The monomer feed composition for the bead copolymerizations are given in Table 1.

Measurement of the Rate of Sulfonation

Copolymer beads only in the 20 - 30 mesh range were used for studying the rate of sulfonation. About 5 g. of the copolymer beads were preswollen in 100 ml. of distilled ethylene dichloride (Fisher Certified Reagent) overnight, and the excess ethylene dichloride was removed by vacuum filtration on a sintered glass Buchner funnel. Twenty milliliter of concentrated sulfric acid prepared from 8 parts of 97.5% sulfuric acid (Baker Chemical Co.) and 1 part of 30% fuming sulfuric acid (Fisher Scientific Co.) was used to flush the swollen beads through a wide, long-stemmed funnel into a 250 ml., 3-neck round bottomed flask to which 130 ml. of the same acid had been added and maintained at a constant temperature of 80°C in an oil

Table 1.

Composition for Bead Copolymerizations

Exp.No.	Wt. of p-DVB,g.	Wt. of m-DVB,g.	Tot.wt. DVB,g.	Wt. of Styrene,g.	Wt. % of p-DVB
1.	0.0	1.6780	1.6780	15.4867	0.0
2.	0.2113	1.5714	1.7827	16.4005	11.85
3.	0.3624	1.4011	1.7635	16.2239	20.55
4.	0.3998	1.2009	1.6007	14.7262	24.98
5.	0.4626	0.7470	1.2096	11.1281	38.24
6.	0.7748	1.0542	1.8290	16.8265	42.36
7.	0.9646	0.8556	1.8202	16.7455	52.99
8.	1.1297	0.6530	1.7827	16.4014	63.37
9.	1.4402	0.2463	1.6865	15.5155	85.40
10.	1.4815	0.0	1.4815	13.6087	100.00

bath. The flask was half immersed in the bath and was fitted with a stirrer, a stopper and an air condenser closed with a silica gel drying tube. When all the beads were in the acid, stirring was started and the speed of stirring was so regulated to ensure that the beads were uniformly dispersed in the acid medium. Approximately the same speed was maintained in the sulfonations of different samples. Bead samples were taken out at a regular time intervals and washed with decreasing strengths of sulfuric acid as previously described by Wiley and Venkatachalam.[2] The sulfonated beads were finally washed several times with distilled water until the washings were free from any acid. The beads were then allowed to stand in distilled water overnight, at the end of which they were washed two or three times more with distilled water.

The rate of sulfonation was followed by determining the total capacity of the beads for different time intervals by the salt splitting method[18] as follows: The washed sulfonated beads were dried in a vacuum oven at 80°C for five days to a constant weight. After cooling, about 0.2500 g. of the dried beads were weighed quickly and added to a 250 ml. beaker containing 100 ml. of 0.02 N. potassium chloride. The mixture was stirred magnetically for one hour to achieve complete equilibrium. The liberated acid was then titrated against 0.1000 N. sodium hydroxide solution to an end point of pH 7. During the titration the reaction mixture continuously was

Table 2.

Rates of Sulfonation[a] of Polystyrene Crosslinked with 8% of para- and meta-Divinylbenzene Mixture.

Exp.No. Tim,min.	1	2	3	4	5	6	7	8	9	10
20			1.09	1.01						
30					1.51					0.16
50			2.57	2.99						
60					3.32	0.80	0.78	0.68	1.35	0.57
80				4.73						
90			4.39		5.08	1.78				
120	0.40		5.23	5.18	5.25		1.87	1.93	2.67	1.13
150					5.41	3.10		2.30		
180		1.28					2.57		4.09	
210		1.55				4.11		3.08		2.35
240	0.75								5.25	
270		1.93				5.49		4.22		
300										3.57
330							4.89			
360	1.15									
420		3.28								
540	2.08									

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[a] Capacity in milliquivalent per gram is tabulated.

being stirred magnetically. The pH was followed with a pH meter. The capacity as milliequivalents per gram of dry beads was calculated using the following formula:

$$\text{Total Capacity} = \frac{\text{ml. of NaOH soln. x N. of NaOH soln.}}{\text{grams of dry sample}}$$

The capacities at different time intervals of each sulfonated copolymer are shown in Table 2.

Results and Discussion

As mentioned in the previous part of this thesis, the structures of copolymers obtained from the copolymerizations of styrene with chemically pure isomeric divinylbenzenes are likely to be different because of their different characteristics in the copolymerizations. If this is the case, one should expect that the polystyrenes cross-linked with a mixture of meta- and para-divinylbenzene would be different from those crosslinked solely with meta- or para-divinylbenzene, and that polystyrenes crosslinked with various ratio of meta and para isomer also would be different from one another in their structures. It has been shown[2] that the measurement of the rates of sulfonation of polystyrene beads copolymerized with divinylbenzenes, a method which is based on the increase in the capacity of the sulfonated beads with sulfonation time, enables one to compare the structural differences between the beads copolymers. Hence, it is not unreasonable to expect that the rates of sulfonation of bead copolymers prepared from styrene and divinylbenzene mixture in which the ratio of the two isomers varies may also differ. Using concentrated sulfuric acid[11] is one of the simplest methods to sulfonate these bead copolymers. The preswelling of the beads is necessary. It greatly accelerates sulfonation because it loosens the chains. Since the sulfonation of these copolymer beads has been reported to proceed from the outer surface toward the center, care was taken to have a uniform stirring speed throughout the entire series of experiments.

The data in Tables 1 and 2 are represented in Figure 1 where capacities were plotted against time of sulfonation and the number on each line refers to the experiment number given in Table 1 or 2. The data show that the polystyrene beads crosslinked with 8 mole % of divinylbenzene have markedly different rates of sulfonation as the meta to para ratio of the two isomers varies. For example, the beads crosslinked with 63% p-divinylbenzene in the 8 mole % of divinylbenzene have the low capacity of 1.93 meq./g. after two hours of sulfonation comparing to the corresponding value of 5.18 meq./g. observed for the beads crosslinked with 25% para isomer (in the mixture) in two hours of sulfonation. In order to see more clearly the changes in the sulfonation rates of the bead copolymers as the ratio of para and meta isomer varies, the initial slopes of the rate curves (in meq./g./hr.) are given in Table 3 and are represented in Figure 2. For compositions containing 20 to 40% of p-divinylbenzene, in the 8 mole % of divinylbenzene used as crosslinking agent, the rate of sulfonation is enhanced by a factor of up to four. Except for the copolymer beads crosslinked with pure meta-divinylbenzene, for which the rate of sulfonation is very low (about 0.2 meq./g./hr.), a variety of compositions, outside the 20-40% of p-divinylbenzene range, show sulfonation rates of 0.5 to 1.5 meq./g./hr.. For compositions containing 20 to 40% of p-divinylbenzene (in the 8 mole %

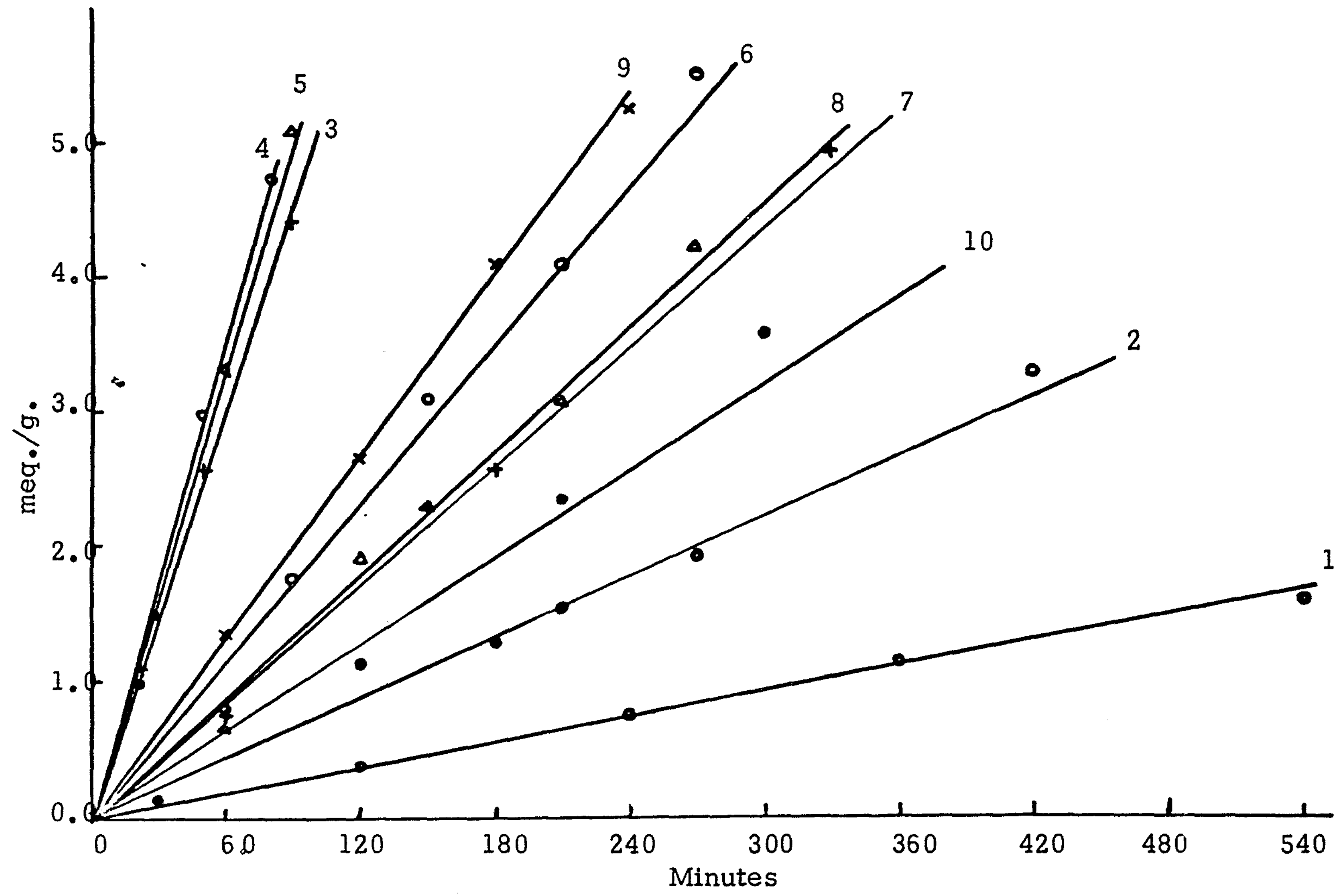


Figure 1. Rates of Sulfonation of Polystyrene crosslinked with Various Divinylbenzene Mixtures.

of divinylbenzene) the values are 2.8 to 3.9 meq./g./hr..

In addition, the data show that the copolymer beads crosslinked with 8 mole % meta-divinylbenzene have a much lower rate of sulfonation (0.21 meq./g./hr.) as compared to the rate of sulfonation of copolymer beads crosslinked with 8 mole % para-divinylbenzene (0.69 meq./g./hr.).

Since the monomer reactivity ratios give an indication of the propagation reactions taking place in the copolymerizations, the structural interpretation of the above results, obtained with pure para and pure meta isomers, can be explained by the differences in the values of the monomer reactivity ratios for the copolymerizations of styrene with these two isomeric divinylbenzenes. The monomer reactivity ratios for the styrene/divinylbenzene series[19] are r_1 (styrene) = $0.605/r_2$(meta) = 0.88 at lower (1.8 to 3.7%) conversions, r_1 (styrene) = $1.27/r_2$(meta) = 1.08 at higher (2.7 to 7.5%) conversions, and r_1 (styrene) = $0.77/r_2$(para) = 2.08. These values appear to suggest that the copolymerization of styrene with p-divinylbenzene results in a structure with a tightly crosslinked nucleus connected by long chains of polystyrene. In comparison, the styrene/m-divinylbenzene copolymer would be expected to have a structure in which the crosslinks are more widely distributed than in the styrene/p-divinylbenzene copolymer. And it has been shown[20] that the distance between the meta-crosslinking in divinylbenzene is smaller (5.5A°) than that between the para crosslinking (5.8A°). Thus it seems that meta

Table 3.

