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HOMOPOLYMER AND COPOLYMER SOLUBILITY:

METHYL GROUP EFFECTS IN STYRENE BASED SYSTEMS

by

David J. Goldwasser

A dissertation submitted to the Graduate
Faculty in Engineering in partial fulfillment
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ABSTRACT

The specific effects of composition and structure on the behavior of polymer solutions are not well understood. In seeking to clarify this situation, we have undertaken an experimental study of the solution properties of well tailored polymers prepared via the living polymer technique: namely, homopolymers and copolymers of styrene, α-methyl styrene and p-methyl styrene. Thus, we are studying how the concentration and placement (in the repeat unit structure) of the methyl group affects homopolymer and copolymer solubility.

In accordance with the findings of previous investigators, we observed an increase in copolymer solubility over that observed by linear interpolation between the parent homopolymers. This effect is most pronounced in plots of theta-temperatures (Θ) versus composition which actually show minima. It is also manifested in Flory-Huggins parameters obtained for moderately concentrated (3% to 25% by volume) toluene solutions. Comparison of our results with the few available in the literature suggest that this phenomenon may be quite general, if not universal. Solubility under Θ-conditions is partly explained with the solubility parameter concept. The magnitude of the

effect appears to be identical in both toluene at 37°C and at the Θ-condition for a variety of solvents; this reinforces the notion that increased solubility arises fron inter-mer repulsions which should be, as a first approximation, independent of solvent. Finally, it is obvious that methyl groups manifest a stronger influence on polymer solution properties than may have been previously appreciated.

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I. INTRODUCTION

The thermodynamic properties of a solution are governed by a series of molecular and submolecular scale processes. It is of practical and theoretical importance to understand these phenomena Nonetheless, the behavior of pure substances and solutions in the liquid state is poorly understood even for low-molecular-weight compounds. Because polymer solutions involve more factors than ordinary solutions, their study presents far greater difficulties.

The solution properties of polymers have been described theoretically by considering the effects governing properties individually For example, in the Flory-Huggins Theory (1-3) the two principal phenomena are the mixing process which gives rise to an entropy term, and a change in the energy environment of a polymer which gives rise to an interaction free energy (or enthalpy) term. More sophisticated models include additional more complex phenomena, but the descriptions of polymer solutions remain inadequate for many purposes. A major obstacle to a more thorough understanding is our lack of knowledge of the molecular factors controlling the equilibrium state.

The long range goal of this research is to expand our understanding of how such molecular factors as functional groups, repeat unit structure, copolymerization, and tacticity affect polymer solution behavior. In order to accomplish this, we will obtain comprehensive, reliable, thermodynamic data on model polymer solutions. This kind of information, noted for its paucity, should be useful in developing new theories or correlations of polymer solution behavior.

In the current research program, we have studied how methyl groups influence polymer solution behavior by the careful construction of an experimental system. Specifically, we have studied the solution properties of a series of well-tailored homopolymers constructed from closely related styrene-based monomers; namely, styrene, α-methyl styrene and to limited extent p-methyl styrene. Differences in the solution properties of the materials of interest could then be attributed to specific differences in repeat unit structure; namely, the number and location of methyl groups. These differences, in turn, will be manifested in chain stiffness and interactions. Polymers were synthesized by the anionic living-polymer reaction to produce amorphous materials with narrow molecular weight distributions. In addition the copolymers were homogeneous and random. It should be noted too, that despite their commercial importance, copolymers have been largely neglected. Our study will help fill this void.

Since the repeat units of the polymer are similar, one might suspect that only small, perhaps unmeasureable, differences exist. As a first step, we undertook an exploratory study to see if the materials actually exhibited significantly different behavior. This included a search for experimental parameters that were sensitive to the subtle differences in our materials. The second virial coefficient (SVC) in toluene, the Θ-temperature in poor solvents and the empirically determined Flory-Huggins parameter, χ, in moderately concentrated toluene solutions, were the primary parameters investigated. The measurement of SVC's is subject to considerable scatter, whereas χ can be ascertained with better confidence. The Θ-temperature, which can be determined easily and accurately, is sensitive to difference in solution properties; hence it is an excellent parameter for comparing solution properties. In fact, minima in Θ-temperature with copolymer composition were the most pronounced property difference observed.

Two salient findings emerged from this study. Random copolymers are generally more soluble than their parent homopolymers, and methyl groups affect polymer solubility in more complex ways than is normally appreciated. That is, although styrene and α-methyl styrene are chemically similar, they differ sufficiently to produce intermer repulsions which increase copolymer solubility. In fact, comparison of our solubility data with the few available in the literature for copolymers indicates that the phenomena may be quite general, if not universal. The solubility parameter concept could be extended to explain and amplify some of these concepts, but in other instances this attempt resulted in less than satisfactory results. Evidently, entropic contributions arise, and the complex influence of methyl groups cannot be explained in terms of simple interaction energy effects. Studies of the solubilities of other styrene based monomers will be required to aid in the clarification of this situation.

II. LITERATURE SURVEY

A. Introduction

Polymer solutions are usually divided into two groups according to their concentrations. Dilute solutions contain less than 1% to 2% polymer by volume, and concentrated solutions contain greater than 10% polymer by volume. The intermediate range has received virtually no attention in the literature. In dilute solutions polymer molecules are pictured as randomly coiled chains existing as isolated clouds in a sea of solvent. Concentrated polymer solutions are pictured as a homogeneous mass of solvent and entangled polymer chains. Different theoretical and analytical techniques are used to study each type of solution.

The literature on polymer solution thermodynamics is voluminous. Considerable effort has been devoted to developing theoretical models for describing dilute and concentrated solutions; but, to date, no completely satisfactory theories have been published. Experimental studies of dilute polymer solutions are much more common than those on concentrated solutions. All experimental investigations are fraught with difficulties. The solution properties of copolymers, despite their commercial importance, have received little attention in the open literature.

Those aspects of the literature which bear directly on this research are reviewed in the following sections.

B. Concentrated Solution Theory

1. Introduction

Concentrated polymer solutions can be depicted as a homogeneous mass of solvent and entangled chains. The concentration at which chain combination becomes important depends on molecular weight. The properties of interest are heats, entropies, free energies and volume changes of mixing, as well as phase equilibria.

The natural thermodynamic variable to describe solutions is the Gibbs free energy of mixing since all thermodynamic properties including phase equilibria can be computed from it. The theoretical problem is to propose molecular models and thereby devise adequate expressions for ΔG_m. This is difficult since the condensed state and liquid solutions are not well understood even for small molecules. Two diverse approaches have been followed. Some investigators have developed expressions for ΔG_m via first principles using molecular models coupled with statistical mechanics. Others have proposed empirical expressions for ΔG_m. The former approach has the great advantage that experimentally determined parameters are related to a specific model for the behavior of a polymer solution and hence to molecular processes. The empirical approach has resulted in expressions for ΔG_m that describe the behavior of hydrogen-bonded polymer-solvent systems. These systems cannot be described in terms of current theories.

2. The Flory-Huggins Theory

The oldest and best known theory for describing polymer solutions was independently developed in the early 1940 s by Flory (1) and Huggins (2,3). These authors used the classical lattice model approach to obtain an expression for the entropy of mixing:

$$(1) \quad \Delta S_m = -R(n_1 \ell n v_1 + n_2 \ell n v_2)$$

where ΔS_m is the entropy of mixing, n is the number of moles, v is volume fraction, and subscripts 1 and 2 refer to solvent and polymer respectively. Note that this expression contains no lattice or chain stiffness parameter. Because ΔS_m depends on the ratio of the number of polymer conformations in the amorphous solid and solution, the effect of chain stiffness cancels. Equation 1 was combined with a Van Laar enthalpy of mixing equation

$$(2) \quad \Delta H_m = RT\chi n_1 v_2$$

to yield the well known Flory-Huggins equation for the Gibbs free energy of mixing

$$(3) \quad \Delta G_m = RT(n_1 \ell n v_1 + n_2 \ell n v_2) + RT\chi n_1 v_2$$

where χ is the interaction parameter. For the first system investigated in detail -- rubber and benzene -- χ was found to be a constant at fixed temperature, which lent support to the theory.

As a result of numerous studies, it was found that the theory suffers from two serious shortcomings. Even in nearly athermal solutions, χ may range as high as from 0.3 to 0.5. If χ merely represented enthalpic effects, it would be zero in nearly athermal solutions. This fact indicates that χ contains entropic as well as enthalpic components, and equation 2 should be interpreted as a free energy instead of as an enthalpy. Furthermore, it has been found that χ may depend quite strongly on concentration, a circumstance not accounted for by this theory.

The Flory-Huggins theory is the polymer solution analogue of regular solution theory. This parallel can be seen by comparing the equations for ΔG_m that follow:

<u>Regular Solution Theory</u>

(4) $\Delta G_m = RT(n_1 \ell n x_1 + n_2 \ell n x_2) + An_1x_2$

<u>Flory-Huggins Theory</u>

(5) $\Delta G_m = RT(n_1 \ell n v_1 + n_2 \ell n v_2 + \chi n_1 v_2)$

where x refers to mole fraction, and subscripts 1 and 2 in regular solution theory refer to the two species in the solution. In polymer solutions, volume fraction replaces mole fraction. The development of equations for ΔH_m in both theories is almost identical. For regular solutions, ΔS_m is calculated from the ratio of the number of arrangements of cells containing the solution components in a lattice of equal sized cells to the number of arrangements in the pure state. The computation of the number of conformations of a polymer molecule in solution can be viewed simply as a restriction on random mixing in regular solutions.

In spite of its many shortcomings, the Flory-Huggins theory represented a significant advance in that it predicted qualitatively all the peculiar properties of polymer solutions, and it is still widely used - in large part because of its simplicity. The Θ-temperature, a concept of considerable practical and theoretical importance, is based on the Flory-Huggins theory. Furthermore, polymer solubility can be treated with this theory coupled with the solubility parameter concept provided the entropic quality of χ is recognized. We will make use of this in later sections.

3. Corresponding States Theory

In the past several years Flory and his coworkers (4,5,8) have developed a corresponding states theory for solutions of ordinary molecules as well as polymers. An inherent difficulty with the lattice model approach is that it does not account for the properties of the pure fluids, which can be significantly different for polymer solutions, and should be accounted for by any theoretical treatment.

Following the work of Prigogine et al. (7-11) Flory developed a partition function which can be used to describe ordinary molecules, polymers and their solutions:

$$Z = (\text{const})(\gamma(v^{1/3} - v^{*1/3})^3)^{rNC}\exp(-E_o/kT) \tag{6}$$

where E_o is the intermolecular energy; (rNC) represents the total number of intermolecular degrees of freedom; r is the number of segments per species; N is the number of species; C restricts the degree of freedom by accounting for the location of neighboring mers in the chain. The term $\gamma(v^{1/3} - v^{*1/3})^3$, after Tonks (12), accounts for the free volume where v is volume per segment and v^* is the hard core volume per segment. The properties of the pure components are expressed in terms of a reduced partition function:

(7) $Z = (\text{const})(\tilde{v}^{1/3} - 1)^{3rNC}\exp(rNC/\tilde{v}\tilde{T})$

and a simplified equation of state

(8) $\tilde{T} = (\tilde{v}^{1/3} - 1)\tilde{v}^{4/3}$

where $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ are defined as

$$\tilde{v} = v/v^*$$
$$\tilde{T} = T/T^* = 2v^*CRT/S\eta$$
$$\tilde{p} = p/p^* = 2p^{*2}/S\eta$$

S is the number of contact sites per segment and η is a constant characterizing the energy of interaction. The reducing parameters can be calculated from the volume coefficient of expansion $\alpha = (1/V)(\partial V/\partial T)_p = 0$, the compressibility $\gamma = (\partial p/\partial T)_V$ and the specific volume of the pure components. Aside from a combinatorial entropy term the same form of the reduced partition function is obtained for solutions, but the definitions of $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ depend upon concentration of the solution.

To develop an expression for ΔG_m, Flory assumed random mixing which he described by the Flory-Huggins expression for ΔS_m. Residual contributions to ΔG_m and ΔS_m were computed from the solution partition function as were expressions for ΔH_m and ΔV_m. The final equations contain two parameters S_2/S_1, the ratio of segment contact areas, and X_{12}, an interaction energy term. S_2/S_1 was established from model studies, and X_{12} was obtained (preferably) from ΔH_m. Flory et al. compared, measured and calculated values of X_{12} and ΔV_m. In general this theory predicted the form of the variation of X_{12} with solution composition from parameters obtained from measurements of ΔH_m or ΔV_m. The demonstration of the importance of equation of state effects upon polymer solutions is the key point.

4. The Maron Theory

Maron and his coworkers developed an empirical equation for ΔG_m (13-15). The chief feature of their equation is that $RT\mu n_1 v_2$, which is analagous to $RT\chi n_1 v_2$ in the Flory-Huggins theory, is taken to be an interaction free energy term. The symbol μ replaces χ which is represented by an arbitrary function of concentration and temperature, fit to experimental results. For many polymer systems, such as polystyrene in cyclohexane (16), μ is a linear function of concentration up to about 50 percent by volume of polymer.

Maron also introduces terms to account for changes in free volume on mixing. Our unpublished calculations for the system they studied reveal that these terms make negligible contributions. In addition, their theoretical justification is obscure.

5. The Segment Interaction Equation

Heil and Prausnitz (17) proposed an equation for ΔG_m based on the concept of local volume fraction first suggested by Wilson (18) and later investigated in detail by Prausnitz and his associates (19,20). Their equation contains only two empirical parameters per solvent-polymer pair, $(g_{12} - g_{11})$ and $(g_{12} - g_{22})$, and it can readily be extended to describe multicomponent systems plus those which show strong interactions such as hydrogen bonding. The equation below can be used to predict phase equilibria in binary and multicomponent systems. It is rather cumbersome in form, and it was not derived from first principles; hence, the exact meaning of the parameters is not clear.

$$(9)\quad \Delta G_m/RT = n_1 \ln \epsilon_{11} + s_2 n_2 \ln \epsilon_{22} + (1 - s_2) n_2 \ln v_2 + n_1 \epsilon_{21} (g_{12} - g_{11})/RT + n_2 \epsilon_{12} s_2 (g_{12} - g_{22})/RT$$

where $\epsilon_{11} = v_1/(v_1 + v_2 \exp(-(g_{12} - g_{11})/RT))$, $\epsilon_{21} = 1 - \epsilon_{11}$, $\epsilon_{22} = 1 - \epsilon_{12}$, s_2 is the number of segments in the polymer chain and

$\epsilon_{12} = (v_1 \exp(-(g_{12} - g_{22})/RT))/(v_1 \exp(-(g_{12} - g_{22})/RT) + v_2)$

The main weakness in this equation from our point of view is that it was not founded on molecular principles.

C. The Solubility Parameter Concept

1. Introduction

Intermolecular forces are an important factor in determining solubility. The solubility parameter, δ, defined as $(\Delta U_V/V_1^c)^{1/2}$, the square root of the energy of vaporization of a compound divided by its molecular volume is a measure of total intermolecular forces; hence, it is an important tool in predicting and explaining solubility or the phenomena which depend on intermolecular forces. Hildebrand first proposed the concept in 1916 (21). Scatchard (22) related the concept to regular solution theory in 1931, and Hildebrand reviewed it thoroughly in his book in 1950. The relationship between the solubility parameter and solution thermodynamics is reviewed in the next section after which its use in describing polymer solubility is discussed.

2. Regular Solution Theory

As originally formulated by Hildebrand in 1929, the regular solution Gibbs free energy of mixing was given by

$$(4) \qquad \Delta G_m = RT\ (n_1 \ell n \chi_1 + n_2 \ell n \chi_2) + An_1\chi_2$$

The entropy of mixing term —— easily derived from lattice model statistics —— is the same as for an ideal solution.

$$(10) \qquad \Delta S = -R(n_1 \ell n \chi_1 + n_2 \ell n \chi_2)$$

When the concept of the regular solution was first formulated, it was assumed that an athermal solution would necessarily exhibit ideal solution behavior. Years later it was found that this is not the case for polymer solutions; that is, their solution behavior deviates widely from ideality even when no heat effects are observed. In 1953 Hildebrand reformulated the concept to embrace all solutions for which thermal agitation was sufficient to provide completely random mixing. This interpretation still permits the separation of enthalpic and entropic contributions to the free energy of mixing.

The enthalpy of mixing term, An_1x_2, for low molecular weight species is derived below. The derivation for polymer solutions closely parallels it. Consider a lattice with coordination number z containing randomly mixed A and B molecules. The total energy of the system is given by

$$(11) \quad U = (N_{AA}w_{AA} + N_{BB}w_{BB} + N_{AB}w_{AB})$$

where N is a number of bonds, w is the energy of a bond and the subscripts refer to AA, BB and AB bonds respectively.

If the molecules are randomly mixed $N_{AB} = zx_AN_B$, $N_{AA} = zx_AN_A/2$, and $N_{BB} = zx_BN_B/2$, where N_A and N_B refer to the number of A and B molecules in the system. Then

$$(12) \quad U = z\bar{A}(w_{AA}x_A^2/2 + w_{BB}x_B^2/2 + x_Ax_Bw_{AB})$$

and

$$(13) \quad \Delta U_m = U - U_A - U_B = z\bar{A}Wx_Ax_B$$

where

$$(13A) \quad W = w_{AB} - (w_{AA} + w_{BB})/2$$

and $\bar{A}$ is Avagadro's number. If $\Delta(PV) = 0$, $\Delta U_m = \Delta H_m$, and $\Delta H_m = Ax_Ax_B$ with

$$(13B) \quad A = \bar{A}zW$$

A simple relationship can be developed between regular solution theory and the solubility parameter provided dispersion forces are the only intermolecular interactions. Recall that $\Delta U_A^* = -\bar{A}zw_{AA}/2$ and $\Delta U_B^* = -\bar{A}zw_{BB}/2$. If dispersion forces are the only type, $\bar{A}zw_{AB}/2 = -(\Delta U_A\Delta U_B)^{1/2}$. Then recalling equations 13, 13A and 13B

---

[*] Energy of vaporization

(14) $A = -(2(\Delta U_A \Delta U_B)^{1/2} - (\Delta U_A + \Delta U_B)) = (\Delta U_A^{1/2} - \Delta U_B^{1/2})^2$

Thus

(15) $A = (\delta_A - \delta_B)^2 \bar{v}^o$

where $\bar{v}^o = (x_A v_A^o + x_B v_B^o)$. Thus, the regular solution parameter A can be calculated from solubility parameters via equation 15 provided only dispersion forces exist. Since δ can be easily computed from pure component data, reasonable estimates of the solution properties of compounds, which satisfy the assumptions, can be made without experiment.

Regular solution theory can qualitatively predict phase behavior, azeotropes and endothermic mixing. Since it is based on restrictive assumptions, it should be expected to apply to few real solutions. Evidently, more sophisticated models are needed to represent real solutions.

3 The Solubility Parameter Concept in Polymeric Systems

The solubility parameter concept finds considerable application in polymeric systems. Selection of the mixed or pure solvents can require considerable experimental effort. By using the solubility parameter concept, the number of experiments can be reduced It can also be used to predict the Flory-Huggins parameter and to predict swelling.

The solubility parameter is a measure of total intermolecular forces. As originally formulated the theory treats dispersion forces only, whereas real systems often involve other types as well In order to extend the solubility parameter concept to these systems, it is resolved into components due to dispersion (London), polar, induced polar and hydrogen bonding forces. Methods are available to measure or estimate dispersion forces (24-25). Techniques have been developed to estimate polar and induced polar forces (25-27). No completely successful technique has yet been shown to treat hydrogen bonding effects, but several approximate methods are available (27-30).

Two different techniques have been developed which use the solubility parameter concept to correlate and predict polymer solution properties; both are based on the resolution of the solubility parameter into components due to different types of intermolecular forces. The first technique developed by Hansen (27) and Crowly, Teague and Lowe (31) is used to predict and correlate polymer solubility. Results of solubility experiments are often presented on three-dimensional figures whose axes are different molecular force components. The coordinate space is divided into soluble and non-soluble regions; each polymer requires its own chart. Once this figure has been established, the solvent power of a solvent can be estimated by consulting the chart. A section of a three-dimensional solubility plot at fixed value of hydrogen bonding parameter is presented in figure 1.

A more quantitative technique for predicting solution properties was devised by Blanks and Prausnitz (26). They devised a method for estimating χ, the Flory-Huggins parameter in polymer systems that do not exhibit hydrogen bonding. As previously explained, χ, the Flory-Huggins parameter contains a large entropic contribution. Hence, one can write

(16) $\chi = \chi_H + \chi_S$

After examining data for many systems, Blanks and Prausnitz assigned a mean value of 0.34 to χ_S, which they subsequently used for all polymer systems. Various techniques were used to calculate χ_H according to the polarity of the poly-

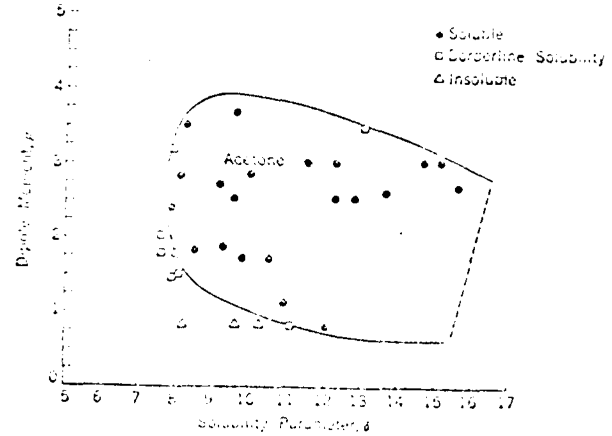

Figure 1. Cross-section of Cellulose Nitrate Solubility Plot Through γ = 10(H1) (31)

mer and solvent. In non-polar polymer-solvent systems

$$(17) \quad \chi_H = v_S(\delta_P - \delta_S)^2/RT$$

where v_S is the molecular volume of the solvent and subscript P and S refer to polymer and solvent. Different methods are used to estimate χ_H if the solution components are polar. For polar polymer-solvent systems

$$(18) \quad \chi_H = (v_S/RT)((\lambda_S - \lambda_P)^2 + (\tau_S - \tau_P)^2)$$

where τ and λ are the polar and non-polar components of δ. In polar-nonpolar systems

$$(20) \quad \chi_H = (v_S/RT)((\lambda_S - \lambda_P)^2 + (\tau^2 - 2\psi))$$

where ψ is an empirically determined function of λ of the non-polar component times τ. Their technique was found to be reasonably accurate.

The solubility parameter of low molecular weight compounds can be computed directly from their heats of vaporization, whereas an assortment of indirect methods must be used for polymers because they do not vaporize. The simplest method is to use δ of the repeat unit as an estimate of polymer solubility parameter. Small (32) devised a method of calculating them from group contributions. The solubility parameter of a solvent that produces maximum swelling in a lightly cross-linked polymer is often used as an estimate; this technique can give erroneous results. Other methods are available but they are often unsatisfactory.

A number of factors limit the application of the solubility parameter concept. Principally, the solubility parameter of a polymer cannot be determined unambiguously, and a range of values is often reported. The separation of the solubility parameter into molecular force components is empirical, although Bagley (24) has suggested a technique for measuring dispersion forces. Hydrogen bonding effects are not well understood. Since the solubility parameter is based on the Flory-Huggins theory, the weaknesses of this theory add additional limitations.

Aside from its eminent usefulness, the main theoretical virtue of the solubility parameter concept is that it relates polymer solution properties to molecular force effects. Although theories have been developed which relate molecular phenomena to solution thermodynamics, they rarely contain the specific effects of molecular factors such as stiffness, mer geometry or intermolecular forces on solution thermodynamics. (An exception to this is Flory's corresponding states theory.) Thus if solution properties are compared, the solubility parameter concept can give us some information about the influence of molecular forces on observed properties.

D. Dilute Solution Theory

1. Introduction

In dilute solutions (less than 1% or 2% by volume) molecules are pictured as random coils existing as isolated clouds in a sea of solvent. Since this model differs markedly from the concentrated solutions case, in that the solution is heterogeneous on a molecular scale rather than homogeneous, different analytical treatments are employed in dilute solution theory. The Gibbs free energy of mixing is still the natural thermodynamic variable. In addition to free energies, polymer conformations are studied in dilute solutions. Relationships have been devised to relate the thermodynamic parameters with molecular dimensions.

2. Elementary Thermodynamics

The free energies of dilute polymer solutions are presented in the form of a virial equation for $\overline{\Delta G}$, as shown

$$(20) \qquad \overline{\Delta G}_1 = RT\, \ln a_1 = -RT(A_1 c + A_2 c^2 \dots)$$

where A_i is the ith virial coefficient, c is the concentration in grams/liter, a_1 if the activity and the bar superscript denotes partial molal quantities. The equation is so arranged that the activity of the solvent is 1.0 at infinite dilution of polymer. Activities and second virial coefficients (SVC) are commonly obtained from osmometry or light scattering measurements.

Information about A_1, the first virial coefficient, can be obtained by considering the equation for ΔG_m of an ideal solution whose free energy is given by; $\Delta G_m = RT(x_1 \ln x_1 + x_2 \ln x_2)$. In dilute solutions $\overline{\Delta G}_1 = RT \ln x_1 = -RT(x_2 + (1/2)x_2^2 + \dots)$. Since $x_2 \approx x_2/x_1 = v_1^o c/M_2$ where M_2 is the polymer molecular weight. Hence,

$$(21) \qquad \overline{\Delta G}_1 = -RTv_1^o(c/M_2 + v_1^o c^2/2M_2^2 + \dots)$$

Since the solvent is ideal at infinite dilution

$$(22) \qquad A_1 = v_1^o/M_2$$

Information about A_2, the SVC, can now be obtained by considering the Flory-Huggins equation

$$(23) \qquad \overline{\Delta G}_1 = RT(\ln(1-v_2) + (1 - v_1^o/v_2^o)v_2 + \chi v_2^2)$$

where v_1^o/v_2^o is the ratio of solvent to polymer molecule volume. In dilute solutions

$$(24)\qquad \overline{\Delta G}_1 = -RT((v_1^o/v_2^o)v_2 + (1/2 - \chi)v_2^2 + \ldots)$$

Concentration can be expressed in terms of grams/liter by using the following; $v_2 = c/\rho_{polymer}$. Comparison of equations 20 and 24 suggests that the SCV is related to $(1/2 - \chi)/\rho^2_{polymer}$.

The Θ-temperature [illegible]ameter of polymer solution theory, can [illegible]oint. The excess Gibbs free energy [illegible]on second and higher powers of concent[illegible] the square of the concentration in d[illegible]e equation 20 and 21.) We can then wri[illegible] $v_2^2(\psi-\kappa)$ where $\overline{\Delta S}_1^* = R\psi v_2^2$ and $\overline{\Delta H}_1^* = RT\kappa v_2^2$. It is convenient to express the difference $(\psi-\kappa)$ as follows;

$$(25)\qquad (\psi-\kappa) = \psi(1 - \Theta/T) = (1/2 - \chi)$$

where $\Theta = \kappa T/\psi$. When $\psi=\kappa$, $\Theta=T$; or equivalently, $\chi=1/2$, the excess Gibbs free energy due to segment-solvent interaction is zero. Other properties of polymer solutions at Θ conditions are discussed in subsequent sections.

$\overline{\Delta H}_1^*$ and $\overline{\Delta S}_1^*$ are the enthalpy and entropy components of $\overline{\Delta G}_{1Excess}$.

3. Molecular Dimensions

Useful information can be derived about the dimensions of polymer chains and the distribution of chain sizes from elementary model analysis. If a chain is made up of $\sigma+1$ randomly oriented elements of length L, the root-mean-square end-to-end distance derived from random walk theory is

$$\overline{h^2} = \sigma L^2 \tag{26}$$

If the angle between bonds is restricted to free rotation on a valence cone of angle θ, then

$$\overline{h^2} = \sigma L^2(1+\cos\theta)/(1-\cos\theta) \tag{27}$$

For the freely rotating polymethylene chain

$$\overline{h^2} = 2\sigma L^2 \tag{28}$$

If additional restrictions are placed on free rotation to obtain more realistic models, the form of equation 26 is retained, but different coefficients appear. In general,

$$\overline{h^2} = \sigma\beta^2 \tag{29}$$

where β takes on numerical values characteristic of individual polymers.

Polymer chain dimensions are obtained most directly via light scattering as an average radius of gyration. For a freely orienting polymer chain, the relationship between radius where v_1^o/v_2^o is the ratio of solvent to polymer molecule volume. In dilute solutions

$$(24) \quad \overline{\Delta G}_1 = -RT((v_1^o/v_2^o)v_2 + (1/2 - \chi)v_2^2 + \dots)$$

Concentration can be expressed in terms of grams/liter by using the following; $v_2 = c/\rho_{polymer}$. Comparison of equations 20 and 24 suggests that the SCV is related to $(1/2 - \chi)/\rho^2_{polymer}$.

The Θ-temperature, an important parameter of polymer solution theory, can be introduced at this point. The excess Gibbs free energy of mixing, which depends on second and higher powers of concentration, is proportional to the square of the concentration in dilute solution. (Compare equation 20 and 21.) We can then write $\overline{\Delta G}_{1Excess} = RTv_2^2(\psi-\kappa)$ where $\overline{\Delta S}_1^* = R\psi v_2^2$ and $\overline{\Delta H}_1^* = RT\kappa v_2^2$. It is convenient to express the difference $(\psi-\kappa)$ as follows;

$$(25) \quad (\psi-\kappa) = \psi(1 - \Theta/T) = (1/2 - \chi)$$

where $\Theta = KT/\psi$. When $\psi=\kappa$, $\Theta=T$; or equivalently, $\chi=1/2$, the excess Gibbs free energy due to segment-solvent interaction is zero. Other properties of polymer solutions at Θ conditions are discussed in subsequent sections.

$\overline{\Delta H}_1^*$ and $\overline{\Delta S}_1^*$ are the enthalpy and entropy components of $\overline{\Delta G}_{1Excess}$.

3. Molecular Dimensions

Useful information can be derived about the dimensions of polymer chains and the distribution of chain sizes from elementary model analysis. If a chain is made up of $\sigma+1$ randomly oriented elements of length L, the root-mean-square end-to-end distance derived from random walk theory is

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If additional restrictions are placed on free rotation to obtain more realistic models, the form of equation 26 is retained, but different coefficients appear. In general,

$$\overline{h^2} = \sigma \beta^2 \tag{29}$$

where β takes on numerical values characteristic of individual polymers.

Polymer chain dimensions are obtained most directly via light scattering as an average radius of gyration. For a freely orienting polymer chain, the relationship between radius of gyration and end-to-end distance is given by $\overline{R_g^2} = \overline{h^2}/6$. The dimensions of real polymers at the Θ-conditions are often characterized by the ratio, X, of the measured chain radius of gyration, $R_{g,o}$, to that calculated from equation 28. Thus, since $R^2_{g,of} = \sigma L^2/3$

$$X = [3\overline{R^2_{g,o}}/\sigma L^2]^{1/2}$$

The following gives the segment density distribution in spherical coordinates of a freely orinting polymer chain, one end of which is fixed at the origin while the other end is contained within a spherical shell of volume $4\pi r^2 dr$.

$$(30) \qquad \rho(r)dr = \frac{\exp(-3r^2/2\sigma L^2)4\pi r^2 dr}{[L(2\pi\sigma)^{1/2}/3]^3}$$

This expression can be modified to give the density of segments around the center of mass of the polymer molecule.

The foregoing rudimentary treatments are based on volumeless polymer segments. For real chains, certain conformations will be forbidden because of excluded volume effects. Hence, real chains will be more extended than ideal chains. This phenomenon is known as the intrachain-excluded-volume effect.

The environment in which a polymer chain exists will influence its dimensions. In a good solvent it will expand since the environment is favorable, whereas in a poor solvent it will contract since the environment is unfavorable. If a solvent is sufficiently poor, the contraction produced by the poor solvent will cancel the expansion produced by the intrachain-excluded-volume effect; then, a polymer molecule will behave as a volumeless freely orienting polymer chain. These conditions are met at the Θ-conditions.

4. Dilute Solution Theory

There are several ways of approaching the analysis of dilute polymer solutions. An elegant method was developed by B. H. Zimm (43) who applied the McMillan-Mayer theory (44) to polymer solutions. This theory treats an osmotic equilibrium situation and obtains an expression for the osmotic pressure which is formally the same as the virial equation for a nonideal gas. The analogy arises because the virial equation of state treats a relatively small number of molecules which exert intermolecular forces, whereas osmotic equilibria involves a small number of molecules dispersed in a fluid which exert intermolecular forces. The second, third and higher virial coefficients in osmotic pressure equilibria correspond to two body, three body, etc. interactions, while the corresponding virial coefficients in osmotic pressure equilibria correspond to two molecule, three molecule, etc. interactions. The theory permits reduction of a many body problem to sucessively two body problems, three body problems, etc.

The osmotic pressure, π, is given by

$$(31)\qquad \pi/RT = \sum_n B_n (v_1^o c/M_2)^n + v_1^o c/M_2$$

where B_i is the ith virial coefficient. The SVC is given by

$$(32)\qquad B_2 = -1/2 \int_0^\infty [\exp(-w(r)/kT)] 4\pi r^2 dr$$

where w(r) is the energy needed to bring molecules from infinity to a distance of separation r. The polymer molecules can be represented as a sphere of uniform polymer segment density which is not affected when two spheres overlap. Integration yields the following result:

(33) $$B_2 = s^2 V^o(1/2 - \chi)(1 - 0.324(1/2 - \chi)V^2/V^o V_o + \ldots)$$

where V^o is the segment volume, s is the number of segments in the polymer molecule, V_o is the volume permeated by a polymer molecule and $V = sV^o$. If a Gaussian distribution is used to replace a uniform sphere the constant in equation 33, 0.324 is replaced by 0.354.