Rates of Sulfonation (meq./g./hr.) of Polystyrene Crosslinked with 8 mole % Mixture of m- and p-Divinylbenzene

Exp.No.	1	2	3	4	5	6	7	8	9	10
Wt.of p-DVB[a]	0.0	11.85	20.55	24.98	38.24	42.36	52.99	63.37	85.40	100.0
meq./ g./hr.	0.19	0.39	2.78	3.60	3.27	1.16	0.87	0.90	1.32	0.64

[a] Percentage of p-divinylbenzene in the 8 mole % of divinylbenzene mixture.

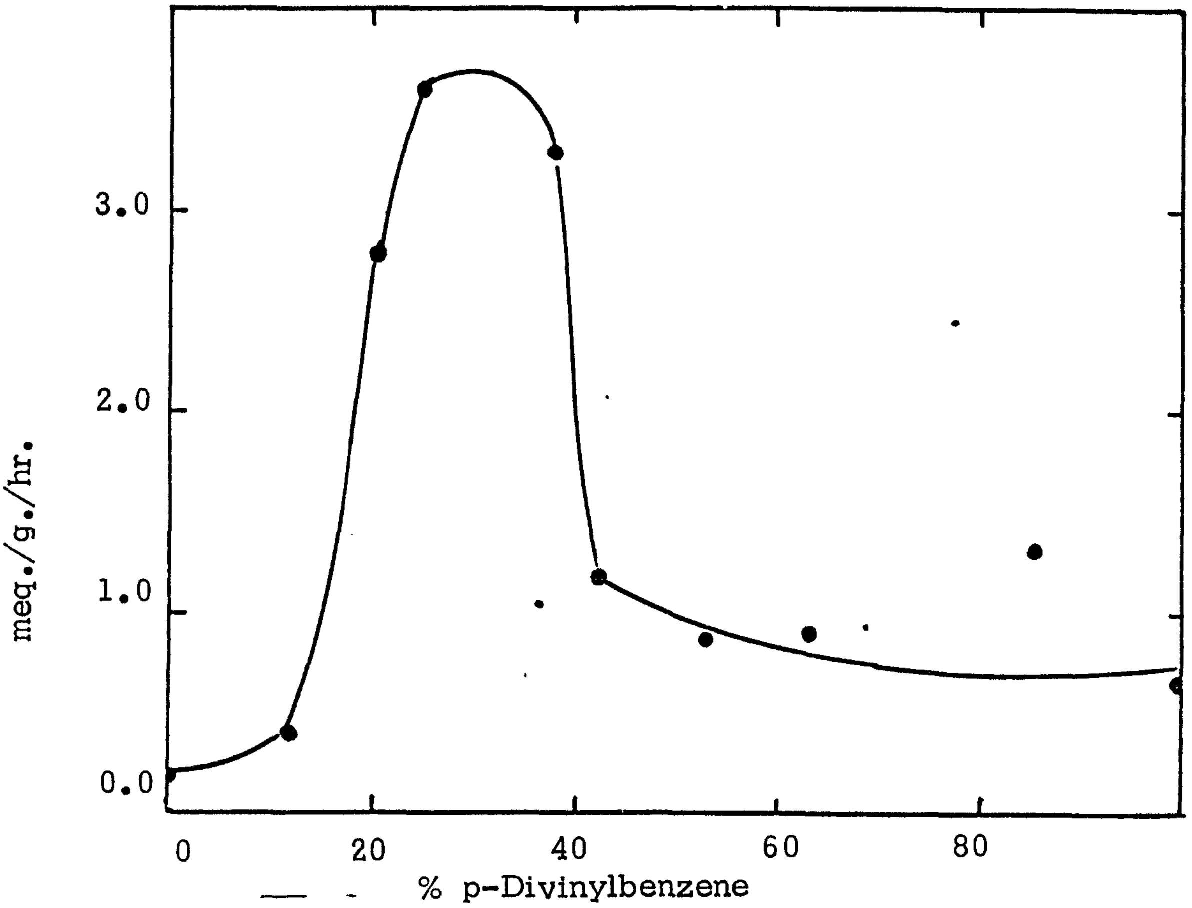


Figure 2. Rates of Sulfonation in meq./g./hr. of Copolymer Beads.

crosslinkages do not provide large enough holes for the sulfonating species (the exact nature of which is not known) to diffuse through. Therefore the meta crosslinked copolymer shows a lower rate of sulfonation compared to the para crosslinked copolymer beads.

Although it might be premature to describe the exact structures of the copolymer beads crosslinked with a mixture of meta- and para-divinylbenzenes without information about kinetic studies for the ternary copolymerization of these three (styrene and the two isomeric divinylbenzenes) compounds, the rates of sulfonations for these copolymer beads indicate that the primary gel network structure is different in these bead copolymers and that the structure formed from the mixture of 30% of p-divinylbenzene (70% meta isomer) is characteristically significant in determining a maximum for the rate of sulfonation. Presumably the interstices of the network in the copolymer beads crosslinked with divinylbenzene mixture of 30% para isomer are of the optimum size to allow access of the sulfonating species to the reacting benzenoid rings in the copolymer.

The following comments concern the isolation of para-divinylbenzene from commercial divinylbenzene by complexing with cuprous chloride as described in the "Experimental" section. Even today after decades of study, it cannot be said that pure para-divinylbenzene is readily available commercially. Techniques for the synthesis of pure para-divinylbenzene have been studied in detail. A useful method is decarboxylation of p-phenylene-β, β-diacrylic acid.[21] The uses of vapor phase chromatography in the separation and purifications of isomeric divinylbenzenes from commercial divinylbenzene also have been reported previously.[22,23] However, these methods are not practical because they are time-consuming and give low yields. In the synthetic methods the yields always were found to be around 30%. The preparative gas chromatographic separation of p-divinylbenzene requires at least two passes of the commercial divinylbenzene through the fractionation column to get pure monomer. This involves a considerable loss of material. Therefore, a possible new method of isolating p-divinylbenzene from commercial divinylbenzene has been studied. The use of complexes in the separation of hard to separate mixtures of aromatic compounds has been employed,[24, 25] and recently p-divinylbenzene was reported[15,16,17] to form a solid complex with cuprous chloride at an optimum ratio of 1:1 at 0-5°C. The possibility of using this complex formation to separate p-divinylbenzene from commercial divinylbenzene was investigated and convenient experimental procedures were described in the previous section. By this method one can easily get highly concentrated p-divinylbezene from commercial divinylbenzene. In order to obtain highly pure p-divinylbenzene (99.5 % or more) the concentrated sample need be passed only once through the vapor phase gas chromatograph.

Summary

The kinetic studies on the sulfonation of polystyrene crosslinked with 8 mole % divinylbenzene, in which the meta/para ratio of the two isomers was varied over the entire range, show that the rates of sulfonation of these beads are remarkedly sensitive to the isomeric (para/meta) composition of the mixture of the two divinylbenzenes used in preparing the copolymers. Thus, beads crosslinked with 20 to 40% para isomer sulfonate much faster than do those crosslinked with the divinylbenzene mixture of the compositions outside the 20 to 40% range of para-divinylbenzene. For example, at 80°C 25% para (in the 8 mole % of divinylbenzene) crosslinked beads sulfonate to a capacity of 4.73 meq./g. in 80 minutes, whereas, the beads crosslinked with 53% para isomer acquire a capacity of 2.57 meq./g. in 180 minutes at the same temperature.

The difference in the rates of sulfonation has been explained on the basis of the network structure of the copolymers. It appears that the interstices of the network in the copolymer beads crosslinked with 20 to 40% p-divinylbenzene have the optimum size for the sulfonating species to permeate and react with bezenoid rings. The copolymer beads used for this rate study were prepared at 80°C for 20 hours by using 0.1 weight % solid benzoyl peroxide as the initiator and 0.4 % solution of carboxymethyl cellulose ether sodium salt in water as the dispersion agent. The meta-divinylbenzene

used in this work was prepared by methods developed previously in this laboratory. The para isomer was also prepared by a newly developed method based on the formation of an insoluble complex between cuprous chloride and p-divinylbenzene and subsequent separation using preparative gas chromatograph.[26]

Bibliography

1. R. H. Wiley et al, J. Phys. Chem., 68, 1776 (1964).

2. R. H. Wiley et al, Cf. Reference 41 cited in Part I "Copolymerization Kinetics."

3. R. H. Wiley et al, Cf. Refrence 43 cited in Part I "Copolymerization Kinetics."

4. R. H. Wiley, G. DeVenuto, and F. E. Martin, J. Macromol. Sci. (Chem.), A1, 635 (1967).

5. R. H. Wiley and E. Reich, J. Polymer Sci., A6, 3174 (1968).

6. H. S. Thompson, J. Royal Agr. Soc. Engl., 11, 68, (1850).

7. J. T. Way, J. Royal Agr. Soc. Engl., 11, 313 (1850); 13, 123, (1852).

8. E. Lemberg, Z. Deut. Geol. Ges., 22, 335 (1870); 28, 519 (1876).

9. R. Gans, Jahrb. Preuss. Geol. Landesanstalt (Berlin), 26, 179 (1905); 27, 63 (1906).

10. B. A. Adams and E. L. Holmes, J. Soc. Chem. Ind., 54, 1-6T, (1935).

11. G. F. D'Alelio, U. S. Patent, 2,366,007 (1945).

12. R. H. Boundy and R. F. Boyer, Cf. Reference 45 cited in Part I "Copolymerization Kinetics."

13. T. K. Venkatachalam, Cf. Reference 46 cited in Part I "Copolymerization Kinetics."

14. R. H. Wiley and E. E. Sale, Cf. Reference 16 cited in Part I "Copolymerization Kinetics."

15. D. Rubenstein and J. R. Snyder, U. S. Patent, 3,217,051 (1965).

16. P. D. Meek and D. Rubenstein, U. S. Patent, 3,217,052 (1965).

17. D. Rubenstein and E. R. Winiarczyk, Ind. Eng. Chem., 50, 1553 (1958).

18. W. C. Bauman and J. E. Eichorn, J. Am. Chem. Soc., 69, 2830 (1947).

19. R. H. Wiley et al, Cf. Reference 18 cited in Part I "Copolymerization Kinetics."

20. S. P. Chang, Ph. D. Thesis, University of Louisville (1963).

21. R. H. Wiley and R. H. Hobson, J. Am. Chem. Soc., 71, 2429 (1949).

22. R. H. Wiley and R. L. Dyer, J. Polymer Sci., A2, 3153 (1964).

23. R. H. Wiley, G. Devenuto, and T. K. Venkatachalam, J. Gas Chromatog., 5, 590 (1967).

24. W. D. Schaeffner, W. S. Dorsey, D. A. Skinner, and C. G. Christian, J. Am. Chem. Soc., 79, 5870 (1957).

25. P. de Radzitsky and J. Hanotier, Ind. Eng. Chem. Proc. Design Devel., 1, 10 (1962).

26. The author is indebted to Mr. J. M. Looney, Cosden Chemical Company, for providing him with the details on such a separation as used in their laboratories.

PART III

POLYMERIZATION KINETICS OF PURE META- AND PARA-DIVINYLBENZENE

Introduction

In the previous parts of this thesis it has been shown that meta- and para-divinylbenzene have quite different characteristics and that the second vinyl groups of these two isomers have dissimilar effects on the copolymerizations with monovinyl monomers.