Flory (34) developed an equation relating the expansion of a polymer chain from its random walk conformation induced by the presence of solvent. The driving force for chain expansion is the decrease in free energy produced by dilution; this force is opposed by an elastic force created by stretching the polymer chain from its random walk conformation. At equilibrium $(\partial G/\partial \alpha)_{T,P} = 0$ with $\Delta G = \Delta G_m + \Delta G_{elastic}$. This calculation yields

(34) $$\alpha^5 - \alpha^3 = 2C_m(1/2 - \chi)M^{1/2}$$

where $C_m = (27/(2^{5/2}\pi^{3/2}))(\bar{v}^2/N\bar{v}_1^o)(\bar{h}_o^2/M)^{-3/2}$

$\bar{h}_o$ is the end-to-end dimensions of a polymer chain at Θ conditions (for an unperturbed chain); α is the ratio of polymer end-to-end distance to that for the unperturbed chain; $\bar{v}$ is the specific volume of the polymer; N is Avagadro's number and $\bar{v}_1^o$ is the volume of the solvent molecule.

This equation provides a connecting link between thermodynamic interactions and chain dimensions. Note that when $\chi = 1/2$, or equivalently $T = \Theta$, $\alpha = 1.0$. Hence random flight statistics are followed at Θ conditions. In the amorphous solid $\bar{v}_1^o$ is very large indicating that $\alpha = 1.0$; therefore, random flight statistics are followed in the amorphous solid. To rephrase these results, according to theory interchain excluded volume effects disappear at Θ conditions and in the amorphous solid.

5. Intrinsic Viscosity

Of all the measurements performed on polymer solutions, intrinsic viscosities are the easiest to execute. Hence, much attention has been devoted to relating intrinsic viscosities to molecular weight and polymer chain dimensions.

Two rudimentary models have been conceived to study the hydrodynamics of polymer chains. These models provide useful limits to the behavior of polymers and serve as a starting point for the construction of more complex theories. In the free draining model, the solvent penetrates the polymer, but the flow perturbations do not interact with each other. With this model the intrinsic viscosity is simply proportional to the molecular weight (34). In the equivalent sphere model the polymer molecule is assumed to behave as a rigid sphere not penetrated by solvent. If the behavior of a polymer molecule can be represented as a rigid inpenetrable sphere, the intrinsic viscosity of a polymer molecule would be proportional to M^a, where $a = 0.5$ in Θ-solvent, and $a > 0.5$ in better solvent media.

Flory and Fox (47-48) proposed the following equation relating polymer chain dimensions, molecular weight and intrinsic viscosity.

$$(35) \qquad [\eta] = \Phi(\overline{h^2})^{3/2}/M$$

where Φ was introduced as a universal constant. The value of Φ was found experimentally to be somewhat smaller than predicted from the Kirkwood-Riseman theory (46,34). Equation 35 can be rewritten using the relationship $(\overline{h^2})^{1/2} = \alpha h_o$ where h_o is the root-mean-square end-to-end distance of a polymer molecule at Θ conditions as

$$(36) \qquad [\eta] = \Phi(h_o^2/M)^{3/2} M^{1/2} \alpha^3$$

Since (h_o^2/M) should be independent of molecular weight

$$(37) \qquad [\eta] = KM^{1/2}\alpha^3$$

where $K = \Phi(h_o^2/M)^{3/2}$ = constant. At Θ conditions where $\alpha = 1$.

$$(38) \qquad [\eta] = K_\Theta M^{1/2}$$

The constant Φ has been found to vary slightly with solvent power (49). A key assumption in this development was that α is the same whether obtained from light scattering or intrinsic viscosity measurements. Since the processes involved are fundamentally different, there is no reason to believe a priori, that they should be equal. Although it is possible to calculate polymer chain dimesions with equation 38, more assumptions are required than for light scattering.

6. Stochmayer-Fixman-Kurata Method for Detrmining Unperturbed Dimensions

Chain dimensions under Θ conditions are of considerable theoretical interest. To compute Θ dimensions from intrinsic viscosity measurements K_Θ is required, which can be obtained by measuring intrinsic viscosity at the Θ-temperature in a given solvent. Another technique for obtaining K_Θ was developed by Stockman, Fixman and Kurata (SFK) (50-51); They proposed $[\eta]/M^{1/2}$ to be a linear function of $M^{1/2}$ with intercept K_Θ for a given polymer. The slope of the SFK plot will decrease with decreasing solvent power; the slope is zero for a solvent a Θ conditions. The technique, which has been studied in detail (52-56), has several limitations. Extrapolations from good solvent data must be made with care since the slope is large. Curvature has been noted in these plots at molecular weights above 500,000 (52-55).

E. Phase Equilibria and the Θ-Temperature Concept

Polymer solvents are usually classified in two ways: good solvents and poor solvents. Good solvents are those in which phase separation cannot be induced by heating or cooling, whereas poor solvents are those in which phase separation can be induced. Some other methods of measuring polymer solvent power are second virial coefficients, Flory-Huggins parameters and the exponent a in the Mark-Houwink equation

(39) $[\eta] = KM^a$

A phase diagram for a series of polymers differing in molecular weight is shown in figure 2. Curves of this sort have several salient features: (a) The critical temperature, T_c, increases with increasing molecular weight, (b) In the vicinity of T_c the phase diagrams tend to be quite flat, and (c) The curves are skewed over to the solvent side of the phase diagram, whereas binary phase diagrams of low molecular weight compounds tend to be centrally located.

The thermodynamic criteria for phase separation is that the chemical potential of each component in each phase is equal. If this condition is applied to the Flory-Huggins equation, the following relations are obtained:

(40) $v_{2\ \text{critical}} = 1/(1 + (v_2^o/v_1^o)^{1/2})$

(41) $\chi_{\text{critical}} = (1 + (v_2^o/v_1^o)^{1/2})^2/(2(v_2^o/v_1^o))$

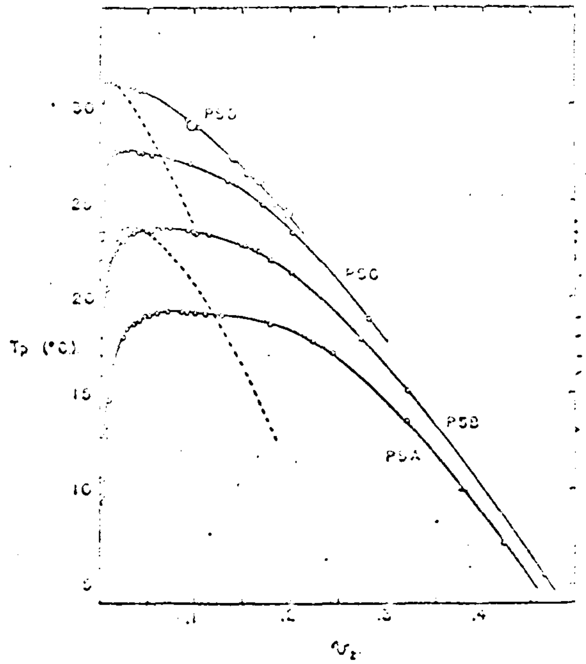

Figure 2. Precipitation temperatures T_p for polystyrene fractions in cyclohexane plotted against polymer volume fractions v_2. Theoretical curves are shown for two of the fractions. (33)

where v_2^o and v_1^o are the molecular volumes of the polymer and solvent and critical refers to the concentration at the highest precipitation temperature. At infinite molecular weight $v_{2\ \text{critical}} = 0$ and $\chi_{\text{critical}} = 1/2$. As the polymer molecular weight increases, Flory-Huggins theory predicts $v_{2\ \text{critical}}$ decreases. Observations of actual polymer-solvent phase diagrams (e.g., figure 2) bears this out (33). Substituting equation 41 into equation 25 yields

$$(42) \qquad [\ 1/2 - (1 + (v_2^o/v_1^o)^{1/2})/(2(v_2^o/v_1^o))] = \psi(1 - \Theta/T)$$

or

$$(43) \qquad 1/T_c = (1/\Theta)(1 + b/M^{1/2})$$

with $b = v_1\rho/\psi$, where T_c is the polymer critical temperature and ρ is the density. Thus, Θ can be evaluated in a plot of $(1/T_c)$ versus $(1/M^{1/2})$ by extrapolating to infinite molecular weight. At the Θ-temperature (the critical temperature of polymer of infinite molecular weight) $\chi = 1/2$. This aspect of the Θ-temperature concept is widely used, and its predictions are repeatedly borne out.

Further, Θ-temperatures can be used as a measure of solubility. For a series of polymers with different Θ-temperatures in a given solvent, polymer solubility increases with decreasing Θ-temperature.

Since most polymers are polydisperse, the actual phenomena involved in phase equilibria are more complicated.

Real systems are not binary but multicomponent. Koningsveld and his associates have examined this situation in detail (34-35). For practical purposes one would desire to know the average molecular weight best for characterizing a polymer for phase equilibria. Flory and Schultz (33) report a weight or z average is better than a number average molecular weight for these purposes.

F. Copolymer Solution Thermodynamics

Despite the commercial importance of copolymers, their solution properties have received little attention because of experimental difficulties. The few systems investigated were examined only in dilute solutions. In order to study copolymers, one must be able to measure not only their molecular weight distribution but also their gross composition and monomer arrangement along the chain backbone. Heterogeneities in any of these properties will complicate their analysis.

Random copolymers behave in solution very much like homopolymers, and their solution properties can be described by the same theories that apply to homopolymers (37,38). Block copolymers can show more complex behavior (39). Kotaka et al (80) has investigated the effects on copolymer solution properties produced produced by random, alternating and block copolymerization.

The random copolymers systems investigated in detail to date are styrene-methyl methacrylate (37,40), styrene-methyl acrylate (38), styrene-acrylonitrile (41), and methyl methacrylate-methyl acrylate (42). SVC's, phase equilibria, Θ-temperatures, molecular dimensions, and intrinsic viscosity-molecular weight relationships were determined.

The unperturbed molecular dimensions of styrene-acrylonitrile and styrene-methyl acrylate random copolymers were found to vary linearly with composition, whereas a modest nonlinear variation was observed for copolymers of styrene and methyl acrylate. With one exception (40), this information was obtained from intrinsic viscosities. Light scattering is a better technique for obtaining molecular dimensions, but this method is fraught with difficulties when applied to copolymers.

SVC's were measured for styrene-methyl acrylate, styrene-methyl methacrylate, and methyl acrylate-methyl methacrylate copolymers. The SVC's of these copolymers are larger than those obtained by linear interpolation between those of the parent homopolymers (see figure 3 for example). For styrene-acrylonitrile copolymers in methylethylketone, a nonsolvent for polyacrylonitrile, a sharp maximum in SVC was observed near the mid composition point (figure 4). The magnitude of the SVC at the maximum was about the same as that for polystyrene in toluene. This indicates that methylethylketone is a good solvent for the copolymer.

The relative increase in SVC for random copolymers has been tentatively attributed to intermer repulsions. The following equation has been proposed to describe the effects of intermer repulsions to a first approximation.

It can be written with various measures of interactions and concentration (40,37).

(44) $$\chi_{copolymer} = \chi_a w_a + \chi_b w_b - w_a w_b \chi_{ab}$$

where w is the weight fraction of monomer in the polymer, subscripts a and b refer to the comonomers, χ is the Flory-Huggins parameter of respective parent homopolymers and χ_{ab} is the intermer repulsion term. The intermer repulsion term, $w_a w_b \chi_{ab}$, causes the Flory-Huggins parameter of the copolymer to be different from that obtained by linear interpolation. Two observations about the solution behavior of copolymers can be drawn from equation 44. (1) To a first approximation χ_{ab} should be independent of solvent. (2) χ_{ab} should increase as the chemical dissimilarity of the comonomers increases. This is illustrated by comparing the differences in SVC for copolymers of styrene and acrylonitrile with styrene and methyl acrylate (figures 3 and 4).

As shown in figures 5 and 6, plots of Θ-temperature vs. composition show minima near the midcomposition points for styrene-methyl methacrylate copolymer in cyclohexanol and styrene-methyl acrylate copolymers in 2-methyl cyclohexanol. Since Θ -temperatures are quite sensitive to changes in interaction parameters, they are an excellent tool for examing solution properties. These Θ-temperature minima, like the SVC results, have been attributed to the effects of intermer repulsions.

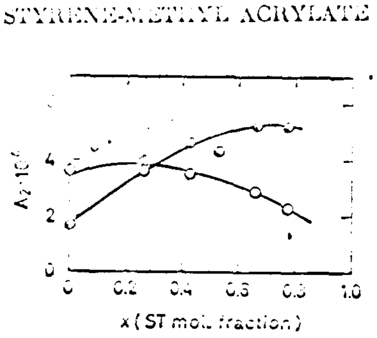

Figure 3. Composition dependence of A_2: (O) by light scattering in butanone and [illegible] by osmometry in toluene. The molecular weight is taken as 2.0×10^5. (36)

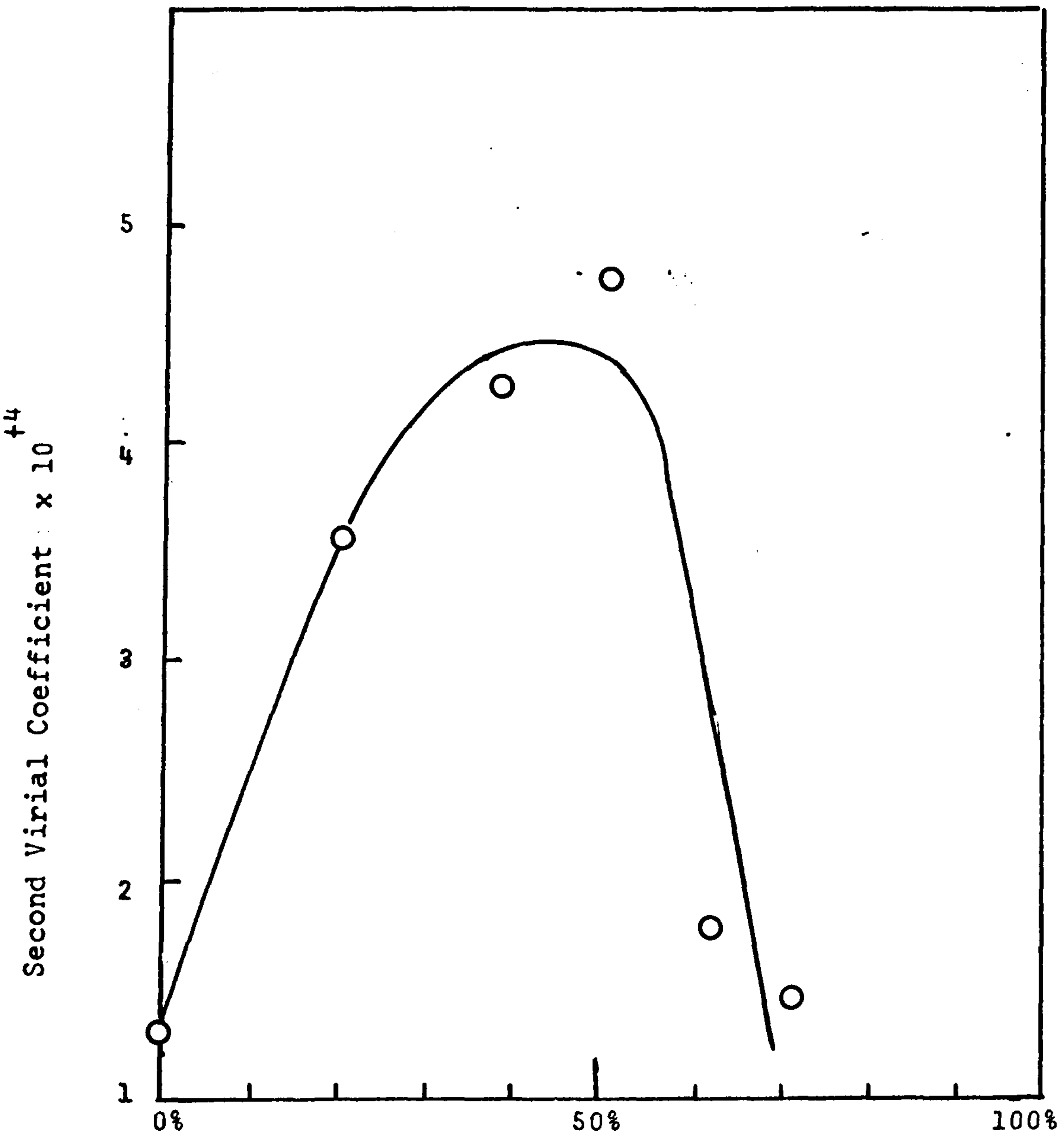

Figure 4 : Second Virial Coefficients for Polystyrene and Styrene-Acrylonitrile Copolymers in Methylethylketone after Shimura (41)

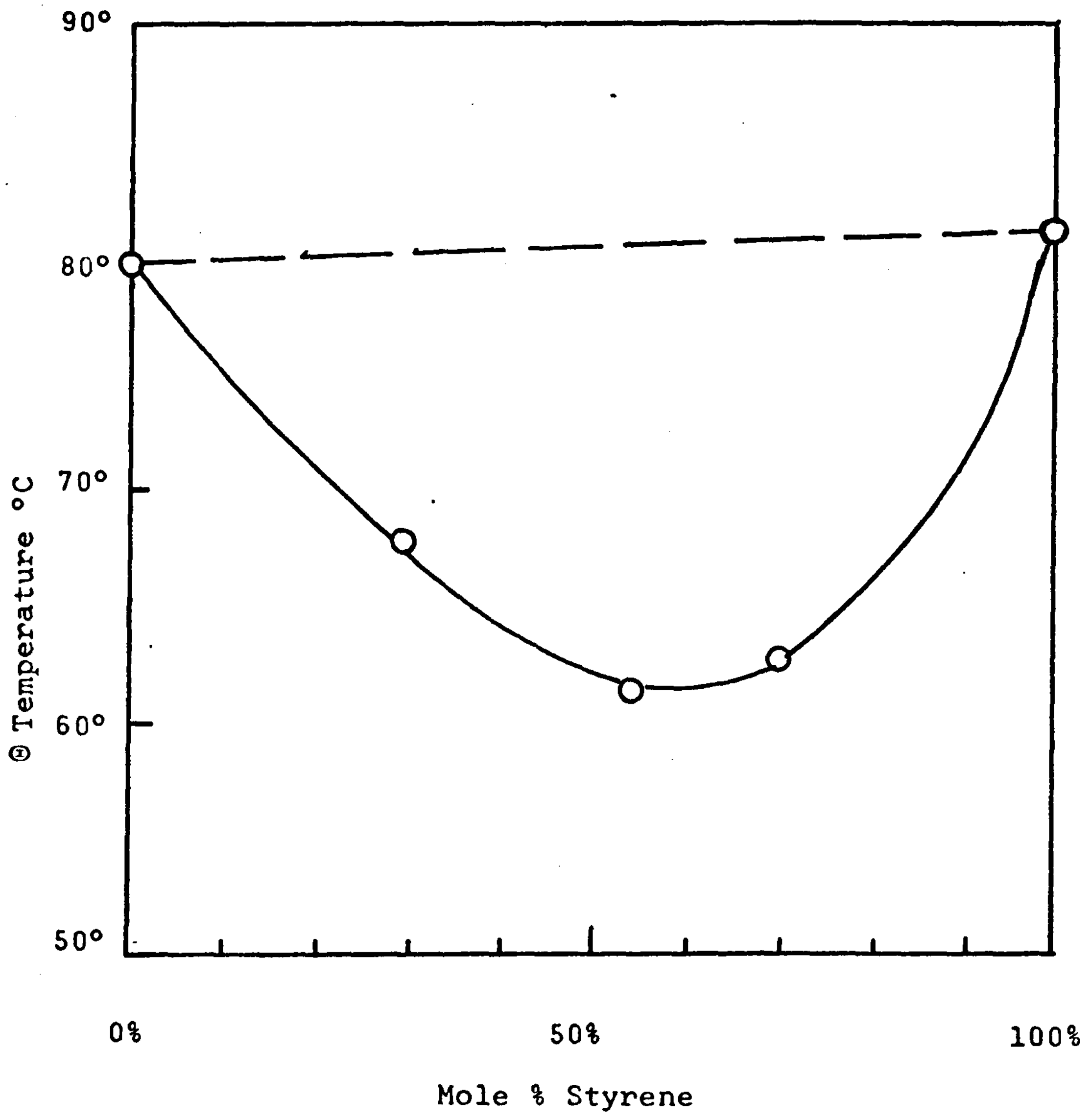

Figure 5 : Θ **Temperatures** of Styrene-Methyl Methacrylate Homopolymers and Copolymers in Cyclohexanol after Kotaka (37)

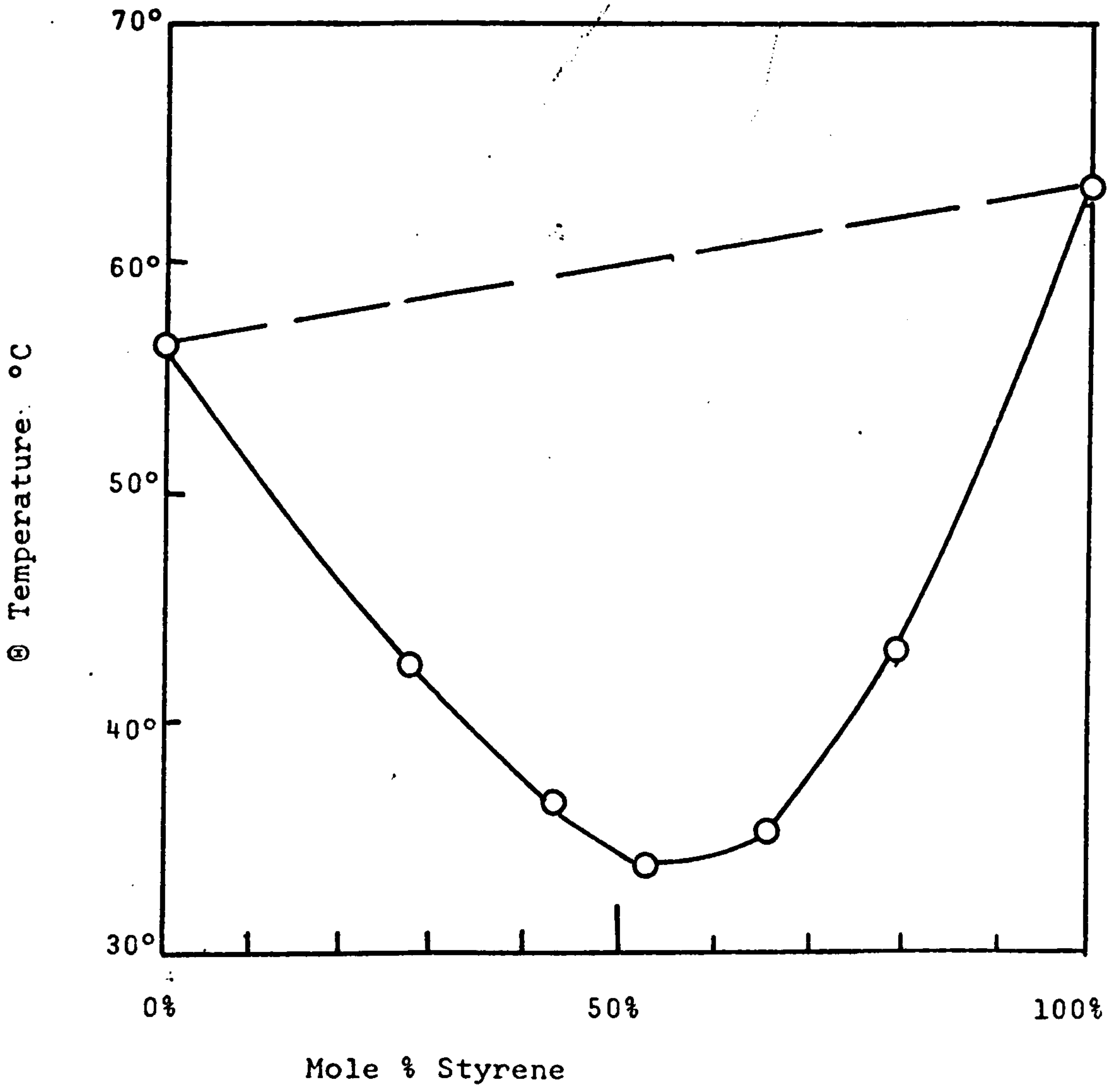

Figure 6 : Θ Temperatures of Styrene-Methyl Acrylate Homopolymers and Copolymers in 2-Methylcyclohexanol after Matsuda (38)

III. EXPERIMENTAL

Since one objective of this research was to interpret differences in solution properties in terms of molecular factors, it is essential that the polymers be well characterized. Thus, efforts were made to determine or eliminate properties of our materials that could complicate the interpretation of their solution properties. Several such factors are discussed in the following sections.

In order to lend clarity and continuity to the following, the detailed discussion of the experimental procedures and the tabulated data are located in the appendices.

A. Polymer Preparation

The polymers are prepared via the anionic living polymer techniques to produce linear, amorphous, homogeneous materials as well as random copolymers, all with narrow molecular weight distributions. An apparatus based on that of F. Wenger (57-58) was assembled from standard taper glassware parts. The reactions were run at $-78^{\circ}C$ in tetrahydrofuran under high vacuum (1.5 to 10 microns) using sodium-biphenyl as the initiator. In order to produce copolymers with uniform backbone composition, two precautions were followed. The mixed monomers were distilled slowly over a six hour reaction time into the reaction vessel. The monomer reservoir contained a large excess of monomer to prevent drift in monomer composition during distillation. The slow distillation time was necessary because styrene is considerably more reactive than α-methyl styrene. If the mixed monomers had been added more quickly than they could react, a polymer whose core was rich in styrene and whose ends were rich in α-methyl styrene would have been formed.

B. Characterization Techniques

1. Basic Measurements

The copolymer compositions were determined by material balances of monomers around the reaction vessels. The solution compositions used in these calculations were measured by gas chromatography.

Number average molecular weights were determined via osmometry in toluene at 37°C using a Mechrolab Model 501 High Speed Osmometer* with S&S 08 membranes**. A linear plot of Π/c vs. c represented the data adequately (where Π is the osmotic pressure and c is the concentration of polymer in grams per cm^3).

Intrinsic viscosities of the polymers were measured in toluene at 30.0°C with Cannon-Ubbehlode viscometers having efflux times greater than 150 seconds. Viscosity average molecular weights were computed for polystyrene, poly(α-methyl styrene) and poly (p-methyl styrene) using the Mark-Houwink correlations with constants determined by Papazian (56), Sirrianni (59) and Tanaka et al. (52), respectively. Since the Mark-Houwink correlation constants have not been published for styrene-α-methyl styrene copolymers, viscosity average molecular weights $\bar{M}v$ were computed from

$$(45) \quad \bar{M}_v = w_S \bar{M}_{v,S} + w_{MS} \bar{M}_{v,\alpha MS}$$

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* Hewlett Packard Inc.

** Arro Laboratories, Joliet, Illinois

where w_s and $w_{\alpha MS}$ are weight fractions of styrene and α-methyl styrene in the copolymer and $\bar{M}_{v,S}$ and $\bar{M}_{v,\alpha MS}$ are the viscosity average molecular weights of polystyrene and poly (α-methyl styrene) computed from the copolymer intrinsic viscosity. This equation should be valid provided copolymer molecular dimensions vary linearly with composition. As discussed in Appendix I, the unperturbed molecular dimensions of polystyrene, poly (α-methyl styrene) and a 24 weight percent styrene copolymer were found to be the same within experimental error (Table 12); therefore, equation 45 should apply.

Softening points were measured to within $\pm$ 3°C with a Dupont Model 941 Thermomechanical Analyzer. A ten gram probe weight and a heating rate of 5°C/minute were used.

2. Tacticity

Tacticity can profoundly influence the physical properties of a polymer. The most familiar manifestation of this effect is exhibited by polypropylene which in the atactic form is an amorphous, rubbery material and which in the isotactic form is a crystalline , tough thermoplastic.

High resolution NMR is a powerful tool for investigating polymer tacticity (79). Information is usually obtained about triads (i.e., three consecutive monomer units) and measurements are made on 5 percent to 20 percent solutions of polymers in inert solvents.

The tacticity of polystyrene produced by the living polymer reaction has not been determined. Poly(α-methyl styrene) produced by the living polymer reaction has been reported to consist largely of syndiotactic and heterotactic triads plus an isotactic concentration of 0.13 (61). The assignment of peaks in poly(α-methyl styrene) is, however, subject to controversy.

C. Properties of Polymers

1. Molecular Weight Distributions

A series of homopolymers of styrene and α-methyl styrene plus copolymers of 24, 50 and 69 weight percent styrene were prepared. The properties of these materials are given in Tables 1 to 5. The ratio of ($\bar{M}_v/\bar{M}_n$) was used as a measure of the molecular weight distributions of these materials. The molecular weight distributions of the poly (α-methyl styrene) and some of the polystyrene samples were quite narrow. The molecular weight distributions of some of the copolymers were not as narrow as desired, but they proved adequate for our purposes.

Table 1. Polystyrene

Sample Number	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\frac{\bar{M}_v}{\bar{M}_n}$
III-8	366	460	1.26
III-5	224	310	1.38
III-1	202	215	1.07
III-7	169	225	1.33
III-2	165	170	1.03
III-9	129	145	1.13
Pressure Chemicals	97.4	---	1.06*
III-6	50.9	73	1.43

* Material specifications provided by Pressure Chemical Inc.

Table 2. Poly(α-methyl styrene)

Sample Number	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\frac{\bar{M}_v}{\bar{M}_n}$
IV-5	278	300	1.08
IV-4	194	195	1.00
IV-1	142	127	0.90
IV-3	127	127	1.00
IV-2	122	120	1.01
IV-7	68.6	69	1.00
IV-8	56.7	59	1.04
IV-6	46.9	42	0.90

Table 3. 24% Styrene Copolymer

Sample Number	Wt. % Styrene	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\frac{\bar{M}_v}{M_n}$
V-46	23.7	51.7	63	1.2
V-47	23.5	107.4	109	1.0
V-49	25.1	180	217	1.2
V-48	25.2	205	337	1.65

Table 4. 50% Styrene Copolymer

Sample Number	Wt. % Styrene	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\frac{\bar{M}_v}{M_n}$
V-36	47.9	106	150	1.4
V-37	53.0	163	245	1.5
V-38	50.0	253	305	1.2

Table 5. 69% Styrene Copolymer

Sample Number	Wt. % Styrene	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_v \cdot 10^{-3}$	$\frac{\bar{M}_v}{\bar{M}_n}$
V-42	70.5	90.5	121	1.3
V-44	70.4	139	220	1.6
V-45	67.6	352	402	1.15

2. Tacticity

High resolution NMR measurements were made on 10% solutions of polystyrene and poly(α-methyl styrene) in carbon tetrachloride. Our study was not definitive. Peaks attributed to heterotactic and syndiotactic triads were observed in our poly(α-methyl styrene) spectra (61), but no appreciable isotactic concentration was detected.

3. Sequence Length Distribution

Analysis based on an idealized kinetic model shows that random copolymers should be produced by the synthesis technique used in this study. As is discussed in Appendix B.1, styrene reacts much more rapidly than α-methyl styrene, and when a drop of monomer is added to the reaction vessel, much of the styrene will react before the α-methyl styrene, If the comonomers are added dropwise to the reaction vessel and only as fast as they react, the polymer backbone will contain short segments whose composition changes periodically from styrene-rich to α-methyl styrene-rich. In a typical reaction between 300 and 600 drops of mixed monomer are added yielding about 600 to 1200 blocks per polymer molecule. Since the average polymer molecule of molecular weight 100,000 contains about 1000 monomer units, the average length of a block will be only several monomer molecules. Thus, the copolymers should have random structures, controlled in large part by mixing.

Evidence for the absence of gross inhomogeneities, resulting from long runs of blocks was obtained from softening point measurements. The softening point of grossly incompatible copolymers will show two breaks in their temperature versus modulus curves. The softening point curves showed only one break; and, as shown in figure 7, the softening point varied linearly with copolymer composition.

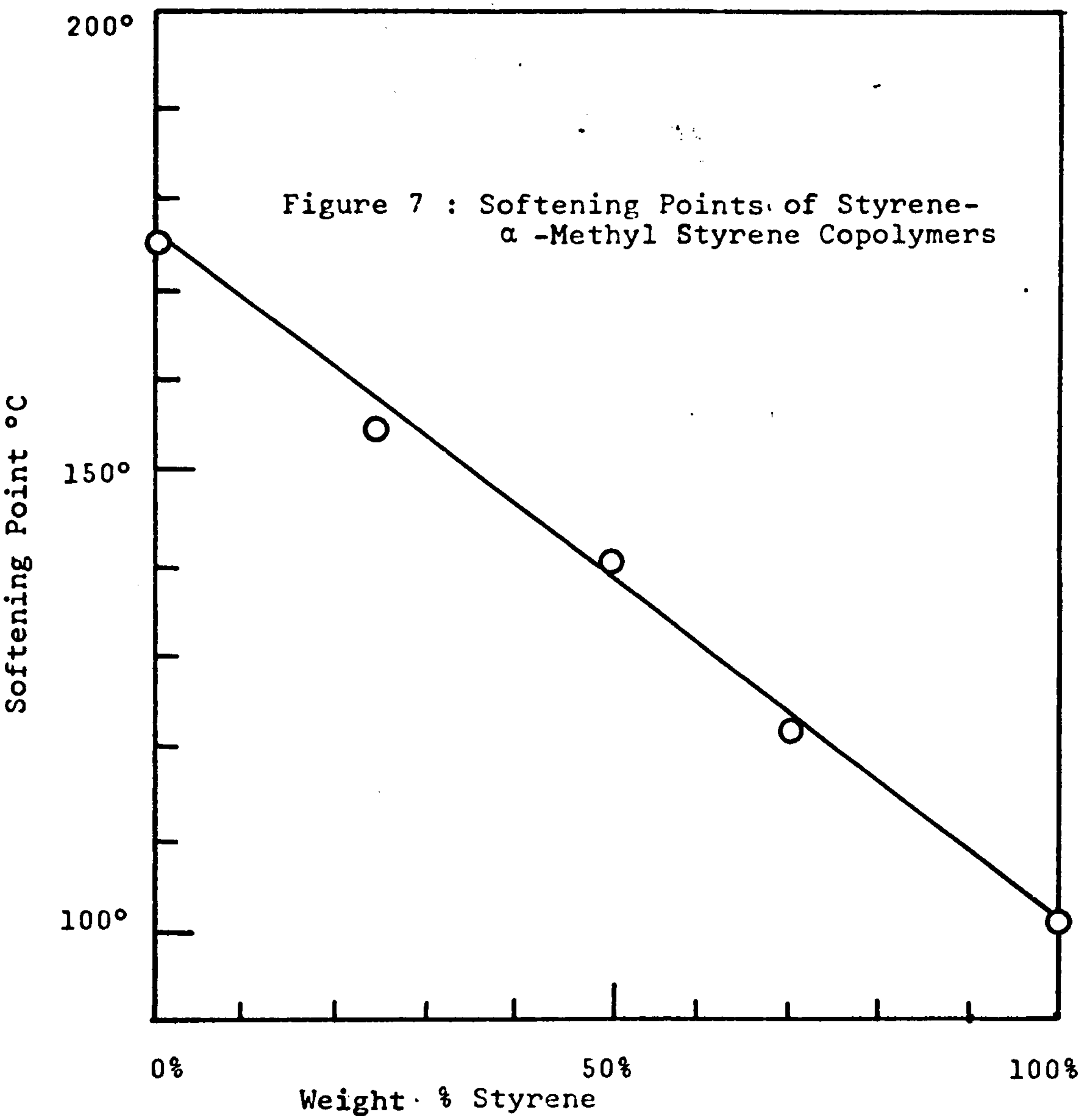

Figure 7 : Softening Points of Styrene-
α -Methyl Styrene Copolymers

D. Measurement of Solubility

Three quantities were used as measures of solubility: second virial coefficients, Flory-Huggins parameters and Θ-temperatures.