The polyfunctional monomers like meta- or para-divinylbenzene form a chemical structures of macroscopic dimensions, a so called infinite network. The occurrence of a sharp gel point is of foremost significance among the physical characteristics of the nonlinear three dimensional polymer formations. Wiley and DeVenuto[1] have shown that it was possible to obtain viscometric data for the kinetics of the pre-gelation period in the polymerization of meta- and para-divinylbenzene and their data showed significant differences in the overall polymerization rates for the two isomers.

In order to understand further the details of the polymerization kinetics of these two divinyl monomers, overall polymerization rates of the two isomers, gel times, and the conversions at gel points were determined in the present study.

Overall reaction rates for the pre-gelation periods were measured dilatometrically and the gel points were determined using rotating magnetic stirrers in the reaction cells. Based on these analyses, it has been shown that 1) the overall reaction rate for both isomers is proportional to the square root of the initiator concentration;

2) the dependences of the gel-times for the two divinylbenzens on the square roots of the initiator concentrations are different; and 3) the dependences of the conversions at the gel-points for the two isomers on the square roots of the initiator concentrations are different.

Historical

A short review on the previous research on polymerization kinetics is made in this section to provide some background for this work.

Polymerization reactions have been known for over a century and during most of this time their study was scrupulously avoided by chemists since they are non-distillable, non-crystalline, form no crystalline derivatives, and generally are quite resistant to the methods of classical organic chemistry. In recent years chemical methods applicable to high molecular weight substances have been developed, physical chemists have become intrigued with their properties, and the role of polymeric substances in natural biochemical systems has become widely recognized. Moreover, it has been noticed that many polymers are of industrial importance.

The processes of polymerization were divided by Carothers and Flory[2] into two groups known as condensation and addition polymerization or, in more precise terminology, step-reaction and chain-reaction polymerization. Condensation or step-reaction polymerization is entirely analogous to condensation in low-molecular weight compounds. In polymer formation the condensation takes place between two polyfunctional molecules to produce one larger polyfunctional molecule with the possible elimination of a small molecule such as water. Polyamides and polyesters are prime examples of condensation polymers.

Addition or chain-reaction polymerization involves chain reactions in which the chain carrier may be an ion (either a cation or an anion) or a reactive substance with one unpaired electron called a free radical. Polystyrenes and polyethylenes are typical examples of addition polymers. In this section only addition polymerization by a free radical chain mechanism will be considered. In 1839 Simon[3] reported the conversion of styrene to a gelatinous mass. Berthelot[4] in 1866 first applied the term polymerization to the process. Polymerization of isoprene to a rubberlike substance and depolymerization of a vinyl polymer to its monomer and other products as well by heating to elevated temperatures were then subsequently reported.[5] Polymethacrylic acid was prepared in 1880 by Fittig and Engelhorn[6] and in 1910 Stobbe and Posnjak[7] proposed a cyclic structure composed of four, five, or possibly more structural units for polystyrene. Lebedev[8] and Harries,[9] working separately, polymerized butadien and both of them proposed the cyclooctadiene structure to polybutadiene on the basis of their structural study of this polymer. However, Lebedev[10] subsequently assigned chain structures for polybutadiene and for rubber.

In an important paper published in 1920 Staudinger[11] deplored the prevailing tendency to formulate polymeric substances as association compounds held together by "partial valences" or other forces. He specifically proposed chain formulae for polystyrene and polyoxymethylene (paraformaldehyde), which are the ones accepted at the present time and he suggested a chain mechanism for a vinyl polymerization. However, an alternative mechanism of a stepwise reaction involving hydrogen transfer[12] was seriously considered as late as 1936. The controversy was settled by Flory's analysis[13] of kinetics of vinyl polymerization in 1937 in which he showed that radical polymerization proceeds by initiation, propagation, and termination steps, typical of chain reactions in low-molecular weight species.

The addition polymerization of unsaturated monomers by a free radical chain mechanism can be initiated by light, heat or peroxides, and has following characteristics: 1) the majority of monomers have the structure $CH_2{=}C<$, i.e., with one end of the double bond unsubstitututed, and are free from allylic C-H bonds; 2) monomer concentration decreases steadily throughout the reaction; 3) the growing polymer radical adds repeating units one at a time to the chain; 4) polymer molecular weight changes little over a considerable extent of the reaction; 5) the reaction mixture contains only monomer, high polymers, and very little part of growing chain. The following free radical polymerization mechanism and kinetics offer an explanation for the above general characteristics of vinyl polymerizations. The simpliest such scheme is one in which three processes, as mentioned above, are involved: chain initiation, radical addition to a double bond, and radical destruction. The process of chain initiation involves two steps, the first being the generation of a pair of free radicals $R\cdot$ by decomposition of the initiator I (e.g., benzoyl peroxide or azobisisobutyronitrile),

$$I \xrightarrow{k_d} 2\,R\cdot \qquad (1)$$

and the second the addition of the radical to the double bond of a monomer M to yield a chain radical

$$R\cdot + M \xrightarrow{k_a} M_1\cdot \qquad (2)$$

where the k's in these and subsequent reactions are rate constants, with subscript designating the reactions to which they refer. The adduct formed from a vinyl monomer is here represented by $M_1\cdot$. Not all of the radicals produced in step (1) necessarily regenerate the chain radicals according to step (2). Some of them may be lost through side reactions. In the propagation steps the polymeric free radical chains grow by successive addition of monomers to the radicals $M_1\cdot$ and to their successors:

$$\begin{aligned} M_1\cdot + M &\xrightarrow{k_p} M_2\cdot \\ M_2\cdot + M &\xrightarrow{k_p} M_3\cdot \end{aligned} \qquad (3)$$

or in general $\quad M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$.

Since radical reactivity is presumed to be independent of chain length, the same reaction rate constant k_p is written for each propagation step.

The termination step involves annihilation of the active center through bimolecular reaction between a pair of chain radicals. This may occur by combination

$$M_n\cdot + M_m\cdot \xrightarrow{k_{tc}} M_{n+m} \qquad (4)$$

or by disproportionation through transfer of a hydrogen atom

$$M_n\cdot + M_m\cdot \xrightarrow{k_{td}} M_n + M_m\cdot \qquad (4')$$

where M_{n+m}, and M_m represent inactive polymer molecules having the numbers of units indicated by the subscript in each case. Except where it is necessary to distinguish between the two mechanisms the termination rate constant will be denoted k_t hereafter. Equations (1), (2), (3), (4), and (4') describe the mechanism of vinyl polymerization initiated by free-radical initiator in a form amenable to general kinetic treatment. The rates of the three steps (initiation, propagation, and termination) may be written in terms of the rate constants and the concentrations of the species involved. It follows, then, that the disappearance of monomer may be represented as

$$-\frac{d(M)}{dt} = k_i(R.)(M) + k_p(M.)(M) \qquad (5)$$

where (M.) represents the total concentration of all chain radicals irrespective of size. Since the number of monomer molecules reacting in step (2) is insignificant compared with those consumed in the propagation step (3), it is clear that the disappearance of monomer is essentially uninfluenced by the initiating rate $k_i(R.)(M)$, so

$$-\frac{d\ (M)}{dt} = k_p(M.)(M) \qquad (6).$$

The rate of change of radical concentration may be expressed as the difference between their rate of formation and their rate of destruction (by termination):

$$\frac{d(M\cdot)}{dt} = k_i(R\cdot)(M) - 2k_t(M\cdot)^2 \qquad (7)$$

where the factor 2 enters as a result of the disappearance of two radicals at each incidence of the termination reactions (4) or (4'). Chain radicals by virtue of their great reactivity simply do not last long when compared with the process of converting monomer to polymer. Therefore, a steady-state assumption can be applied for the rate of change of radical concentration. Hence

$$k_i(R\cdot)(M) = 2k_t(M\cdot)^2 \qquad (8)$$

Furthermore the steady-state assumption can be applied for the rate of change of initiating radical concentration:

$$\frac{d(R\cdot)}{dt} = 2fk_d(I) - k_i(R\cdot)(M) = 0 \qquad (9)$$

where the factor f represents the fraction of the radical formed by Eq. (1) which is successful in initiating chains by Eq. (2) and (I) is the initiator concentration. From above equations finally one gets

$$-\frac{d(M)}{dt} = k_p(M)\,(k_d f(I)/k_t)^{1/2} \qquad (10)$$

If R_p is the rate of polymerization and R_i is the rate of chain initiation, one may simplify Eq.(10) to

$$R_p = k_p(M)\,(R_i/2k_t)^{1/2} \qquad (11)$$

This equation shows that in the early stages of the reaction, the overall rate of polymerization should be proportional to the square root of the initiator concentration and, if f is independent of the concentration of monomer (M), to the first power of the monomer concentration. An extensive study of various monomer-initiator combinations has abundantly confirmed the relationship between the rate of polymerization and the square root of the initiator concentration and this experimental fact confirms the bimolecular mechanism of polymer radical termination process, whether by combination or disproportionation. If the initiator efficiency f is independent of monomer concentration and the initiator concentration does not vary much during the course of polymerization, then the transformation of monomer to polymer should be by first order, i.e., the polymerization rate should be proportional to the monomer concentration. In some systems, such as the benzoyl peroxide-initiated polymerization of styrene in toluene[14] and polymerizations of d-sec-butyl-α-chloroacrylate[15] and vinyl-ℓ-B-phenylbutyrate[15] in dioxane solution initiated by benzoyl peroxide, the reaction is accurately first order up to quite high conversions.

The polymerization of certain monomers, either pure or in concentrated solution, shows a marked deviation from first-order kinetics in the direction of an increase in reaction rate with increase in molecular weight. This phenomenon is termed autoacceleration or the gel effect. Although it also is called the Trommsdorff effect,[16] this phenomenon was first observed by Norrish and Brookman.[17] Data obtained by Schulz and Harborth[18] illustrate behavior quite dissimilar from that in first-order kinetics. They polymerized methyl methacrylate in mass and at various concentrations in benzene with benzoyl peroxide as an initiator in a dilatometer. The dilatormeter was employed to follow the polymerization by observation of the decrease in volume of the polymerizate, which is due to the higher density of polymer than of monomer. At monomer concentrations up to approximately 40% the polymerization process was first order. When the monomer concentration was increased to higher values, a great acceleration of the polymerization rate was observed when the conversion reached 15 to 40%. The acceleration occurs at a higher conversion when the monomer is more dilute. Moreover, the molecular weight of polymer formed at concentrations leading to autoacceleration increased sharply. Autoacceleration in the rate of polymerization occurs also with other monomers.[19] The homologous acrylates and methacrylates exhibit a tendency to autoacceleration, as do acrylic and methacrylic acids and acrylonitrile. In the polymerization of methyl acrylate without diluent,[19] it sets in before a conversion of one per cent has been reached. Autoacceleration also occurs in the polymerizations of styrene and vinyl acetate,[20] but to a lesser degree than for methyl acrylate or methyl methacrylate.

It is now generally believed that this phenomenon can be explained by a large reduction in the termination rate constants in relation to the propagation rate constants. This decrease in k_t is believed to arise from the high viscosity of the monomer-polymer mixture when the concentration rises to the levels mentioned earlier. The decrease in termination rate leads to an increase in overall polymerization rate and in molecular weight, since the lifetime of the growing chain increases. The measurements of the absolute values of the individual rate constants have furnished further proof of this explanation. In the polymerization of methyl methacrylate the termination rate constant has been found to decrease by about 100 times during the autoacceleration phenomenon, whereas k_p does not appear to change. At quite high conversions (70 to 90%), but long after propagation has become diffusion controlled, the rate of polymerization drops to a very low value.

The overall rate of polymerization has been followed by several methods, such as titrimetric determination of the reduction in unsaturation by Wijs solution[21] or bromine,[22] observation of changes both in ultraviolet[23] and infrared[24] absorption spectra, measurement of the molecular diamagnetic susceptibility[25] of the reaction mixture at certain time intervals, measurement of increase in refractive index[26] during polymerization, and weighing of produced polymer after certain time of polymerization. The above analytical methods are in part

1) extremely laborious, 2) time consuming, 3) of rather low accuracy, and 4) difficult in regard to the design of the required equipment. The most convenient method of rate measurement for liquid phase polymerization is the dilatometric method.[27] This arises in part, at least, from the high sensitivity of the technique which results from the large difference in density between polymer and monomer. Also it has been demonstrated[28] that there is a linear relationship between the densities of monomer-polymer mixtures and their composition. From known densities of monomer, d_m, and polymer, d_p, or specific volumes of monomer, V_m, and polymer, V_p, the volume contraction for 100% conversions can be calculated:

$$\text{volume contraction for 100\% conversion} = K = \frac{1/dm - 1/d_p}{1/d_m} = \frac{V_m - V_p}{V_m}$$

The extent of polymerization (% conversion) after polymerization time t is calculated by the equation:

$$U = \frac{V_t}{K\,V} \times 100 \qquad (12)$$

where U, V, and V_t are % conversion, initial volume of monomer, and observed volume contraction at polymerization time t, respectively.

If the heat of polymerization is known, a reasonably accurate measure of the course of reaction can be obtained by use of an isothermal calorimeter.[29] Essentially polymerization is carried out in a small sealed tube immersed in a liquid in equilibrium with its own vapor at its boiling point. Under these conditions heat released from the reacting system will bring about the evaporation of the surrounding liquid. The loss in weight of the assembly will be a measure of the extent of polymerization.

Another important way to follow the rate of polymerization involves viscometry. Recently Wiley and DeVenuto[1] studied the kinetics of the pre-gelation period for the polymerization of divinylbenzene isomers viscometrically and they found that the overall rate of polymerization of meta isomer was greater than that of para compound in both toluene and tert-butylbenzene.

Divinyl monomers, (as contrasted to the monomers containing only one vinyl group or those unsaturated compounds which generally react to add only one monomer) form a three-dimensional, network of crosslinked polymers. Since each act of crosslinking reduces the number of polymer molecules which would otherwise be formed, crosslinked polymers may have very high molecular weights, and, in fact, a sufficiently crosslinked sample may be essentially a single giant molecule. The transition from an initial linear polymer to a crosslinked structure usually occurs quite dramatically in the course of polymerization. The gel point, the appearance of visible gelation in a polymerizing system, may be defined as the point at which large networks (on a molecular scale) are first formed. One of the most widely used method[30] to detect the gel point is to cause a little glass ball to spin or to be in motion in the polymerizing system and the point at which the ball stops spinning or moving is taken as the gel point.

Experimental

Monomers

meta-Divinylbenzene was prepared by a method similar to the one described in the first part of this thesis. The sample used for this work was found to be 99.5+% pure by gas chromatographic analysis with a flame ionization detector (Perkin-Elmer vapor fractometer Model 154D with "R" column), and had b.p. 34°C/1mm. and n_D^{24} 1.5755.

para-Divinylbenzene was supplied by Cosden Chemical Co. with the purity of about 92%. This sample was dissolved in equal parts of benzene and separated by the preparative gas chromatographic method to give pure p-divinylbenzene as previously described in the first part of this thesis. The monomer used for this work was 99.5+% pure by gas chromatographic analysis with a flame ionization detector and had m.p. 29.8°C and n_D^{35} 1.5855.

Solvent

Toluene was used as a solvent throughout this work. A quantity of toluene (Baker Analyzed Reagent) was boiled over sodium for 10 hours and freshly distilled under nitrogen just prior to use. The solvent used for this work had b.p. 110.6°C and n_D^{20} 1.4969.

Initiator

Solid benzoyl peroxide, purified as described in previous works, was used as an initiator throughout this work.

Determination of Densities of Solvent, Monomers, and Polymers

Since the reaction rate was followed dilatometrically at 70°C, first the densities of monomers, polymers, and solvent at 70°C were measured using a 25 ml.-Gay-Lussac pycnometer with the expansion cup (Figure 1). The densities of toluene and monomers at 70°C were obtained by comparing the weights of their samples to that of an equal volume of water of known density at 70°C using the following equation:

$$d_o = \frac{W_o}{W_w} \times d_w$$

where d_o and d_w are the densities of the sample and of water, respectively, and W_o and W_w are the weights of the same volume of the sample and of water, respectively.

When the densities of monomers were measured, a small quantity (about 1000 p.p.m.) of inhibitor (2,6-di-tert-butyl-p-cresol) was added to inhibit polymerization. The volume occupied by the inhibitor was neglected.

Furthermore, since the dried polymer volumes may not be the same as those in solution,[27] the apparent densities of poly(m-divinylbenzene) and poly(p-divinylbenzene) were determined in toluene at 70°C. A certain weight of the polymer obtained as indicated in the section "Determination of Converstion at Gel-Point" was placed in the pycnometer and about 10 ml. of toluene was added to this pycnometer with a dropper. The pycnometer after capping was allowed to stand three days at room temperature and then it was placed in 70°C constant temperature water bath after being filled with toluene. After thermostating, part of the excess liquid was forced out through the capillary into cup C by inserting a ground glass stopper. After a few minutes more in the thermostat, the liquid remaining on the flat surface of the stopper, S, was quickly wiped off with lens paper. The cup was dried with absorbent paper and the pycnometer was reweighed to get the weight of toluene used. From the known values for the densities of toluene and water at 70°C and weight of polymer used, one can calculate the polymer density in the solvent using the equation:

$$dp = \frac{W_p}{V - V_s}$$

where d_p represents the density of the polymer, W_p is the weight of the polymer used, and V and V_s are the volumes of the pycnometer and of the solvent (toluene) used.

The values obtained for the densities of monomers, polymers, and solvent (toluene) at 70°C are given in Table 1. As mentioned in the "Historical" section the densities of monomer and polymer enable volume contractions for 100% conversions to be calculated, and the calculated values using the obtained values for the densities of the two monomers and polymers are included in Table 1.

Table 1.

Densities and Volume Contraction for 100% Conversion at 70°C.

	density of monomer	density of polymer[a]	% contraction for complete reaction
m-DVB	0.8803	1.056	16.43
p-DVB	0.8959	1.072	16.64
Toluene	0.8211		

[a] density of polymer in toluene

Polymerization Rate Determination

The monomer mixtures were prepared by using 10 ml. volumetric flasks at 20°C. The volumetric flask was weighed on a balance and 2.9683 g. of freshly distilled monomer (m-divinylbenzene or p-divinylbenzene) was placed in the volumetric flask through a Pasteur pipette and various amount of benzoyl peroxide (0.00199 to 0.19743 g.) were added to each flask (Table 2 and 3). Toluene was quickly added to the volumetric flasks to make the volume 10.00 ml. at 20°C. During this process the flask was gently vibrated. The weight of toluene used was measured. This mixture was allowed to stand an additional five minutes at room temperature to ensure complete mixing. The monomer mixture prepared by the above method was used in part for the dilatometric study and in part for the determination of gel-time and conversion at gel-time. The monomer sample was charged into

Table 2.

Concentration of Benzoyl Peroxide for the Polymerization of m-Divinylbenzene in Toluene (2.28 mole/l.[d]) at 70°C.

Exp.No.[a]	1	2	3	4	5	6	7	8
Wt.of Benzoyl Peroxide[b]	0.00199	0.00296	0.00751	0.01766	0.02955	0.04428	0.07303	0.19717
Conc.of Benzoyl Peroxide[c]	0.821	1.22	1.30	7.29	12.20	18.28	30.15	81.40

[a] Experiments with the same number in Tables 2, 4, and 6 have the same initiator concentrations.

[b] Weight of Benzoyl Peroxide in 10.00 ml. of monomer mixture.

[c] (mole/l.) x 10^3

[d] The monomer mixture (10.00 ml.) contained 2.9683 g. of m-DVB and 7.8385g. of toluene at 20°C.

Table 3.

Concentration of Benzoyl Peroxide for the Polymerization of p-Divinylbenzene in Toluene (2.28 mole/l.)[d] at 70°C.

Exp.No.[a]	1	2	3	4	5	6	7	8	9
Wt.of Bz_2O_2[b]	0.00208	0.00414	0.00751	0.00753	0.01766	0.02931	0.04435	0.07402	0.19743
Conc.of Bz_2O_2[c]	0.858	1.71	3/10	3.11	7.29	12.10	18.31	30.56	81.51

[a] Experiments with the same number in Tables 3, 5, and 7 have the same initiator concentrations.

[b] Weight of benzoyl peroxide in 10.00 ml. of monomer mixture.

[c] (mole/l.) x 10^3

[d] The monomer mixture (10.00 ml.) contained 2.9683 g. of p-DVB and 7.9105 g. of toluene at 20°C.

the reaction tube of the dilatometer using a glass dropper. The reaction tube (about 3 ml. capacity) was mounted in an evacuation chamber into which the graduated capillary tube (O.D. 0.5 cm.; length 55 cm., the upper end of which had been tightly capped with a small sleeve type rubber stopper) was inserted right up to the reaction tube through an adaptor sealed with a rubber tube. The reaction tube, graduated capillary tube, and the evacuation chamber are shown in Figure 2. The evacuation chamber was connected to a vacuum and a (pre-purified) nitrogen line through a three-way stopcock. Vacuum was applied for five minutes while keeping the monomer sample frozen by dipping the lower part of the chamber into a bath of liquid nitrogen or a dry ice-acetone mixture. Stopping the vacuum pump, nitrogen was allowed to fill the chamber and then the chamber was evacuated for another three minutes. The liquid nitrogen bath was removed and the monomer sample was allowed to melt. The monomer mixture was then frozen and the degassing process was repeated twice more. After the last evacuation the ground glass joint of the graduated capillary tube was carefully inserted into the joint on the reaction tube so as to force the reactants into the capillary. Part of the excess liquid was quickly wiped off with absorption paper. The whole chamber was filled with nitrogen, the dilatometer assembly was taken out of the chamber, and the connection part between the capillary and reaction tube was sealed with mercury (Figure 2).[31] The dilatometer was placed in a constant temperature water bath maintained at 70.00 ±0.01°C.