Second virial coefficients (SVC's) were determined in toluene at 37°C from the osmotic pressure measurements used to calculate $\bar{M}_n$. Plots of $(\Pi/c)^{1/2}$ versus c were used in addition to linear plots of (Π/c) versus c to facilitate comparison with literature results.* The results are tabulated in Appendix A-1 and are shown in figures 8 to 10.

Flory-Huggins parameters of polymer solutions ranging from 3 percent to 25 percent by weight were determined for polystyrene, poly (α-methyl styrene) and a 50 weight percent styrene copolymer in toluene at 37°C by high pressure osmometry. These materials were all of approximately the same molecular weight. The results are tabulated in Appendix A-2 and shown in Figures 11 and 12.

Θ-temperatures were computed from critical temperatures determined by cloud-point measurements using a Flory-Schultz plot (33) of $1/M^{1/2}$ versus $1/T_c$ (°K). Since the copolymers had $(\bar{M}_v/\bar{M}_n)$ ratios of 1.0 to 1.6, the Flory-Schultz plots were smoother when viscosity average rather than number average molecular weights were used.

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* Π is the osmotic pressure and c is the concentration of polymer in grams/cm^3.

These data are presented in Tables 6, 11 and 13 to 18, Appendix A-3, and Figures 13-15. Polystyrene data were obtained from the literature.

E. Unperturbed Chain Dimensions

Unperturbed chain dimensions were determined from intrinsic viscosities measured in toluene and cyclohexane using the Stockmayer-Fixman-Kurata technique. Measurements were made only for poly (α-methyl styrene) and the 24 weight percent styrene copolymers because the other samples were too polydisperse. These results which are presented in Tables 25 and 26, and Figures 29 and 30, and are discussed in detail in Appendix H.

Briefly, it was found that poly (α-methyl styrene) and the 24 percent by weight styrene copolymer had the same unperturbed dimensions within experimental error. An examination of literature data revealed that poly (α-methyl styrene) has somewhat larger unperturbed chain dimensions than polystyrene. Studies of unperturbed chain dimensions of these materials are not fruitful because chain dimensions are not strongly dependent upon repeat unit structure, and the differences in unperturbed chain dimensions of our materials are too small to measure accurately.

IV. SOLUBILITY IN GOOD SOLVENTS

A. Second Virial Coefficients

It is generally found that plots of SVC versus molecular weight are linear on a log-log scale. Figure 8 is such a plot for the data of interest, with the homopolymer points shown closed and the copolymer points shown open; the measurements were made in toluene at 37°C. The polystyrene data lie above those for poly (α-methyl styrene) indicating that polystyrene is more soluble in toluene than poly (α-methyl styrene). All the copolymer data shown in Figure 8 lie above those of poly (α-methyl styrene), and most of them lie between those of polystyrene and poly (α-methyl styrene). On closer examination, the SVC's seem to increase with increasing styrene content at fixed molecular weight. Since the difference in SVC between polystyrene and poly (α-methyl styrene) at fixed molecular weight is not much larger than experimental error, it is difficult to verify this conclusion. In general, as those results indicate, the scatter limits the usefulness of the SVC as a characterizing parameter. This is particularly evident in systems such as styrene and α-methyl styrene copolymers where differences in solutions properties are small.

Figures 9 and 10 are plots of SVC* versus molecular

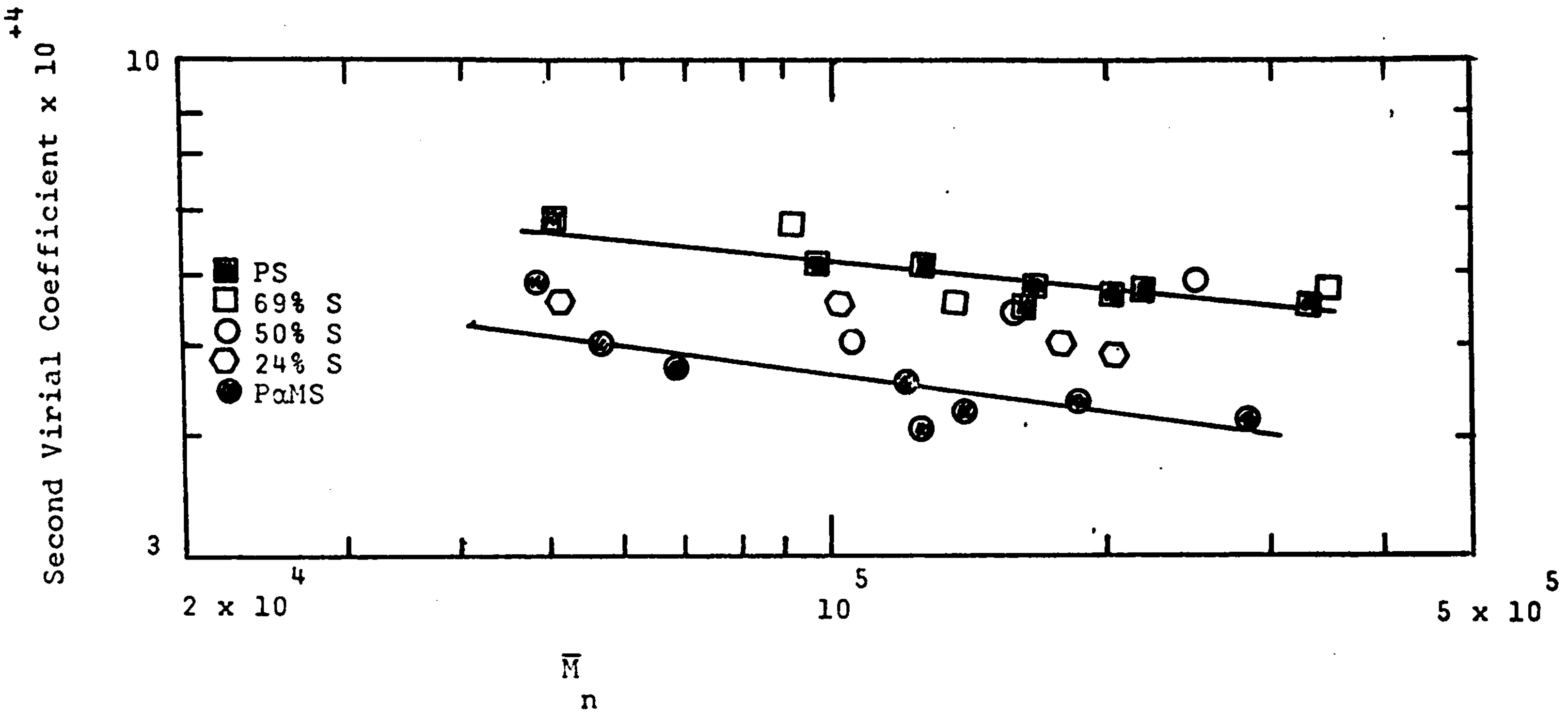

Figure 8 : Homopolymer and Copolymer Second Virial Coefficients in Toluene at 37°C

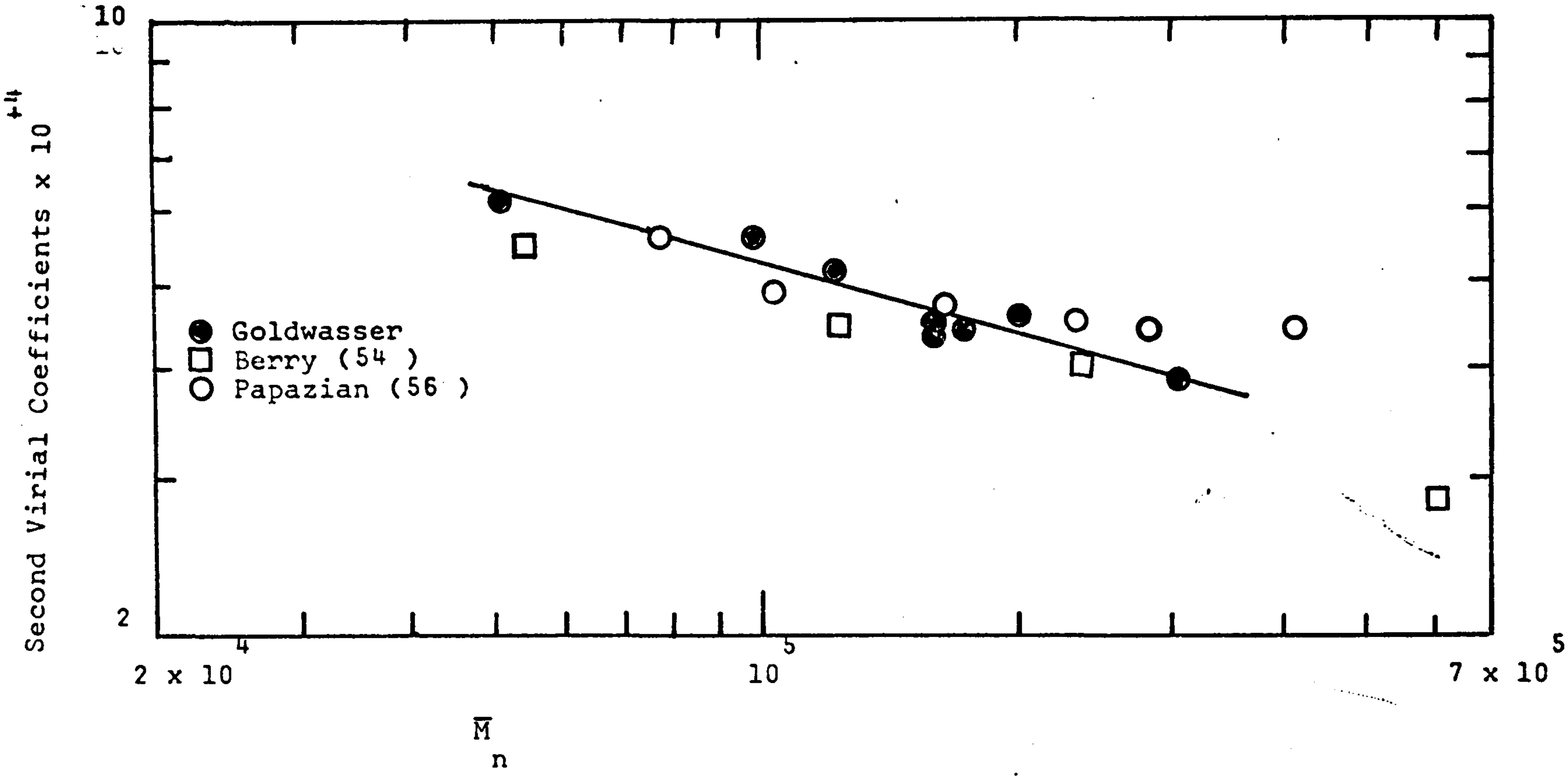

Figure 9 : Polystyrene Second Virial Coefficients in Toluene at 37°C
Comparison with Literature Data

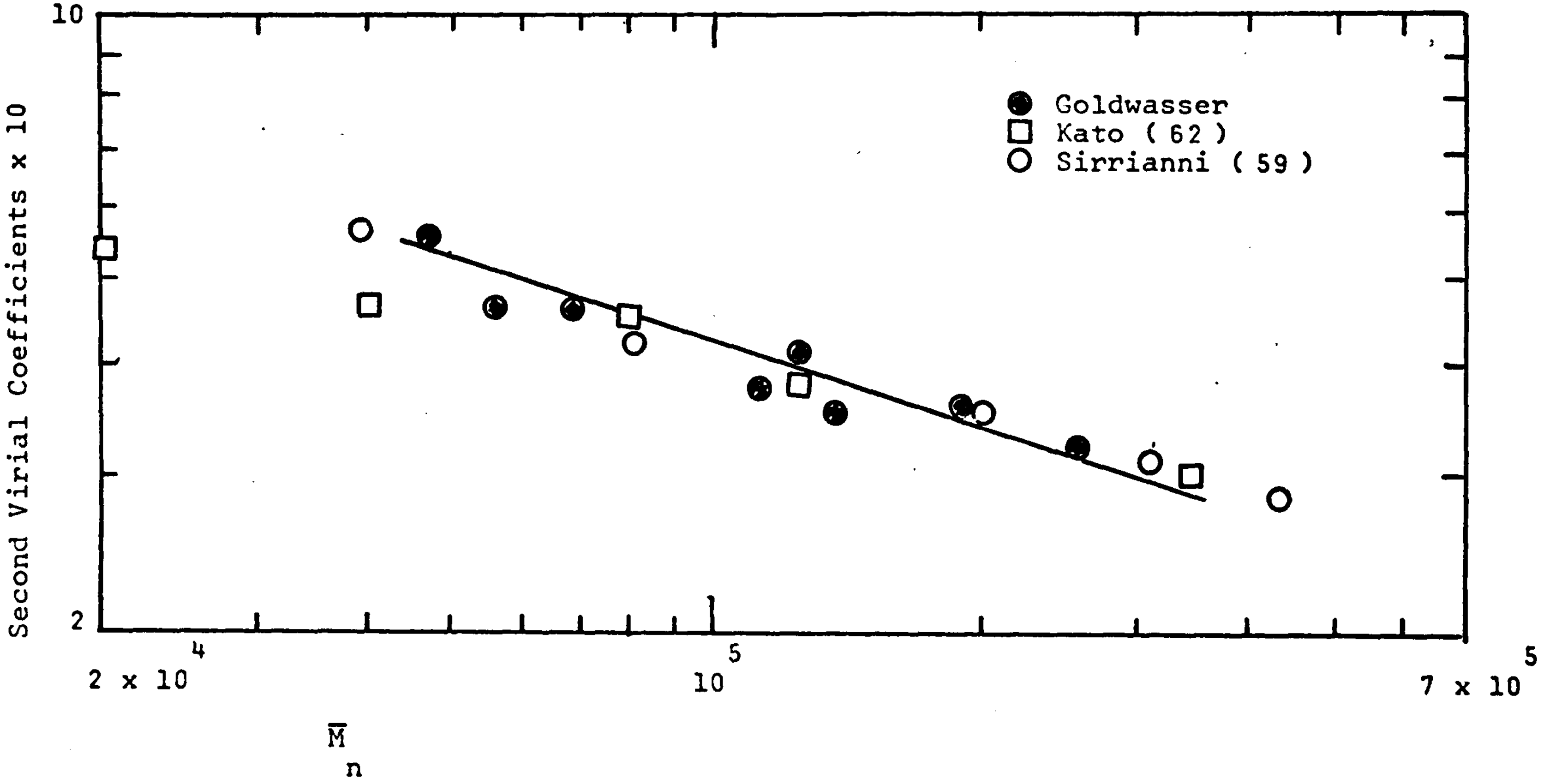

Figure 10 : Poly(α -methyl styrene) Second Virial Coefficients in Toluene at 37°C, Comparison with Literature Data

weight containing the results of Papazian (56) and Berry (54,55) for polystyrene; Sirrianni (59) and Kato et al. (62) for poly (α-methyl styrene); as well as data from this research. The literature data and those from this study are in agreement within experimental error.

* The SVC's used in Figures 9 and 10 were obtained by plotting $(\Pi/c)^{1/2}$ versus c; this was done to permit direct comparison with literature results. See Appendix F-4.

B. Flory-Huggins Parameters

Osmotic pressures were measured for polystyrene, poly (α-methyl styrene) and a 50 percent by weight styrene copolymer (sample V-36) of about the same molecular weight (ca. 100,000) in toluene at 37°C for solutions ranging from 3 percent to 25 percent by weight polymer. The Flory-Huggins parameter χ offers a convenient way of comparing thermodynamic data for relatively concentrated solutions. These data are presented in Appendix A-2 and figure 11. They show χ to be a constant for all three polymers in the concentration range studied. Further χ for polystyrene is smaller than that for poly(α-methyl styrene) which indicates, in agreement with our SVC studies, that polystyrene is more soluble in toluene than poly(α-methyl styrene). The Flory-Huggins constants for polystyrene and the 50 weight percent copolymer are the same.