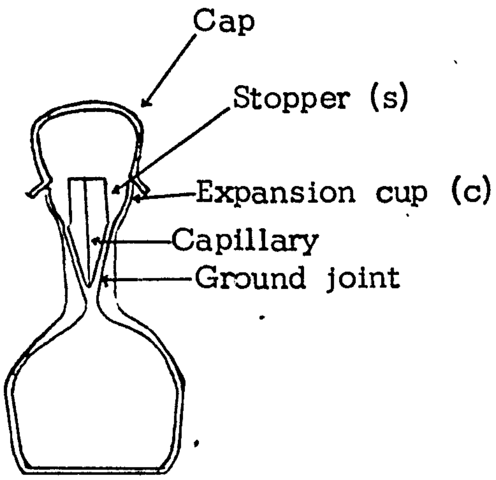
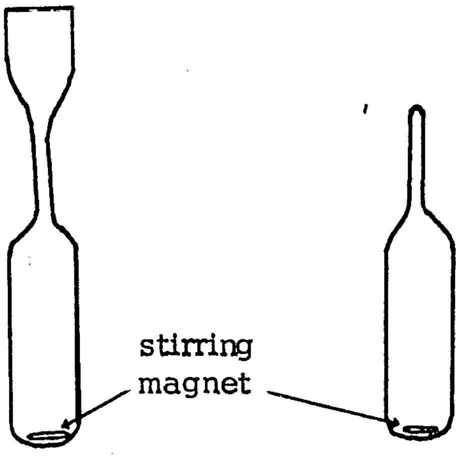


Figure 1. Pycnometer



Before Sealing

After Sealing

Figure 3. Reaction Cell

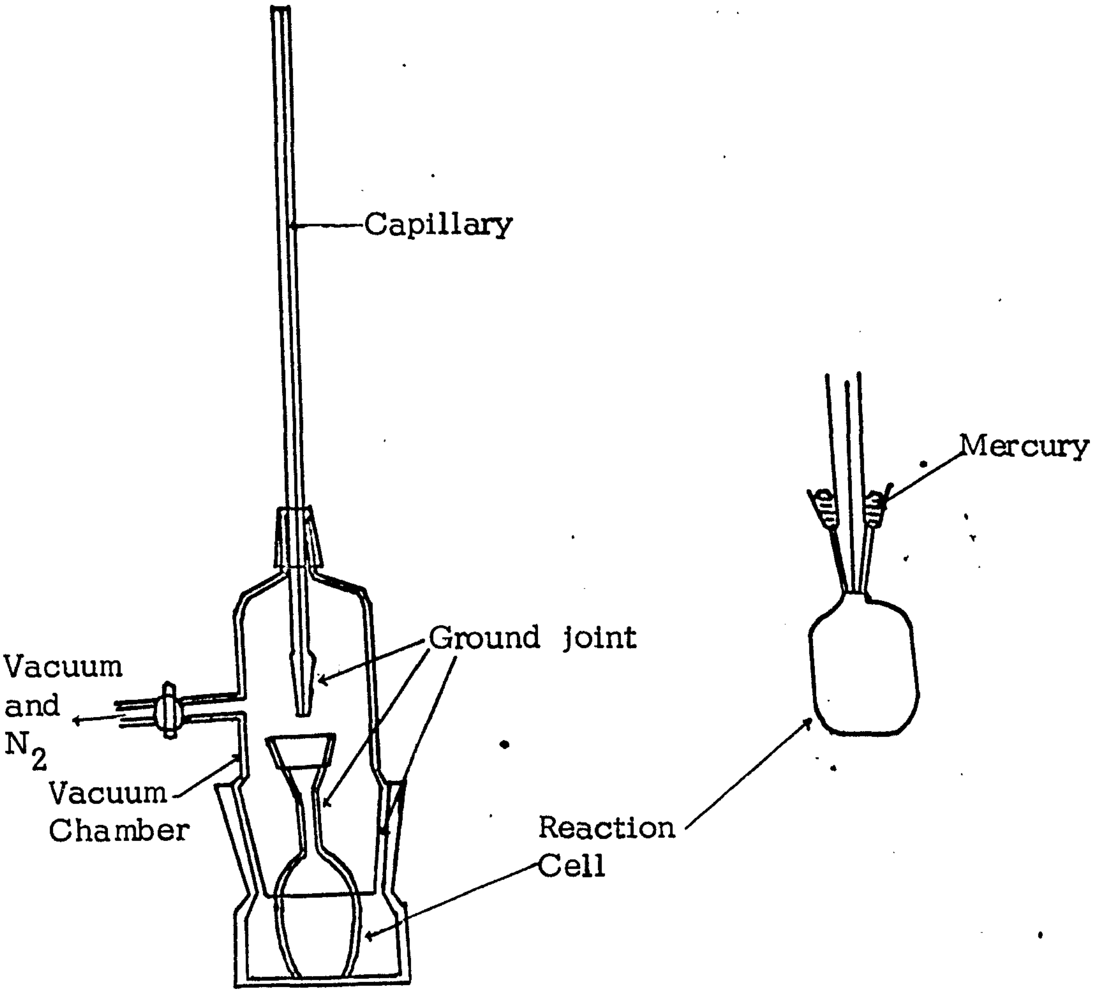


Figure 2. Dilatometer Assembly

Volume contractions were measured at five minute intervals from the moment of the insertion of the dilatometer into the constant temperature bath. It was observed that the volume contraction increased abruptly at the gel point. Past the gel point the liquid column in the capillary was subsequently broken and it was impossible to follow the volume contraction after gelation. All the dilatometric measurements of the volume contractions, except two cases, experiment number 4 in the polymerization of m-divinylbenzene and experiment number 5 in the para-divinylbenzene polymerization (Figure 4), were stopped before gelations occurred. Observed readings (in ml./min.) for the volume contractions for the polymerizations of m- and p-divinylbenzene are given in Tables 4 and 5.

The volumes for all the dilatometer assemblies were determined by measuring the weights of mercury which filled the assemblies at 70°C and are given in the second columns in Tables 4 and 5. The dilatometer capillary was graduated to tenths of a centimeter and it was found that one centimeter division on the capillary corresponded to a volume of 1.995×10^{-3} ml. at 70°C. This was determined by the weights of mercury which filled the capillaries to the various heights.

Gel-Point Determination

All polymerizations were carried out in small glass reaction cells about 4-5 cm. in length and about one centimeter wide, which had

Table 4.

Dilatometric Readings for the Polymerization of m-Divinylbenzene in Toluene (2.28 mole/l.) at 70°C with Benzoyl Peroxide Initiator

Exp.No.	Vol. of monomer mix.taken(ml)[a]	Vol.of monomer (ml)	Reading[b] mm/min	Vol.contraction Vt(ml)x10^4/min.	Vt x10^4/V/min.	Rp[e] x 10 (%conv./min.)
1	3.315	0.8653	0.4486	0.895	1.034	0.63
2	3.028	0.7904	0.5010	0.999	1.264	0.77
3	3.123	0.8152	0.9400	1.875	2.300	1.40
4	2.993	0.7812	1.364	2.721	3.483	2.12
5	3.166	0.8264	2.178	4.345	5.258	3.20
6	3.047	0.7953	2.424	4.835	6.079	3.70
7	2.981	0.7781	2.865	5.715	7.344	4.47

[a] Volume of dilatometer

[b] Average of dilatometer readings of polymerization time 40-200 minutes

[c] Reading (mm.) x 1.995 x 10^{-4} (ml./mm.)

[d] Vt/V = volume contraction/initial monomer volume

[e] Polymerization rate = (Vt/V) x 100/0.1643

Table 5.

Dilatometric Readings for the Polymerization of p-Divinylbenzene in Toluene (2.28 mole/l.) at 70°C with Benzoyl Peroxide Initiator

Exp.No.	Vol. of monomer mix.taken (ml)[a]	Vol.of monomer (ml)	Reading[b] mm/min	Vol.Contraction[c] (ml.) x 10^4/min.	$\frac{V_t}{V}$ x 10^4/min.[d]	Rp[e] x 10 (%Conv./min)
1	3.217	0.8232	0.2675	0.534	0.649	0.39
3	2.997	0.7669	0.5310	1.059	1.381	0.83
5	3.313	0.8478	1.018	2.031	2.396	1.44
7	3.251	0.8319	1.596	3.184	3.827	2.30
8	3.175	0.8125	1.980	3.950	4.862	2.92

[a] Same as dilatometer volume

[b] Average of dilatometer readings of polymerization times 50 - 200 minutes

[c] Reading (mm.) x 1.995 x 10^{-4} (ml./mm.)

[d] V_t/V = volume contraction/initial monomer volume

[e] Polymerization Rate (% conv.) = $(V_t/V) \times 100/K = (V_t/V) \times 100/0.1664$

been made from Pyrex test tubes. The reaction cell used for this work is shown in Figure 3. The reaction cells were stoppered with rubber stoppers and weighed. About three milliliters of the previously prepared monomer sample, which in part had been used for the dilatometric work, was transferred under a nitrogen atmosphere into the reaction cell using a Pasteur pipette and the cell containing the monomer mixture was weighed again after being tightly stoppered. A small Teflon coated magnetic stirrer (O.D. 0.3 cm.; length 1.2 cm.) was quickly placed in the reaction cell under nitrogen and the contents of the cell was frozen by immersing the cell in a bath of liquid nitrogen or a dry ice-acetone mixture. The cell was connected to a vacuum line with efficient traps cooled by a dry ice-acetone mixture or liquid nitrogen. A vacuum was drawn on the system for about five minutes while keeping the monomer mixture frozen, and the monomer mixture was allowed to melt after the pumping was stopped. The monomer mixture was then refrozen and vacuum was applied for another three minutes. This process was repeated twice more. After the final degassing, the monomer mixture was refrozen and sealed under vacuum with a small torch.

The polymerizations were carried out in a $70.00 \pm 0.01^{\circ}C$ water bath by attaching the cells to long glass rods and suspending the cells in the water. As soon as the reaction cells were immersed in the bath, the magnetic stirrers were placed in rotation by an electric stir jack. The magnetic field strength was regulated so as to just rotate the stirrers. The gel-time was taken as the time interval between the immersion of the reaction cell in the constant temperature bath and the time at which the magnetic stirrer ceased rotation. The end point was usually sharp, except at very low initiator concentrations. Exploratory experiments showed that the rotation of the magnetic stirrer ceased at the same gel-time as that observed dilatometrically. The data are given in Tables 6 and 7.

Determination of Conversion at Gel-Point

At the gel-point the above mentioned reaction cell was immediately removed from the bath and frozen in liquid nitrogen or dry ice-acetone mixture. The polymer mixture was thawed and quickly transferred to a 15 ml. centrifuge tube which had been weighed. The reaction cell was rinsed twice with approximately 0.5 ml. of benzene each time and these were added to the centrifuge tube. A small quantity of inhibitor (2,6-di-tert-butyl-p-cresol) was added to the centrifuge tube, and then the polymer produced was precipitated by adding about 10 ml. of methanol. The contents of the centrifuge tube were thoroughly mixed by a pointed stainless steel spatula. The solvent and unreacted monomer were decanted by centrifuging the tube at approximately 4000 r.p.m. on an International Clinical Centrifuge for about 15 minutes. This washing process was repeated twice more without adding inhibitor. After the final decantation the centrifuge tube containing polymer was placed in a vacuum oven after its mouth was covered with filter paper

Table 6.

Gel-Time and Conversion at Gel-Time for the Polymerization of m-Divinylbenzene in Toluene (2.28 mole/l) at 70°.

Exp.No.	Wt.of monomer mix.taken(g.)	Wt.of mono-mer(g.)	Gel-Time (min.)	Wt.of poly-mer(g.)	Con-version (%)
1	3.1671	0.8698	286	0.1487	17.10
2	3.0893	0.8483	238	0.1520	17.92
3	3.3230	0.9121	130	0.1676	18.37
4	2.9895	0.8198	91	0.1531	18.67
5	3.1546	0.8641	61	0.1707	19.75
6	3.2725	0.8952	57	0.1758	19.64
7	3.0188	0.8482	46	0.1852	21.83
8	2.9980	0.8087	33.5	0.2073	25.63

Table 7.

Gel-Time and Converstion at Gel-Time for the Polymerization of p-Divinylbenzene in Toluene (2.28 mole/l.) at 70°C.

Exp.No.	Wt.of monomer mix.taken(g.)	Wt.of monomer(g.)	Gel-Time (min.)	Wt.of Polymer(g.)	Conversion (%)
1	3.1125	0.8491	359.5	0.1233	14.52
2	2.9774	0.8121	260.9 3	0.1134	13.96
3	3.0030	0.8188	180.2	0.1355	16.55
4	3.0045	0.8192	190.2	0.1188	14.50
5	3.1673	0.8628	111.0	0.1400	16.23
6	3.2665	0.8889	91.8	0.1582	17.80
7	3.0688	0.8339	76.2	0.1411	16.92
8	2.8134	0.7625	65.2	0.1502	19.70
9	3.2062	0.8592	54.8	0.1933	22.50

and the polymer was dried in the vacuum oven to a constant weight at 50°C and 1 mm. pressure for 48 hours. The conversion was determined by dividing the weight of the polymer produced into the weight of the monomer used. Observed conversions at gel-times are tabulated in Tables 6 and 7.

Results and Discussion

As metnioned in the "Historical" section about forty years ago by density measurements a linear relationship was demonstrated between the percentage contraction on the original volume of the monomer and the extent of polymerization. This made it possible for many of polymerization rates of various monomers to be followed dilatrometrically. Since it was shown[1] that it is possible to obtain viscometric data for the kinetics of the pregelation period in the polymerization of meta- and para-divinylbenzene, polymerization rates of pure meta- and pure para-divinylbenzenes were measured dilatometrically in toluene solution at 70°C and the results are given in Tables 8 and 9. The conversion data obtained from the dilatometric readings for the polymerization of meta-divinylbenzene (Exp. 4) are represented in Figure 4 and show that the conversion is directly proportional to the polymerization time at intervals up to the gel-time, at about 90 minutes and 19% conversion, at which point the conversion sharply increases. Comparable data for the para isomer (Exp. 5) are also shown in Figure 4 and the conversion is proportional to the polymerization time up to gelation at about 110 minutes and with a conversion of 16%. The same linear dependence of conversion on the polymerization time was observed for all the other polymerizations in the early stages of polymerization (i.e., before gelation).

In the radical polymerization of vinyl compounds the polymeriza-

Table 8.

Polymerization of m-Divinylbenzene in Toluene (2.28 mole/l.) at 70°C with Benzoyl Peroxide Initiator

Exp.No.	Initiator Conc. mole/l. x 10^3	Rate of Polymerization, %/min x 10	Gel-Time min.	Conv. at Gel-time, % conv.
1	0.82	0.63	286	17.10
2	1.22	0.77	238	17.92
3	3.10	1.40	130	18.37
4	7.29	2.12	91	18.67
5	12.20	3.20	61	19.75
6	18.28	3.70	57	19.64
7	30.15	4.47	46	21.83
8	81.40	--	33.5	25.63

Table 9.

Polymerization of p-Divinylbenzene in Toluene (2.28 mole/l.) at 70°C with Benzoyl Peroxide Initiator

Exp.No.	Initiator Concentration mole/l.x 10^3	Polymerization Rate %Conv./min.	Gel-Time min.	Conversion at Gel-Time, % conv.
1	0.86	0.39	359.5	14.52
2	1.71	---	260.9	13.96
3	3.10	0.83	180.2	16.55
4	3.11	---	190.2	14.50
5	7.29	1.44	111.0	16.23
6	12.10	---	91.8	17.80
7	18.31	2.30	76.2	16.92
8	30.56	2.92	65.2	19.70
9	81.51	---	54.8	22.50

tion rates are, in general, proportional to the square root of initiator concentration as expressed by Eq. (10) or (11). To confirm this relationship for the divinylbenzenes, the polymerization rates were measured dilatometrically at various initator concentrations and the results are given in Tables 8 and 9. The polymerization rates in per cent conversion per minute are plotted against the square root of the initator (benzoyl peroxide) concentration over a range of 0.00082 moles/1. to 0.0815 moles/1. in Figure 5, from which it can be seen that the experimental points fall on a straight line for each isomer. The polymerization rates of p-divinylbenzene are about two thirds those of the meta isomer under comparable conditions over this entire range as shown in Figure 5. This relation has been observed in a previous viscometric study[1] for the polymerizations of these two isomers. Since monomers of low resonance stabilization yield polymer radical adducts of low resonance stabilization and high reactivity with monomers in general and monomers of high resonance stabilization yield radical adducts of high resonance stabilization and low reactivity with monomers in general, this result suggests a more resonance stabilized character for para-divinylbenzene and for free radicals derived from it. It seems reasonable to assume that the more stable radical (para derived radical) would have a longer life time and would have more chance to undergo chain termination through bimolecular collision. It is also apparent from the data now available that up to the gel-point the kinetics of

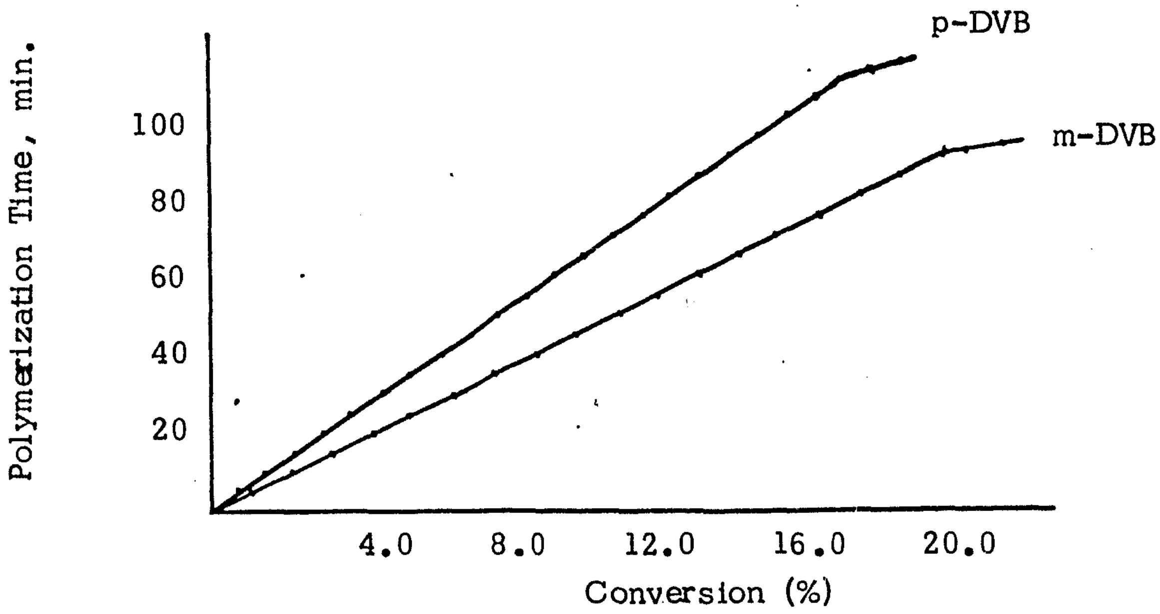


Figure 4. Polymerization of meta- and para-Divinylbenzene at 70°C. Concentration of Divinylbenzene, 2.28 mole/l; of Initiator, 7.29 x 10^{-3} mole/l.

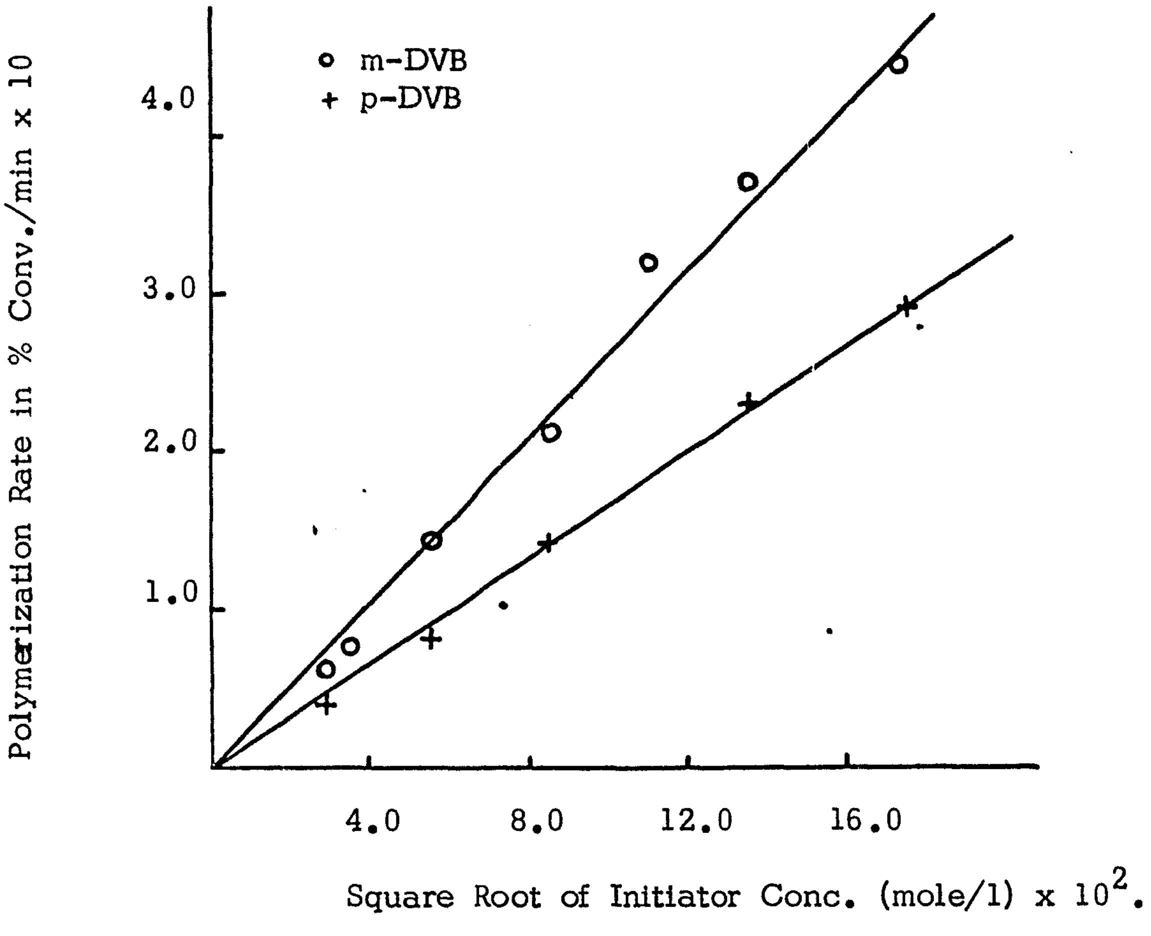


Figure 5. Rates of Polymerizations of meta- and para-Divinylbenzene in Toluene vs. Square Root of the Initiator Concentration.

the polymerizations of the two divinylbenzene monomers have the characteristics shown by typical monovinyl monomers. This is consistent with the generally accepted concept that the second vinyl group of the divinyl monomer is not involved prior to gelation. The second vinyl group appears to function, at least in the divinylbenzenes, as a substituent which modifies the reactivity of the reacting vinyl group.

The measurements of gel time were made by polymerization in the presence of a rotating magnetic stirrer as previously described in the "Experimental" section. At high initiator (benzoyl peroxide) concentrations gelation occurred very suddenly and at lower initator concentrations the transition to a gel was less sudden. The data for the gel-times are given in Tables 8 and 9 and Figure 6 shows the relation between gel-time and the square root of the initiator concentration. It can be seen from this Figure that the times for gelations in the polymerizations of meta- and para-divinylbenzenes are linearly related to the reciprocal of the square root of the initiator concentration for both isomers over the ranges of the initator concentrations used for this study. There is a consistent difference between the two isomers with the shorter gel-time for the meta-divinylbenzene at the same initiator concentration.