Bawn et al. (65) determined χ for polystyrene dissolved in toluene via vapor pressure measurements and found it to be a constant, independent of concentration and temperature. The results from this study and those of Bawn* et al. are presented in figure 12. Evidently, scatter

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* Values of χ were calculated from values of p_1/p_1^o, the ratio of solution to solvent vapor pressure using the equation

$$\chi = [RT \ln(p_1/p_1^o) - (1 - v_1^o/v_2^o)v_2 - \ln(1 - v_2)](1/v_2^2)$$

Volume fractions were computed from weight fractions using a density of 1.06 grams/cm^3 for polystyrene. See Appendix E-4

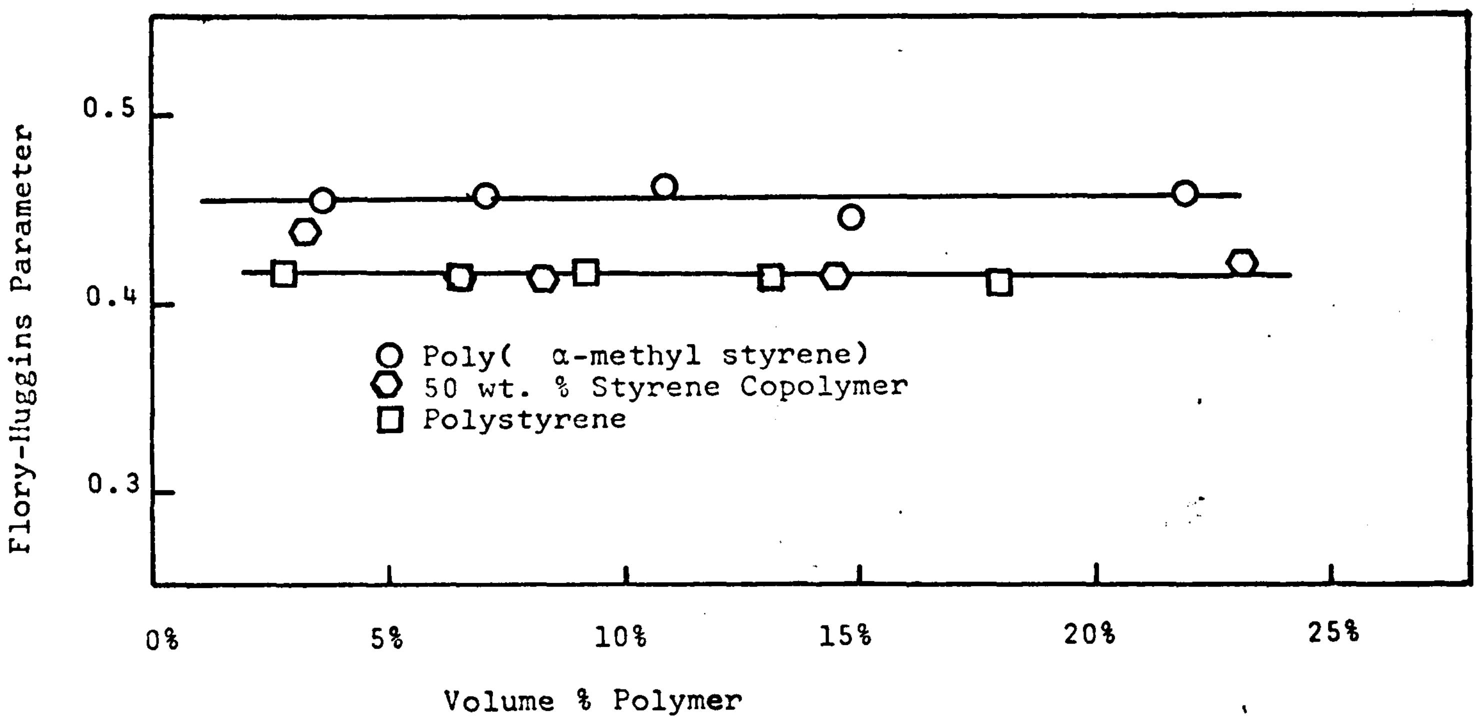

Figure 11 : Flory-Huggins Parameters from High Pressure Osmometry in Toluene at 37°C

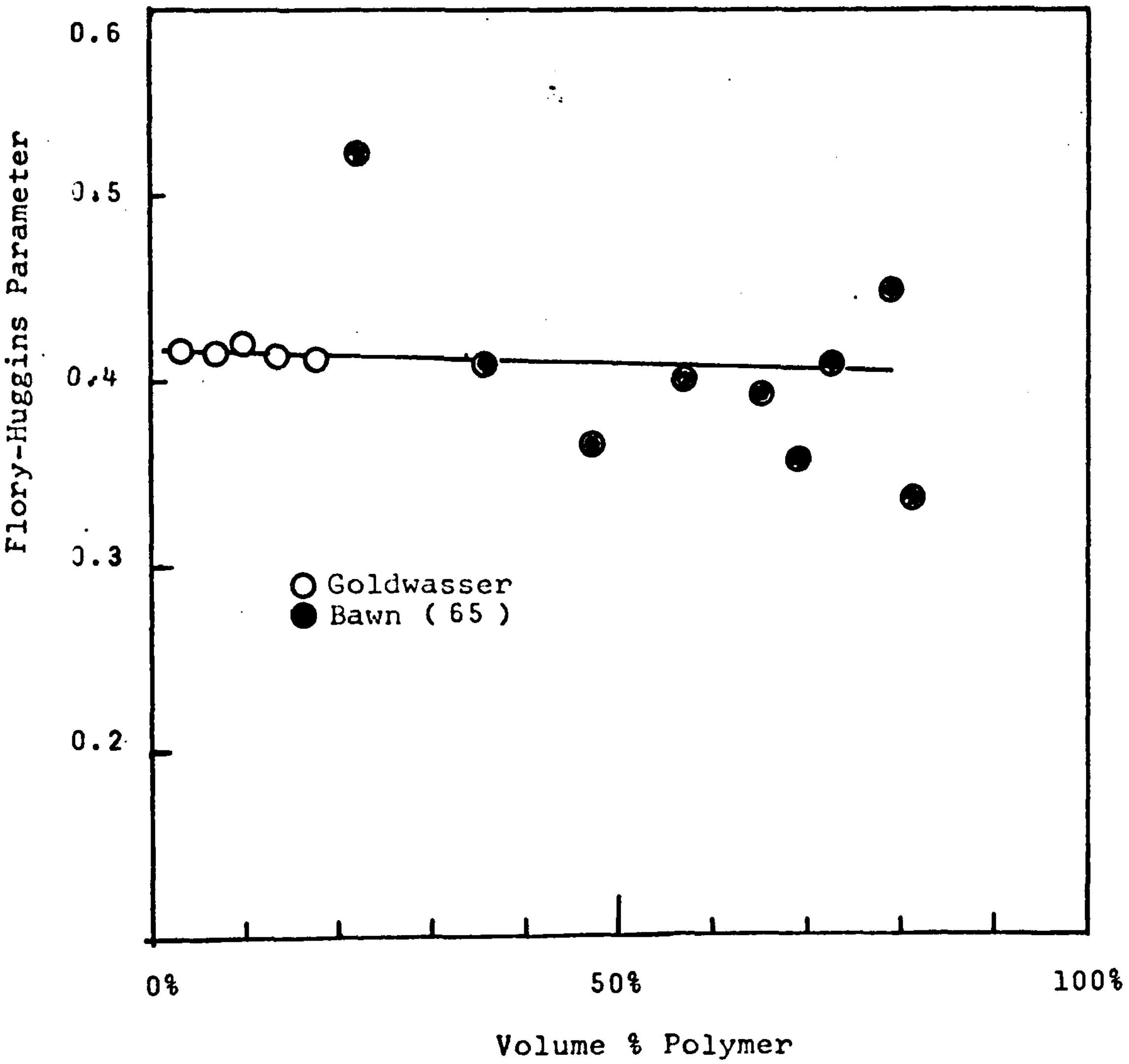

Figure 12 : Comparison of Polystyrene Flory-Huggins Parameters in Toluene

in Bawn's data makes it difficult to make meaningful comparisons.

There are two intrinsic sources of error in vapor pressure measurements. In relatively dilute solutions (less than 40 percent polymer by volume), the difference in vapor pressure between the polymer solution and the solvent is too small to measure with the accuracy needed to obtain reliable values of χ. In very concentrated solutions (>90(vol.)percent polymer), activity changes rapidly with concentration; hence small errors in concentration measurements will yield large errors in χ. Despite its limitations, high pressure osmometry is the superior method for investigating solution properties in solutions containing less than about 40 percent by volume polymer.

C. Discussion

The principal finding to emerge from this phase of the study is that χ for the copolymer V-36 and the polystyrene are about the same. That is, χ for the copolymer is smaller than that obtained by the linear interpolation between the homopolymers χ-values; this indicates that random copolymerization of styrene and α-methyl styrene increases solubility. Since increased solubility in other random copolymer systems has been tentatively attributed to intermer repulsions, we could reasonably hypothesize that these affects might also prevail in this system. This idea is treated in more detail in the following sections.

A comparison of solution properties in dilute and moderately concentrated including the region of the onset of molecular overlap is presented in Appendix F. A smooth transition was observed.

V. SOLUBILITY IN Θ-SOLVENTS

A. Introduction

Measurements of χ in moderately concentrated toluene solutions revealed that χ varied with copolymer styrene content in a way to increase copolymer solubility. Second virial coefficients in toluene indicated that poly(α-methyl styrene) was less soluble than polystyrene, but scatter prevented interpretation of relative copolymer solubility. The Θ-temperature was found to be sufficiently sensitive to warrant extensive study. Unexpected increases in copolymer solubility and rather perplexing variations in homopolymer solubility were observed.

Discussions of solubility in Θ solvents falls into two parts: (1) homopolymer solubility, and (2) copolymer solubility.

B. Homopolymer Solubility

1. Results

The Θ-temperature of polystyrene, poly(α-methyl styrene), and poly(p-methyl styrene) in cyclohexane, methyl cyclohexane, decalin and diethyl succinate are given in Table 6 and the relative solubilities are summarized in Table 7. In cyclohexane, polystyrene and poly(α-methyl styrene) have about the same Θ-temperatures, whereas poly(p-methyl styrene) is soluble at all temperatures. The order of solubility in methyl cyclohexane is polystyrene > poly(α-methyl styrene), whereas in decalin isomers, the order is reversed with poly(α-methyl styrene) > polystyrene. Polymer solubility also varies considerably in diethyl succinate. Polystyrene is soluble in diethyl succinate up to its freezing point, whereas poly(α-methyl styrene) has a Θ-temperature of about 145° C. The Θ-temperature of poly(p-methyl styrene) of 16.5° C falls between that of polystyrene and poly(α-methyl styrene). Thus the order of solubility here is polystyrene >> poly(p-methyl styrene) > poly(α-methyl styrene).

Table 6. Homopolymer Θ-Temperatures

Solvent / Polymer	Cyclohexane	Methyl-Cyclohexane	Cis-decalin	Trans-decalin	Commercial Decalin	Diethyl Succinate
PS	35°C (a)	70°C (a)	13°C (b)	21°C (b)	13°C	Soluble
PpMS	Soluble	----	----	----	----	16.5°C (d)
PαMS	32°C- 37°C (e)	94°C	Probably Soluble	9.5°C (c)	-5.6°C	145°C

(a) Polymer Handbook (67)
(b) G. C. Berry (54)
(c) T. Kato et al. (62)
(d) G. Tanaka et al. (52)
(e) J. Cowie et al. (75)

Table 7. Relative Polymer Solubility Characterized by Θ-Temperature

Solvent	Solubility
Cyclohexane	PpMS[*] >>PS≃PαMS
Methyl cyclohexane	PS>PαMS
Decalin	PαMS>PS
Diethyl Succinate	PS[*] >>PpMS>PαMS

[*] Soluble to the freezing point of the solvent. Hence, this polymer has no Θ-temperature.

2. Discussion

The patterns of solubility among homopolymers are perplexing. Specifically, explanations are required for: (a) the change in relative homopolymer solubility in Θ solvents related to cyclohexane, (b) the variation in solvent power of cyclohexane based solvents, and (c) the large differences in Θ-temperatures in diethyl succinate.

An understanding of these solubility patterns requires a knowledge of the effects of many factors on polymer solution behavior. The influence of intermolecular forces are the best understood molecular factors influencing polymer solution properties, and they can be described to a first approximation in terms of the solubility parameter concept.

The solubility parameter theory can be used to estimate χ and thereby predict relative polymer solubility. Following Blanks and Prausnitz (26), χ_S is assumed constant and equal to 0.34; χ_H is computed from equation 17 for nonpolar polymer-solvent systems from the solubility parameters in Table 8.

$$(17) \quad \chi_H = v_S(\delta_P - \delta_S)^2/RT$$

We now apply equation 17 to predict the order of solubility - an approach which neglects the possible variation of entropic effects among the various polymer-solvent systems. Polymer solubility decreases with increasing values of χ, and hence with increasing values of $(\delta_P - \delta_S)^2$. The solubility parameters for cyclohexane, methylcyclohexane and decalin isomers are smaller than those of the polymers, whereas that for diethyl succinate is larger. Hence, in cyclohexane, methylcyclohexane or decalin one would predict the following order of relative solubility from solubility parameter considerations alone

$$P\alpha MS > PpMS > PS$$

In diethyl succinate the reverse order would be predicted. References to Table 9 shows that equation 17 fails to correctly predict the relative solubility of the polymers in cyclohexane derivative solvents, whereas in diethyl succinate the predicted order is followed. Since the relative solubility of our polymers in cyclohexane derivative solvents cannot be explained in terms of the solubility parameter concept, factors other than those embodied in this theory must be involved.

The solubility parameter concept can also be used to predict the effectiveness of solvents towards polystyrene type polymers. Cyclohexane should be a better solvent than methylcyclohexane and cis-decalin should be a better solvent than trans-decalin according to the solubility parameter theory - two phenomena which were observed. Decalin isomers should also be poorer solvents than cyclohexane - the reverse order was observed.

One possible explanation for the failure of the solubility parameter to predict relative solubility resides in the assumption that χ_S is a constant. Blanks and Prausnitz (26) report that $\chi_S = 0.34 \pm 0.06$; the range in χ_S is sufficient to account for the failure of the theory. In other words, χ_S could vary sufficiently from polymer to polymer to overcome enthalpic effects as described by the usual solubility parameter calculations. Molecular explanations for the variation of χ_S with polymer structure have not been developed as yet.

It should be noted also, that the experimental error in the solubility parameter can be larger than the differences in solubility parameters among the solvents, although data from one source should be internally consistent. It is also difficult to unambiguously estimate the solubility of a polymer. Despite these limitations, the solubility parameter concept offers the best means for resolving the effects of intermolecular forces.

Table 8. Solubility Parameters

Material	δ	Source
cyclohexane	8.19	a
methylcyclohexane	7.82	a
cis-decalin	8.05	b
trans-decalin	7.78	b
diethyl succinate	9.63	
benzene	9.16	a
toluene	8.93	a
o-xylene	9.06	a
m-xylene	8.88	a
p-xylene	8.83	a
α-methyl styrene	9.10	a
styrene	9.33	a
methylethylketone	9.45	a
cyclohexanol	11.4	b
methyl methacrylate	9.23	a
methyl acrylate	9.38	a
acrylonitrile	10.56	a

(cont.)

Table 8 (cont.). Solubility Parameters

Material	δ	Model Compound	Source
Polystyrene	8.84	ethylbenzene	a
Poly(α-methyl styrene)	8.60	isopropylbenzene	a
Poly(p-methyl styrene)	8.65	p-ethyltoluene	a
Poly(methyl methacrylate)	8.64	methyl isobutyrate	a
Poly(methyl acrylate)	9.14	methyl proprionate	a
Polyacrylonitrile	10.73	proprionitrile	a

a. Table of Solubility Parameters, Union Carbide Corp., May 31, 1967

b. Calculated from Vapor Pressure Data in the "Handbook of Physics and Chemistry", The Chemical Rubber Publishing Co.

Table 9. Solubility Predictions

Polymer	$(\delta_P - \delta_S)^2$	Predicted Solubility	Observed Solubility
Cyclohexane			
PS	.424	least soluble	same as PαMS
PpMS	.212	intermediate	most soluble
PαMS	.178	most soluble	same as PS
Methylcyclohexane			
PS	1.04	least soluble	more soluble than PαMS
PpMS	.689	intermediate	------------
PαMS	.610	most soluble	less soluble than PS
Cis-decalin			
PS	.622	least soluble	less soluble than PαMS
PpMS	.360	intermediate	------------
PαMS	.304	most soluble	more soluble than PS
Trans-decalin			
PS	1.12	least soluble	less soluble than PαMS
PpMS	.759	intermediate	------------
PαMS	.672	most soluble	more soluble than PS
Diethyl Succinate			
PS	.622	most soluble	most soluble
PpPS	.962	intermediate	intermediate
PαMS	1.06	least soluble	least soluble

B. Copolymer Solubility

1. Results

Θ-temperatures for polystyrene, poly(α-methyl styrene) and their 24, 50, and 69 weight percent styrene copolymers were determined in cyclohexane, methylcyclohexane and commercial decalin. The results are presented in figures 13 to 15 plus Table 10. As the results indicate, minima in Θ-temperatures occur in the mid-composition range. The minima in Θ-temperature in methylcyclohexane is sharper than that in cyclohexane. Our findings in cyclohexane are supported by Kotliar (74) who measured Θ-temperatures of two styrene - α-methyl styrene copolymers by osmometry. Commercial decalin was not a convenient Θ solvent to use because gels tended to form at low temperatures which made critical temperature measurements difficult. Consequently, measurements were made only for the 69 weight percent styrene samples. The decalin results followed the same pattern as those in cyclohexane and methylcyclohexane.