The relation between the conversion at gel-time and the square root of the initiator concentration (Figure 7) also shows a difference in the behavior of the two isomeric divinylbenzenes. Conversion at

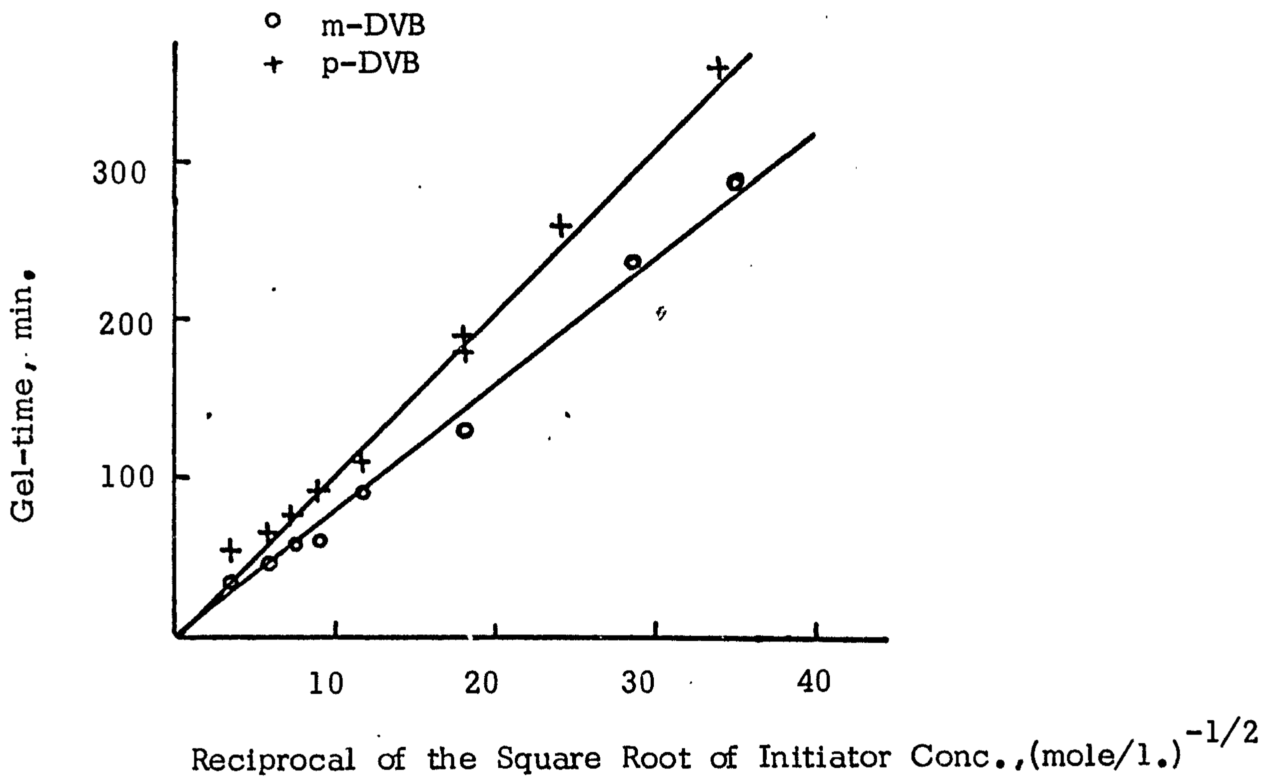


Figure 6. Polymerization of meta- and para-Divinylbenzene in Toluene at 70°C. Gel-time in Minute vs. the Reciprocal of the square Root of Initiator Concentration.

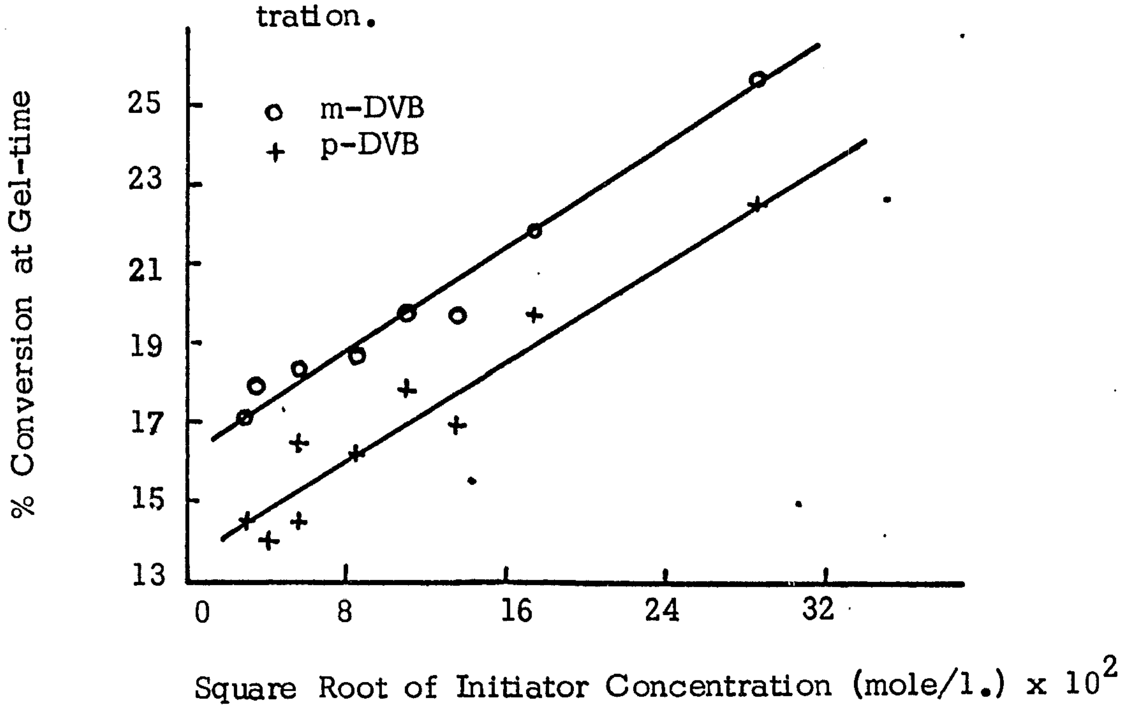


Figure 7. Polymerization of Divinylbenzene in Toluene at 70°C. Conversion (%) at Gel-time vs. Square Root of the Initiator Concentration.

gel-time seems to be linearly related to the square root of the initiator concentration in the polymerizations of both isomers and the conversion at gel-point for the meta isomer is consistently higher than that for the para isomer for the same initiator concentration. The gelation characteristics of the two divinylbenzenes show distinctions which appear to be related to different crosslinking processes. Although the gelation time appears to be a function of rate; i.e., the lower the rate the longer the time to gelation, and thus also is a function of polymer concentration build up, this cannot be the only factor involved because the conversion at gelation also varies for the two isomers. If everything were strictly comparable for the two divinylbenzenes the conversions at gelation should be equivalent. The data given above show this is not so. At every level the more slowly polymerizing para isomer shows a lower conversion at gelation. This fact requires that less para-divinylbenzene monomer be incorporated into the crosslinked network at gelation than meta-divinylbenzene and suggest that there is greater molecular build up prior to crosslinking in the meta derived polymer than in the para derived polymer. In other words, this may be considered as a suggestion that the second vinyl group in the para-divinylbenzene participates in the polymerization reaction earlier than the second vinyl group of the meta isomer. The cross-linking reaction therefore occurs in the earlier stages of the polymerization for the para isomer than for the meta isomer.

It is usually considered that gelation occurs after one, or at most but a few, crosslinkings are produced.[32] The acceleration in the polymerization rates is generally attributed to inhibition, via diffusion control, of the bimolecular termination in a high viscosity medium. The viscosity of a polymer solution varies among polymer types in terms of both molecular shape and size as well as solvent -polymer interaction phenomena. Since the polymers derived from the divinylbenzenes are structurally different from each other, in the polymerizations of the two isomers all of these may be involved and may be involved in different ways for the two isomeric divinylbenzenes.

The following statements concern the densities of the polymers from meta- and para-divinylbenzene and the per cent contraction for the complete polymerization of the two isomers in toluene solvent. It is known that monomer and polymer volumes are not strictly additive in solution[27] and the apparent density of a polymer in a solvent or in its monomer is different from that of the dried polymer. In this study the densities of the meta- and para-divinylbenzene polymers were determined in toluene solution and were found to be 1.056 and 1.072, respectively at 70°C. These values are quite close to the density of polystyrene (1.051)[33] in styrene solution. It has been reported[30] that in the copolymerization of styrene and p-divinylbenzene the densities of the copolymers with various amount of para-divinylbenzene were not so much different from one another and all the values clustered about the values of polystyrene. The volume contractions for 100% conversions for the polymerizations of meta- and para-divinylbenzene at 70°C were 16.43 and 16.64%, respectively. And these values are slightly greater than the value for the polymerization of styrene (16.4%).[34]

Summary

The polymerizations of pure meta- and para-divinylbenzene have been followed dilatometrically in toluene solution for the pre-gelation period at 70°C. Solid benzoyl peroxide was used as the initiator for all the polymerizations. Though the two isomeric compounds are divinyl monomers, the experiments with varying initiator concentration showed that the polymerization rates in per cent conversion per minute are directly proportional to the square root of the initiator concentration (0.00082 moles/l. to 0.0815 moles/l.) for both isomers, which is the characteristic shown by typical monomers. In addition to this, the meta-divinylbenzene polymerizes more rapidly than the para isomer, as was observed in the viscometric studies for the polymerizations of these two divinylbenzenes.

The time to gelation was determined by using rotating magnetic stirrers placed in the polymerization system and the conversion at gel-time was obtained from the weight of the polymer produced up to the gelation. For para-divinylbenzene the gel-time is consistently greater and the conversion at gel-time lower than for meta-divinylbenzene.

The differences in the rates of polymerizations for the two divinylbenzene isomers have been explained on the basis of less resonance-stabilization for the meta-vinylstyryl derived radical.

The distinction between the gelation characteristics of the two isomeric divinylbenzenes has been interpreted in terms of possible different crosslinking processes for the two isomers.

Bibliography

1. R. H. Wiley and G. DeVenuto, J. Polymer Sci., A2, 5347 (1964); A3, 1959 (1965).
2. P. J. Flory, Principles of Polymer Chemistry, Page 27, Cornell University Press, New York, 1953.
3. E. Simon, Ann., 31, 265 (1893).
4. M. Berthelot, Bull. Soc. Chim. France, (2), 6, 294 (1866).
5. G. Wagner, Ber., 11, 1260 (1878).
6. R. Fittig and F. Engelhorn, Ann., 200, 65 (1880).
7. H. Stobbe and G. Posnjak, Ann., 371, 259 (1910).
8. S. V. Levedev and B. K. Merezhkovskii, J. Russ. Phys. Chem. Soc., 43, 1124 (1911),
9. C. Harries, Ann., 395, 211 (1913).
10. S. V. Lebedev, Chem. Abstracts, 9, 798 (1915); J. Russ. Phys. Chem. soc., 45, 1296 (1913).
11. H. Staudinger, Ber., 53, 1073 (1920).
12. G. S. Whitby and M. Katz, J. Am. Chem. Soc., 50, 1160 (1928).
13. P. J. Flory, J. Am. Chem. Soc., 59, 241 (1937).
14. G. V. Schulz and E. Husemann, Z. Physik. Chem. Leipzig, B39, 246 (1938).
15. C. S. Marvel, J. Dec, and H. G. Cooke, J. Am. Chem. Soc., 62, 3499 (1940).
16. E. Trommsdorf, H. Kohle, and P. Lagally, Makromol. Chem., 1, 169 (1948).

17. R. G. W. Norrish, E. F. Brookman, Proc. Roy. Soc. (London), A171, 147 (1939).

18. G. V. Schulz and G. Harborth, Makromol. Chem., 1, 106 (1947).

19. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Am. Chem. Soc., 73, 5395 (1951).