Table 10. Copolymer Θ-Temperatures

Wt. % Styrene	T_{Θ}; °C		
	Cyclohexane	Methylcyclohexane	Commercial decalin
0	32.5	94.4	-5.6
24	26.	71.	---
50	24.	53.	---
69	22.	55.	-2.
100	34.5	70.	13.

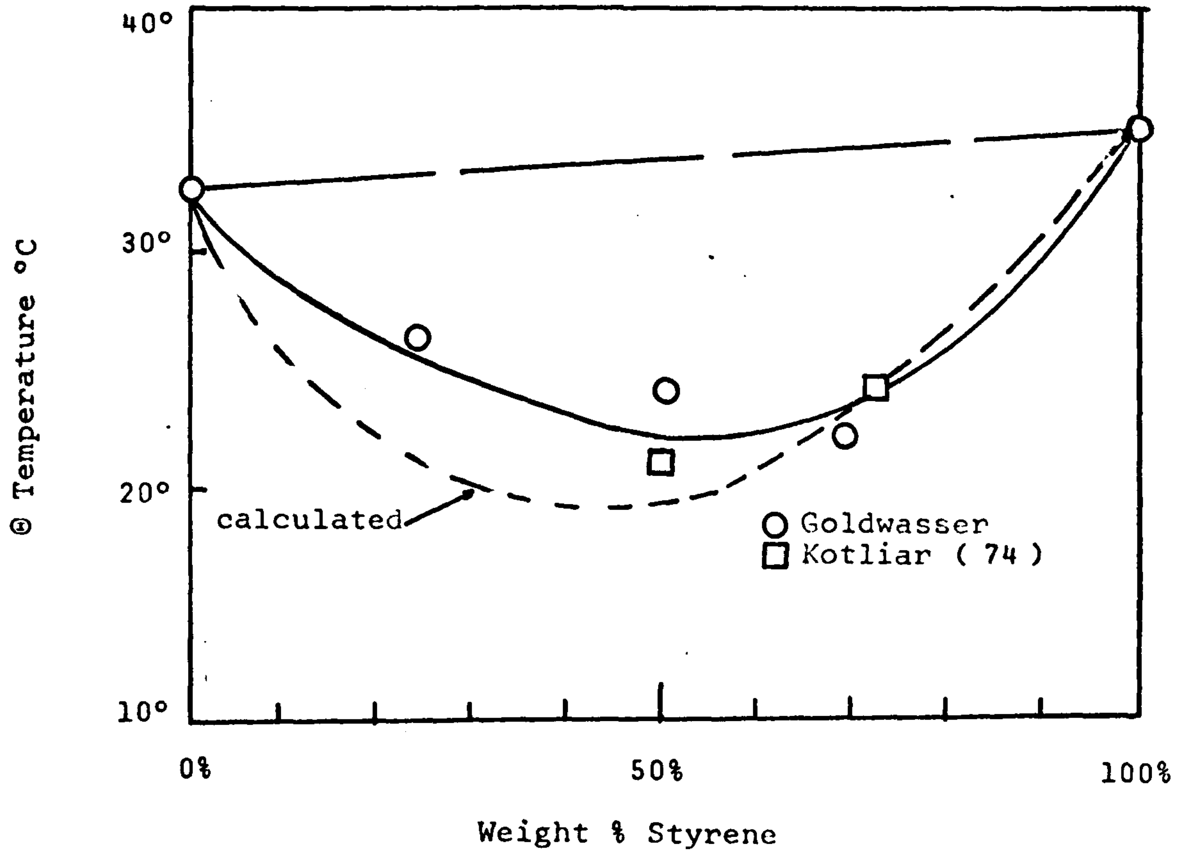

Figure 13 : Θ Temperatures of Styrene- α-Methyl **Styrene Homo**polymers and Copolymers in Cyclohexane

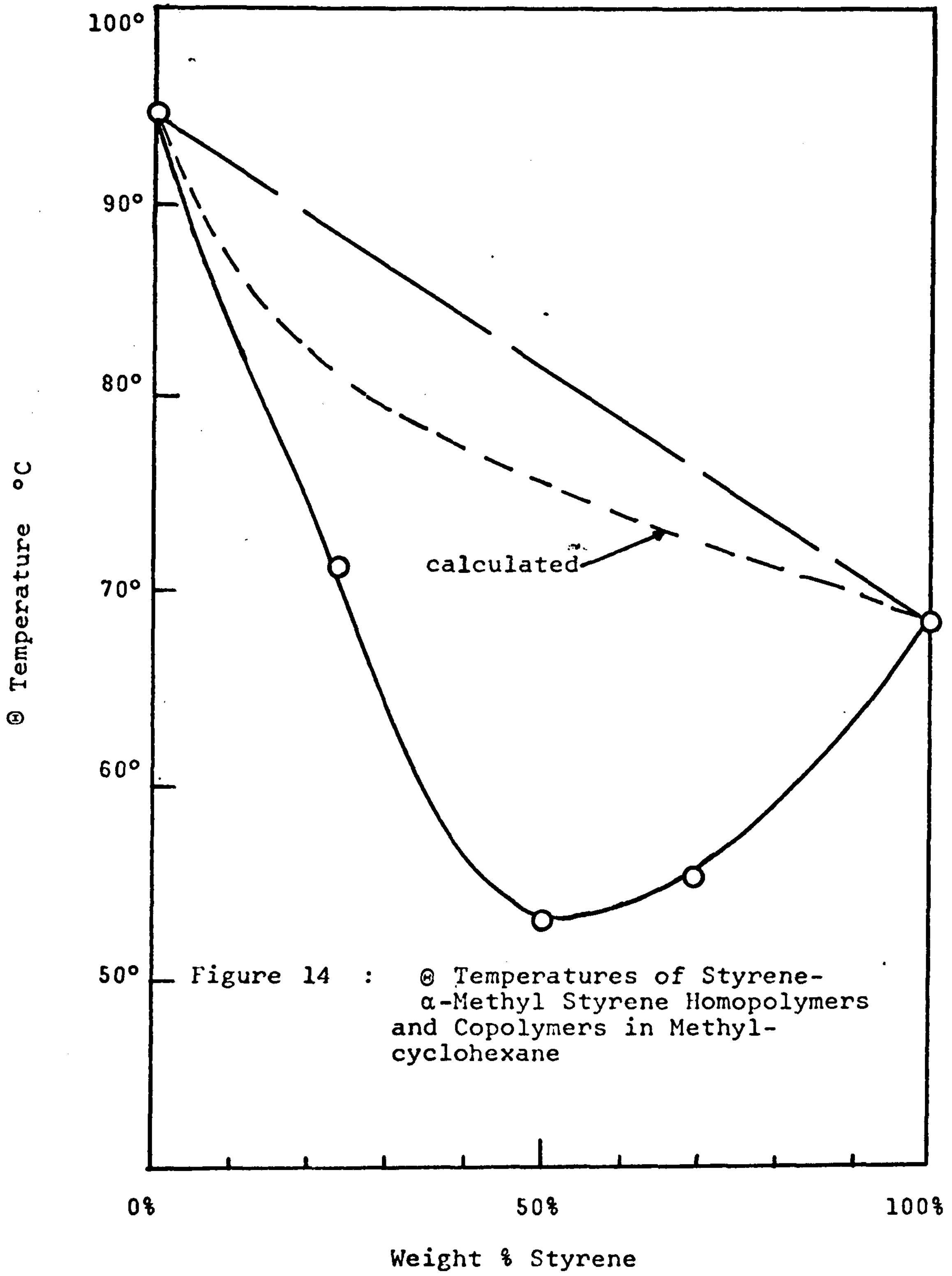

Figure 14 : ⊛ Temperatures of Styrene-α-Methyl Styrene Homopolymers and Copolymers in Methylcyclohexane

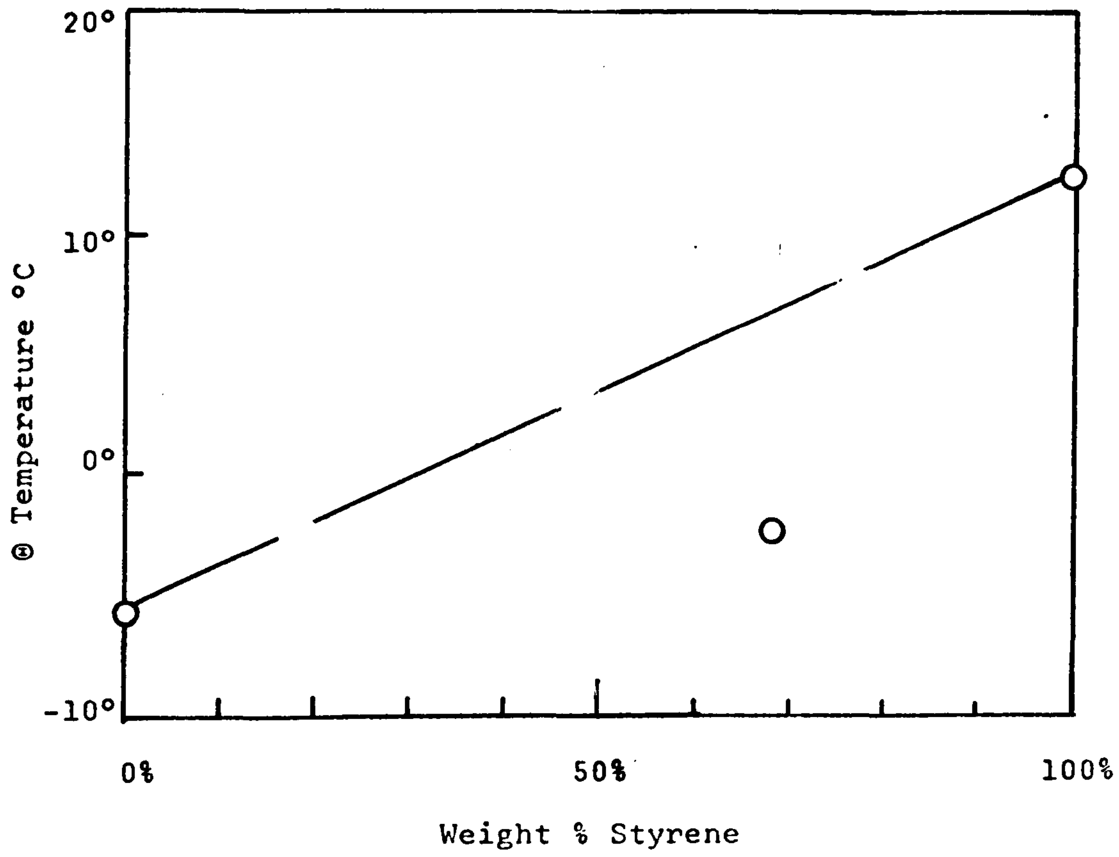

Figure 15: Θ Temperatures of Styrene-α -Methyl Styrene Homopolymers and Copolymers in Commercial Decalin

2. Discussion

Minima in Θ-temperatures have been observed by Matsuda for styrene-methyl acrylate copolymers in 2-methyl cyclohexanol (38)(figure 6) and by Kotaka for styrene-methyl methacrylate copolymers in cyclohexanol (37)(figure 5). Despite the fact that styrene-methyl acrylate and styrene methyl methacrylate systems differ more in structure than the styrene-α-methyl styrene system, the depression in Θ-temperatures observed for these three random copolymers are about the same.

Shimura measured second virial coefficients for styrene-acrylonitrile copolymers in methyl-ethyl-ketone — a non-solvent for polyacrylonitrile (41). A sharp maximum was observed near the mid-composition point (figure 4). The difference in second virial coefficient between polystyrene and the acrylonitrile copolymer with the highest second virial coefficients was three to four times larger than the difference between polystyrene and poly(α-methyl styrene).

Calculation of Intermer Repulsions

Examination of the Flory-Huggins parameters in moderately concentrated toluene solutions and Θ-temperatures in poor solvents for styrene-α-methyl styrene copolymers reveal that copolymer solubility is greater than that predicted by linear interpolation between the parent homopolymers. In other copolymer systems increased solubility has been tentatively attributed to intermer repulsions, but the origins of this phenomena have yet to be examined in detail. It is relatively easy to visualize the origins of intermer repulsions in styrene-methyl acrylate, styrene-methyl methacrylate, and styrene-acrylonitrile copolymers (especially in the latter since the co-monomers are so different in structure), but the same effect in chemically similar, styrene-α-methyl styrene copolymers are harder to understand.

Let us consider two propositions concerning intermer repulsions in styrene-α-methyl styrene copolymers: (a) To a first approximation these repulsions should be independent of solvent. (b) Since the measured increase in solubility of styrene-α-methyl styrene and styrene-acrylate copolymers (as measured by the depression in copolymer Θ-temperatures) are about the same, the magnitude of intermer repulsions in both systems should be about the same. To examine this proposition, we have developed a technique for quantifying the magnitude of intermer repulsions from solubility parameters. Calculations based on this technique and a comparison of χ_{ab}, the intermer repulsions term (see equation 44), obtained in toluene and Θ solvents, support the hypothesis that intermer repulsions are responsible for the increased copolymer solubility.

Comparison of Intermer Repulsions Computed for Polymers in Toluene and Θ Solvents

One consequence of equation 44, which relates copolymer and homopolymer Flory-Huggins parameters, is that χ_{ab},

$$(44) \quad \chi_{copolymer} = w_a\chi_a + w_b\chi_b - w_a w_b \chi_{ab}$$

which represents intermer repulsions should be independent of solvent. Hence, if values of χ_{ab} obtained from measurements of solubility properties in a variety of solvents are about the same, intermer repulsions may be responsible for the increased copolymer solubility. In order to examine this proposition, χ_{ab} must be obtained from measurements of χ in moderately concentrated toluene solutions and Θ-temperature data. From our measurements in toluene (Table 24), χ_{ab} can be readily calculated as 0.08 ± 0.04.

In order to calculate χ_{ab} from our Θ-temperature data let us represent the difference in solubility between the actual copolymer and that obtained by linear interpolation as

$$(46) \quad J = (\chi_{in} - \chi_{me})/(\chi_{me})$$

where subscripts "in" and "me" refer to interpolated and measured respectively. Since $w_a\chi_a + w_b\chi_b = \chi_{in}$, combination of equation 44 with equation 46 yields

$$(47) \quad J = w_a w_b \chi_{ab}/\chi_{me}$$

or

(47a) $\chi_{ab} = J\chi_{me}/w_a w_b$

Here, J represents the relative increase in copolymer solubility and can be computed from our Flory-Huggins parameter data in toluene for our 50 weight percent styrene copolymer from our data in Table 24 as

$$J_{50/50} = (0.434 - 0.416)/(0.416) = 0.05$$

where $J_{50/50}$ is the value of J for a 50 weight percent styrene copolymer. Methods for computing J from values of Θ-temperatures are developed in the following paragraphs from which χ_{ab} is calculated. The validity of proposition (a) can then be examined.

In order to compute the value of $J_{50/50}$ for the copolymers in Θ solvents, values of χ for the homopolymers and copolymers must be obtained at a fixed temperature. To obtain χ_{in}, a method for predicting the variation of χ with temperature must be devised. If χ is strictly enthalpic, (χT) = constant (see Appendix G). Recalling that $\chi = 0.500$ when $T = \Theta$, at any other temperature χ is given by

(48) $\chi = (0.500)\Theta/T$

For a 50 percent by weight styrene copolymer χ_{in} is given by

(49) $\chi_{in} = 0.5\ (0.5(\Theta_a/T) + 0.5\ (\Theta_b/T) = (0.5\Theta_{in}/\ \Theta_{me})$

where subscripts a and b refer to components of the copolymer. Combining equation 49 with 46 and setting $\chi_{me} = 0.5$, we obtain

(50) $J_{50/50} = (\Theta_{in} - \Theta_{me})/\Theta_{me}$

Values of J computed for the 50 percent by weight styrene copolymer in cyclohexane and methylcyclohexane are 0.05 and 0.09 respectively. This calculation serves as an approximate upper bound for the change in χ equivalent to our Θ-temperature minima. In the next paragraph a more sophisticated model is developed.

Representing χ in its entropic and enthalpic components we have

(51) $\chi = \chi_H + \chi_S$

Using the Blanks-Prausnitz (26) value of 0.34 for χ_S, at the Θ-temperature where $\chi = 0.5$, $\chi_H = 0.16$. At the Θ-temperature, ΔH_M and the portion of ΔS_M arising from interactions, ΔS_i, would be given by $\Delta H_M = n_1 v_2 R\Theta(0.16)$ and

$\Delta S_i = n_1 v_2 R(0.34)$. The fraction of ΔG_M arising from interactions, ΔG_i, is

(52) $\Delta G_i = \Delta H_M - T\Delta S_i = n_1 v_2\ R\ (0.16\,\Theta + 0.34T)$

An equation for χ can then be obtained as

$$(53) \quad \chi = 0.16\Theta/T + 0.34$$

This equation predicts a smaller variation of χ with temperature than equation 47; larger values of χ_H yield larger variation of χ with temperature. Equation 53 combined with equation 46 yields values of J for the 50 percent by weight styrene copolymer in cyclohexane and methylcyclohexane of 0.016 and 0.029 respectively. These values are smaller than those obtained previously. These calculations also illustrate the great sensitivity of Θ-temperatures to small changes in χ.