20. A. C. Cuthberson, G. Gee, and E. K. Rideal, Proc. Roy. Soc. (London), A170, 300 (1939).

21. Kia-Khwe and H. N. Alyca, J. Am. Chem. Soc., 55, 575 (1933).

22. G. F. D'Alelio, Experimental Plastics and Synthetic Resins, Page 10, John Wiley & Sons, New York, 1946.

23. J. W. Goodeve, Trans. Faraday Soc., 34, 1293 (1938).

24. E. L. Kropa and R. B. Banes, Am. Chem. Soc. Meeting, 1941.

25. J. Farquharson, Trans. Faraday Soc., 33, 824 (1937).

26. H. W. Mellville and W. F. Watson, Trans. Faraday Soc., 44, 68 (1948).

27. G. V. Schulz and G. Harborth, Angew, Chem., 59, 90 (1947).

28. H. W. Starkweather and G. B. Taylor, J. Am. Chem. Soc., 52, 4708 (1930).

29. L. K. J. Tong and W. O. Kenyon, J. Am. Chem. Soc., 67, 1278 (1945).

30. B. T. Storey, Cf. Reference 53 cited in Part I "Copolymerization Kinetics."

31. G. V. Schulz, G. Henrici, and S. Olive, Z. Elektrochem., 60, 296 (1956).

32. C. Walling, J. Am. Chem. Soc., 67, 441 (1945).

33. M. S. Matheson, E. E. Auer, E. B. Bevilacqua, and E. J. Hart, J. Am. Chem. Soc., 73, 1700 (1951).

34. A. D. Jenkins, Symposium on Techniques of Polymer Science, Report of Royal Institute of Chemistry, London, No. 5, 1956.

PART IV

COMPUTER CALCULATION OF MONOMER REACTIVITY RATIOS

Introduction

The classical methods of determining monomer reactivity ratios for free-radical copolymerizations have been described in the "Historical" section of the first part of this thesis. All of these methods involve polymerization of several different monomer feed compositions to low conversion, recovery and purification of the copolymer formed, compositional analysis, and fitting of the data to the differential form of the copolymer composition equation. All these techniques have a common short-coming with respect to the treatment of the experimental data. In the use of the differential form of the copolymer composition equation the relative monomer concentrations are assumed not to change significantly from the initial values during the copolymerization. However, the copolymer composition, in general, will not be the same as the monomer composition except when $r_1 = r_2 = 1$ or in the special case of azeotropic copolymerization. In all other cases any polymer formed changes the compositions of the monomers remaining, and there will be a continuous drift of copolymer composition with conversion. It has been known[2] that the problem of changes in monomer composition with conversion can be avoided by using an integrated form of the copolymer composition equation to treat the experimental data, but laborious calculations are required, and the tendency has been to avoid it when possible, even at the recognized expense of some loss in accuracy. However, nowadays computers are available to handle the massive calculations.

Montgomery and Fry[1] have written a computer program in Fortran II language to use the Mayo and Lewis'[2] integrated form of the copolymer composition equation, making it possible to include the conversion corrections in the calculations of monomer reactivity ratios.

In the present studies, the monomer reactivity ratios for the copolymerizations of styrene and meta-divinylbenzene, and for styrene and para-divinylbenzene have been calculated by the integrated form of the copolymer composition equation using the reported experimental data.[3] A slight modification of Montgomery and Fry's program was employed for the IBM 1620 computer. The original Format statements were changed to allocate more space for input and output data and an "If (Sense Switch) Statement" was added to print out the output data only when the sense switch 1 was on.

Results and Discussion

The monomer feed composition, conversion and copolymer composition used in the present study for the calculation of the monomer reactivity ratios for the copolymerizations of styrene with meta- and para-divinylbenzene are given in Tables 1 and 3. These experimental results are taken from Wiley and coworkers.[3]

Since the divinylbenzenes have two vinyl groups, this statistical factor was taken into consideration when the initial monomer concentrations were used in the computer program as input data.

The values of monomer reactivity ratios obtained for styrene, M_1, and meta-divinylbenzene, M_2, are given in Table 2 for all twenty combinations of pairs of experiments shown in Table 1. Values of $r_1 = 0.70$ and $r_2 = 1.0$ were obtained as averages of results for all twenty pairs. These values are quite close to the values ($r_1 = 0.605$, $r_2 = 0.88$) obtained by the differential form of the copolymer composition equation using the same experimental data. The differences between the two sets of values suggest that there is some drift in monomer compositions even with such low conversions (1.8 to 3.7%) as were used for this calculation. Montgomery and Fry showed that in the copolymerization of vinyl chloride and vinyl acetate the values of the monomer reactivity ratios calculated, as in this calculation, by a Fortran II computer program using the integrated form of the copolymer composition equation fitted the experimental conversion-composition curve much better than those based on the differential analyses.

Table 1.

Copolymerization of Styrene and m-Divinylbenzene at 80°. Benzoyl Peroxide Initiator.

	Monomer Feed, g.				Copolymer Composition[b]		
No.	Styrene M_1	m-DVB M_2	Wt.-%[a] Styrene	Wt.-%[a] m-DVB	Wt.-% Styrene	Wt.-% m-DVB	Conver. %
1	0.6638	0.4480	42.56	57.44	37.97	62.03	3.72
2	0.4865	0.4280	36.63	63.37	34.46	65.54	1.79
4	0.3913	0.4256	31.49	68.51	29.99	70.01	2.03
6	0.4319	0.6148	25.99	74.01	21.37	78.63	2.10
8	0.1813	0.3872	18.93	81.07	19.02	80.98	2.20

[a] Calculated taking into account the statistical factor of 2 for m-DVB; Wt.-% = $(100\cdot M_1)/(M_1 + 2M_2)$ or $(100 \times 2M_2)/(M_1 + 2M_2)$

[b] Average values of duplicate analyses.

Table 2.

Monomer Reactivity Ratios for the Copolymerization of Styrene and m-Divinylbenzene.

Run.No.	r_1	r_2	Run.No.	r_1	r_2
12	0.6356	1.0026	46	0.8112	1.0005
14	0.6363	1.0025	48	0.8138	1.0010
16	0.6364	1.0012	61	0.2607	1.0024
18	0.6368	1.0011	62	0.2587	1.0027
21	0.7867	1.0025	64	0.2607	1.0024
24	0.7854	1.0028	68	0.2591	1.0020
26	0.7843	1.0078	81	1.0274	0.9999
28	0.7869	1.0010	82	1.0273	0.9998
41	0.8140	1.0014	84	1.0263	0.9999
42	0.8149	1.0019	86	1.0261	0.9999
			Average	0.70	1.00

As one can see from Table 2, experiments 6 and 8 (used as the first members of the pairs) gave values quite different (0.26 and 1.03, respectively) from those obtained from experiments 1, 4, and 6 (taken as the first members of the pairs). Excluding these from the averages (even though there is no basis for doing this) values of $r_1 = 0.75$ and $r_2 = 1.0$ were obtained as averages for 12 pairs of experiments 1, 2, and 4 (used as the first members of the pairs).

Table 4 shows the results for the calculations of the monomer reactivity ratios for the copolymerization of styrene and para-divinylbenzene. Values of $r_1=0.89$ and $r_2 = 2.73$ were obtained as averages of the results for all the twenty combinations of pairs of experiments tabulated in Table 3. These two values are not in very good agreement with the values ($r_1 = 0.77$ and $r_2 = 2.08$) obtained by differential analysis. However, it must be noted that the difference between the two r_2 values is greater than that between the two r_1 values. This also was the case in the copolymerization of styrene and meta-divinylbenzene and in both copolymerizations the r_2's are greater than the r_1's. This fact seems to imply that the use of the integrated form of the copolymer composition equation to calculate the monomer reactivity ratios gives relatively higher values for the higher monomer reactivity ratios (r_2 in the above cases) than for the lower monomer reactivity ratios. This phenomenon was also observed in the copolymerization of styrene and isopropylstyrene which was described in the "Results

Table 3.

Copolymerization of Styrene and p-Divinylbenzene at 80°. Benzoyl Peroxide Initiator.

No.	Monomer Feed, g. Styrene M_1	Monomer Feed, g. p-DVB M_2	Wt.-%[a] Styrene	Wt.-%[a] p-DVB	Copolymer Composition[b] Wt.-% Styrene	Copolymer Composition[b] Wt.-% p-DVB	Conver. %
1	0.6707	0.1804	65.02	34.98	49.60	50.40	0.55
3	0.6022	0.2365	56.01	43.99	42.10	57.90	0.94
5	0.2184	0.2646	29.22	70.78	14.50	85.50	1.72
6	0.2286	0.3166	26.53	73.47	13.59	86.41	1.05
10	0.1984	0.7786	11.30	88.70	6.30	93.70	1.78

[a] Calculated taking into account the statistical factor 2 for p-DVB

[b] Average values of the reported duplicate analyses.

Table 4.

Monomer Reactivity Ratios for the Copolymerization of Styrene and p-Divinylbenzene.

Run.No.	r_1	r_2	Run.No.	r_1	r_2
13	0.9873	3.914	56	0.9894	3.191
15	0.7551	2.890	510	0.9957	3.187
16	0.6803	2.561	61	0.6803	2.561
110	0.5314	1.905	63	0.9619	2.856
31	0.9916	2.937	65	0.9909	2.885
35	0.9879	2.929	610	0.9959	2.885
36	0.9620	2.855	101	0.5314	1.905
310	0.9940	2.944	103	0.9968	2.050
51	0.7551	2.890	105	0.9979	2.050
53	0.9863	3.187	106	0.9977	2.040
			Average	0.89	2.73

and Discussion" section of the first part of this thesis. This also is consistent with the concept that there is more drift in the concentration of more active monomer with conversion than in that of the less active monomer.

As in all methods which contain experimental data, the output from this computer program can not be better than the input, and therefore the compositions of monomer feed and copolymer formed and conversion must be known accurately if good values of r_1 and r_2 are to be obtained. The experimental data for the composition of the copolymer formed as a function of conversion starting with a fixed monomer feed composition which will enable one to examine the accuracy and reliability of the computerized values of the monomer reactivity ratios are not available for the copolymerizations of styrene with meta- and para-divinylbenzene, although they are readily obtainable by known techniques. Therefore, more experimental data are required to get more reliable values of the monomer reactivity ratios for its two copolymerization systems if the integrated form of the copolymer composition equation is to be used.

Summary

The monomer reactivity ratios were calculated for the copolymerizations of styrene and meta-divinylbenzene and of styrene and para-divinylbenzene by the Mayo and Lewis' integrated form of the copolymer composition equation using Montgomery and Fry's computer program in Fortran II language and the reported experimental results for the two copolymerization systems. Values of r_1 (styrene) $= 0.70$ and $r_2 = 1.0$, and r_1 (styrene) $= 0.89$ and $r_2 = 2.73$ were obtained for the copolymerizations of styrene with meta- and para-divinylbenzene, respectively. These values are in fair accord with the values obtained by differential analysis. The differences between the values obtained by the two analyses were explained on the basis of the drift in monomer composition with converstion. More experimental data on the composition of the copolymer formed as a function of conversion starting with a fixed monomer feed composition for the two copolymerization systems are needed in order to get more reliable values of the monomer reactivity ratios using the integrated form of the copolymer composition equation.

Bibliography

1. D. E. Montgomery and D. C. Fry, Cf. Reference 55 cited in Part I "Copolymerization Kinetics."
2. F. R. Mayor and F. M. Lewis, Cf. Reference 6 cited in Part I "Copolymerization Kinetics."
3. R. H. Wiley et al, Cf. Reference 18 cited in Part I "Copolymerization Kinetics."