Values of χ_{ab} computed from Θ-temperature data and from Flory-Huggins parameters measured in moderately concentrated toluene solutions are presented in Table 11. An examination of the results indicates that approximately the same value of χ_{ab} are obtained in toluene, cyclohexane and methylcyclohexane. Hence, to a first approximation, intermer repulsions for styrene-α-methyl styrene copolymers appear to be independent of solvent. This lends credence to the notion that this phenomena is responsible for increased copolymer solubility in this system.

Table 11. Comparison of χ_{ab} Calculated from Solubility Measurements

Solvent	Estimated by	$J_{50/50}$	χ_{ab}
Toluene	a	0.05	0.08±0.04
Cyclohexane	Eq. 48 (b)	0.05	0.10
Cyclohexane	Eq. 53	0.016	0.03
Methylcyclohexane	Eq. 48 (b)	0.09	0.18
Methylcyclohexane	Eq. 53	0.29	0.06

a. Computed directly
b. Eq. 48 gives high estimates

Comparison of Intermer Repulsions Calculated from Solubility Parameters

A method for estimating the magnitude of intermer repulsions has been devised in which the solubility parameter concept is applied to equation 44. First equation 44 is written in terms of the enthalpic portion of $\chi_{copolymer}$.

$$(54) \quad \chi_{H,copolymer} = w_a \chi_{H,a} + w_b \chi_{H,b} - w_a w_b \chi_{ab}$$

Combining no. 17 with equation 54 yields

$$(55) \quad \chi_{H,copolymer} = (v_s/RT)[w_a(\delta_a - \delta_s)^2 + (\delta_b - \delta_s)^2 - w_a w_b (\delta_a - \delta_b)^2]$$

Several calculations can be performed with equation 55 as a basis. First values of $w_a w_b (\delta_a - \delta_s)^2$, which represent intermer repulsions, were calculated for styrene-α-methyl styrene, styrene-methyl acrylate, styrene-methyl methacrylate and styrene-acrylonitrile copolymers and are presented in Table 12. The magnitude of intermer repulsions are about the same for all these copolymers but styrene-acrylonitrile. Thus, provided this calculation is valid, the effects produced by differences in structure as measured by the solubility parameter for styrene and α-methyl styrene are about the same as those produced by differences in structure between styrene and methyl acrylate or styrene and methyl methacrylate. Some supporting evidence for this is given by the fact that reductions in Θ temperatures for styrene-α-methyl styrene and styrene-acrylic copolymers are about the same. The value of the intermer repulsions for styrene-acrylonitrile copolymers is considerably larger than that for other systems as would be expected from the large differences in structure for these monomers.

The value of the solvent-mer interactions were calculated from the first terms of equation 55,

$$w_a (\delta_a - \delta_s)^2 + w_b (\delta_b - \delta_s)^2,$$

and are also given in Table 12. Since cyclohexanol and 2-methylcyclohexanol are hydrogen bonding compounds, solubility parameter estimates of solvent-mer interactions could not be computed. In the styrene-acrylonitrile system the solubility parameter estimates of intermer repulsions and solvent-mer interactions are about the same magnitude for a 50 percent copolymer in methylethylketone. This large value of intermer repulsions accounts for the dramatic increase in solubility that Shimura observed (41).

Θ-temperatures for a random copolymer can be estimated from values of Θ (interpolated) through equation 55 combined with equations 46 and 49.

$$(56) \quad (\Theta_{in} - \Theta_{me})/(\Theta_{me}) = w_a w_b(\delta_a - \delta_b)^2/[w_a(\delta_a - \delta_s)^2 + w_b(\delta_b - \delta_s)^2 - w_a w_b(\delta_a - \delta_b)^2]$$

These calculations were preformed for styrene-α-methyl styrene copolymers in cyclohexane and methylcyclohexane and are shown in Figures 18 and 19. Surprisingly good agreement was obtained in cyclohexane, but poorer agreement was obtained in methylcyclohexane. The good agreement in cyclohexane is probably due to the fact that the calculated polymer-solvent interaction term in cyclohexane is relatively small compared to that in methylcyclohexane. Variations in χ_S with solvent may also be responsible.

In conclusion, the main points of the preceding discussion are: (1) To a first approximation the intermer repulsion term, χ_{ab}, is independent of solvent. (2) Intermer repulsions calculated for styrene-α-methyl styrene copolymers from solubility parameter considerations are about the same magnitude as those of styrene-methyl acrylate and styrene-methyl methacrylate copolymers. These calculations together with the similarity in Θ-temperature depressions observed for styrene-α-methyl styrene, styrene-methyl acrylate and styrene-methyl methacrylate copolymers support the notion that intermer repulsions are primarily responsible for the increase in solubility of styrene-α-methyl styrene copolymers.

Table 12. Calculated Intermer Repulsions

Copolymer	Solvent	Solvent - mer interaction $(0.5(\delta_S-\delta_A)^2$ $(0.5(\delta_S-\delta_B)^2)$	Intermer repulsions $(0.5)^2(\delta_A-\delta_B)^2$
S - αMS	cyclohexane	0.295	0.014
S - αMS	methylcyclohexane	0.824	0.014
S-Methyl acrylate	2-methylcyclohexane	- - - (a)	0.0225
S-Methyl methacrylate	cyclohexanol	- - - (a)	0.010
S-Acrylonitrile	methylethylketone	1.18	0.893

(a). Cyclohexanol is a hydrogen bonded solvent. Hence, this calculation cannot be made.

VI. METHYL GROUP EFFECTS

A goal of this research was to gain insight as to the effects of methyl groups on polymer solution behavior. Calculations of χ_{ab}, the intermer repulsion parameter in Equation 44, from solubility measurements in toluene and several Θ-solvents showed the increase in copoylmer solubility to be approximately independent of solvent type, and values of intermer repulsions calculated for styrene-α-methyl styrene and styrene-acrylate copolymers were of the same order of magnitude. Together with similarities in Θ-temperature depression between styrene-α-methyl styrene and styrene-acrylates, these results suggest that repulsive interactions produced by the presence of methyl groups are responsible for the increase in copolymer solubility in this system. To our knowledge such estimates of methyl group effects have not been reported before. It is certainly larger than one might expect, inasmuch as the methyl group is often considered "innocuous". Explanations for all the phenomena we observed have not been devised, particularly for the relative solubility of the homopolymers in chemically similar Θ-solvents. Before further definitive statements can be made, additional work is necessary, particularly with a variety of solvent systems (pure as well as mixed) and with such methyl group containing monomers as p-methyl styrene.

VII. SUMMARY AND CONCLUSIONS

The thermodynamic behavior of some styrene-based model polymer systems has been studied in a variety of ways. This study was undertaken to elucidate the influence of methyl groups on polymer solution behavior as well as to explore the solution behavior of random copolymers. The materials of interest were the homopolymers and copolymers constructed from styrene and α-methyl styrene plus, to a limited extent, p-methyl styrene. The polymers were synthesized by the living polymer technique to obtain monodisperse, amorphous polymers as well as homogeneous, random copolymers. The solvents were toluene, which is a good solvent, plus cyclohexane, methylcyclohexane, commercial decalin and diethyl succinate, in which the polymers of interest exhibit Θ temperature. Several parameters were employed to characterize solubility: second virial coefficients in toluene, Θ-temperatures, and Flory-Huggins parameters in moderately concentrated toluene solutions.

We obtained an increased copolymer solubility over that obtained by linear interpolation between the parent homopolymers. This phenomena is most pronounced in plots of Θ-temperature versus copolymer composition which actually show minima.

It is also manifested in the Flory-Huggins parameter obtained from activities. This is the first evidence for the increase in copolymer solubility obtained at moderate concentrations. Scatter inherent in the SVC prevented a definitive interpretation of these results, but they appear to follow the same general pattern of polymer solubility. Comparison of our evidence with the few available in the literature suggest that this phenomena may be quite general. The systems for which increased copolymer solubility have been observed are given in Table 13. Evidence for increased copolymer solubility comes from diverse polymer systems and solvents, and it is observed in a variety of parameters. Specifically, this phenomenon is observed in copolymer systems as chemically dissimilar as styrene and α-methyl styrene or methyl acrylate and methyl methacrylate. Indeed, an increase in solubility produced by such an innocuous group as the methyl group is surprising. Furthermore, it has been observed in good and poor solvents plus hydrogen bonding solvents. Finally, it is manifested in measurements of SVC's, Θ-temperatures and Flory-Huggins parameters. On the basis of these observations one is tempted to advance the notion that such an increase in random copolymer solubility may be a universally occurring phenomenon.

Table 13. Copolymer Systems Exhibiting Increased Solubility

Comonomers	Solvents	Comments	References
Styrene-Methyl Acrylate	2-Methylcyclohexanol	Θ-Temps.	38
Styrene-Methyl Methacrylate	Cyclohexanol	Θ-Temps.	37
Styrene-Acrylonitrile	Methylethylketone	SVC Maxima	41
Styrene-α-Methyl Styrene	Cyclohexane, Methylcyclohexane, Toluene	Θ-Temps. F.-H. Parameters	Current Research
Methyl Acrylate-Methyl Methacrylate	Methylethylketone	SVC	42

An attempt was made to explain the homopolymer solubility data with the solubility parameter theory. Although some of the solubility parameter predictions were followed, the perplexing patterns of homopolymer solubility in chemically similar solvents based on cyclohexane (Table 7) were beyond the scope of the theory as presently formulated. Variations in the entropic contributions to the Flory-Huggins parameter, which are not embraced in the current theory, may be responsible for these results.

The solubility parameter theory was used to support the contention that intermer repulsions are responsible for increased copolymer solubility in the styrene-α-methyl styrene system. First if intermer repulsions dominate, the increase in copolymer solubility should not depend on solvent. Quantitatively, the intermer repulsion term, χ_{ab} in Equation 44, should be independent of solvent. χ_{ab} was calculated for the styrene-α-methyl styrene system from solubility measurements in toluene plus several Θ-solvents and was to be approximately independent of solvent (Table 11). Secondly, stronger evidence was obtained by devising a method to calculate the magnitude of intermer repulsions from solubility parameter considerations. Values ranged from 0.01 to 0.0225 for copolymers of styrene and methyl acrylate, styrene and α-methyl styrene plus styrene and methyl methacrylate (Table 12). The similarity in magnitudes of calculated intermer repulsions between styrene-α-methyl styrene and styrene-acrylate copolymers (systems where the existence of intermer repulsions are comprehensible because of the dissimilarity of the comonomers) supports the hypothesis that intermer repulsions are responsible for the increase in solubility for styrene-α-methyl styrene copolymers. These two calculations together with the similarity in the depressions in Θ-temperature for styrene-α-methyl styrene and styrene-acrylate copolymers are the bas~~i~~es of our theory.

The influence of methyl groups on polymer solubility is considerable as can be seen from the foregoing discussion. Additional experiments will be required before definitive statements can be made.

Studies of SVC's and unperturbed chain dimensions proved less fruitful. SVC's in toluene indicated that polystyrene was more soluble than poly (α-methyl styrene), but scatter prevented a definitive elucidation of copolymer solubility by this technique. Unperturbed dimensions computed from values of K_{Θ} obtained by a SFK plot for poly (α-methyl styrene) and a 24 percent by weight styrene copolymer as well as polystyrene obtained from the literature were the same within experimental error. This perplexing lack of variation of unperturbed chain dimensions with chain stiffness requires further research for an explanation.

APPENDICES

APPENDIX A-1

Solution Properties

Table 14. Poly (α-methyl styrene)

Sample Number	$A_2 \cdot 10^4$ *; mol-cm^3/gm^2	[η]; dl/gm in toluene at 30°C	[η]; dl/gm cyclohexane at 30°C	T_c; °C cyclohexane	T_c; °C methyl-cyclohexane	T_c; °C diethyl succinate	T_c; °C commercial decalin
IV-5	4.2	.847	.416	22.2	----	----	110.5
IV-4	4.4	.609	.332	20.5	69.8	-19.8	-----
IV-1	4.3	.460	.292	----	----	-21.8	-----
IV-3	4.1	.460	.269	17.7	65.6	-22.3	-----
IV-2	4.6	.440	.254	17.1	----	----	99.0
IV-7	4.8	.292	.210	13.8	55.1	----	-----
IV-8	5.1	.260	----	11.4	----	----	86.1
IV-6	5.9	.205	.171	9.2	47.7	-32.	-----

* In toluene at 37°C

Table 15. Polystyrene

Sample Number	$A_2 \cdot 10^4$ *; mol-cm^3/gm^2	[η]; dl/gm in toluene at 30°C	Tc; °C in commercial decalin
III-8	5.5	1.42	6.2
III-5	5.5	1.08	---
III-1	5.7	.838	---
III-7	5.7	.853	---
III-2	5.5	.698	---
III-9	6.1	.610	---
Pressure Chemicals	6.1	----	---
III-6	6.9	.386	---

* In toluene at 37°C.

Table 16. 24 Weight Percent Styrene Copolymers

Sample Number	Weight Percent Styrene	$A_2 \cdot 10^4$ *; mol-cm^3/gm^2	[η]; dl/gm in toluene at 30°C	[η]; dl/gm in cyclohexane at 30°C	T_c; °C cyclohexane	T_c; °C methyl-cyclohexane
V-46	23.7	5.6	.288	.194	8.1	40.5
V-47	23.5	5.8	.421	.249	11.7	47.0
V-49	25.1	5.1	.692	.320	15.9	53.2
V-48	25.2	4.9	.960	.458	18.1	57.0

* In toluene at 37°C

Table 17. 50 Weight Percent Styrene Copolymers

Sample Number	Weight Percent Styrene	$A_2 \cdot 10^{4*}$; mol-cm^3/gm^2	$[\eta]$; dl/gm in toluene at 30°C	T_c; °C cyclohexane	T_c; °C methylcyclohexane
V-36	47.9	5.2	0.558	10.0	38.1
V-37	53.0	5.4	0.796	11.8	40.3
V-38	50.0	5.9	0.940	14.8	42.8

* In toluene at 37°C

Table 18. 69 Weight Percent Styrene Copolymers

Sample Number	Weight Percent Styrene	$A_2 \cdot 10^{4*}$ mol-cm^3/gm^2	[η]; dl/gm in toluene at 30°C	T_c; °C cyclohexane	T_c; °C methyl-cyclohexane	T_c; °C commercial decalin
V-42	70.5	6.8	0.46	9.2	31.1	-19.2
V-44	70.4	5.5	0.767	12.5	32.7	-14.5
V-45	67.6	5.8	1.20	14.8	40.7	-12.3

* In toluene at 37°C

APPENDIX A-2

Osmometry Data

Table 19. Flory-Huggins Parameters of Polystyrene III-9* in Toluene at 37°C

Dilute Solution Data

c; gm/l	$V_2 \cdot 10^3$	Π; gm/cm^2	χ
2.41	2.27	.59	.400
4.82	4.56	1.36	.415
7.24	6.83	2.33	.418
9.65	9.10	3.47	.421

High Pressure Osmometry Data

$w_2 \cdot 10^2$	$V_2 \cdot 10^2$	Π; gm/cm^2	χ
2.617	2.915	26.5	0.415
7.859	6.338	122.5	0.414
11.32	9.266	263.7	0.417
15.93	13.16	599.9	0.413
21.52	17.99	1300.	0.409

* Density 1.06 gm/cm^3

Table 20. Flory-Huggins Parameters of Poly(α-methyl styrene)* IV-3 in Toluene at 37°C

Dilute Solution Data

c; gm/l	$V_2 \cdot 10^3$	Π; gm/cm^2	χ
1.98	1.83	.43	.473
3.96	3.67	.98	.455
5.94	5.85	1.58	.455
7.91	7.32	2.25	.456

High Pressure Osmometry Data

$W_2 \cdot 10^2$	$V_2 \cdot 10^2$	Π; gm/cm^2	χ
4.529	3.591	26.0	.454
8.853	7.086	99.6	.456
13.33	10.95	249.4	.462
18.33	14.99	645.7	.444
26.32	21.91	1592.	.455

* Density 1.08 gm/cm^3

Table 21. Flory-Huggins Parameters of Styrene-α-Methyl Styrene Copolymer V-36* in Toluene at 37°C

Dilute Solution Data

c; gm/l	$V_2 \cdot 10^3$	Π; gm/cm^2	χ
1.88	1.76	.51	.412
3.76	3.51	1.08	.436
5.78	5.40	1.78	.442
7.61	7.11	2.57	.438

High Pressure Osmometry Data

$W_2 \cdot 10^2$	$V_2 \cdot 10^2$	Π; gm/cm^2	χ
4.072	3.255	25.6	.443
8.269	6.668	132.8	.416
11.28	9.154	263.1	.414
18.77	15.48	872.	.415
27.52	23.13	2302.	.420

* Density 1.07 gm/cm^3
Copolymer contains 50 percent styrene by weight

APPENDIX A-3

Flory-Schultz Plots

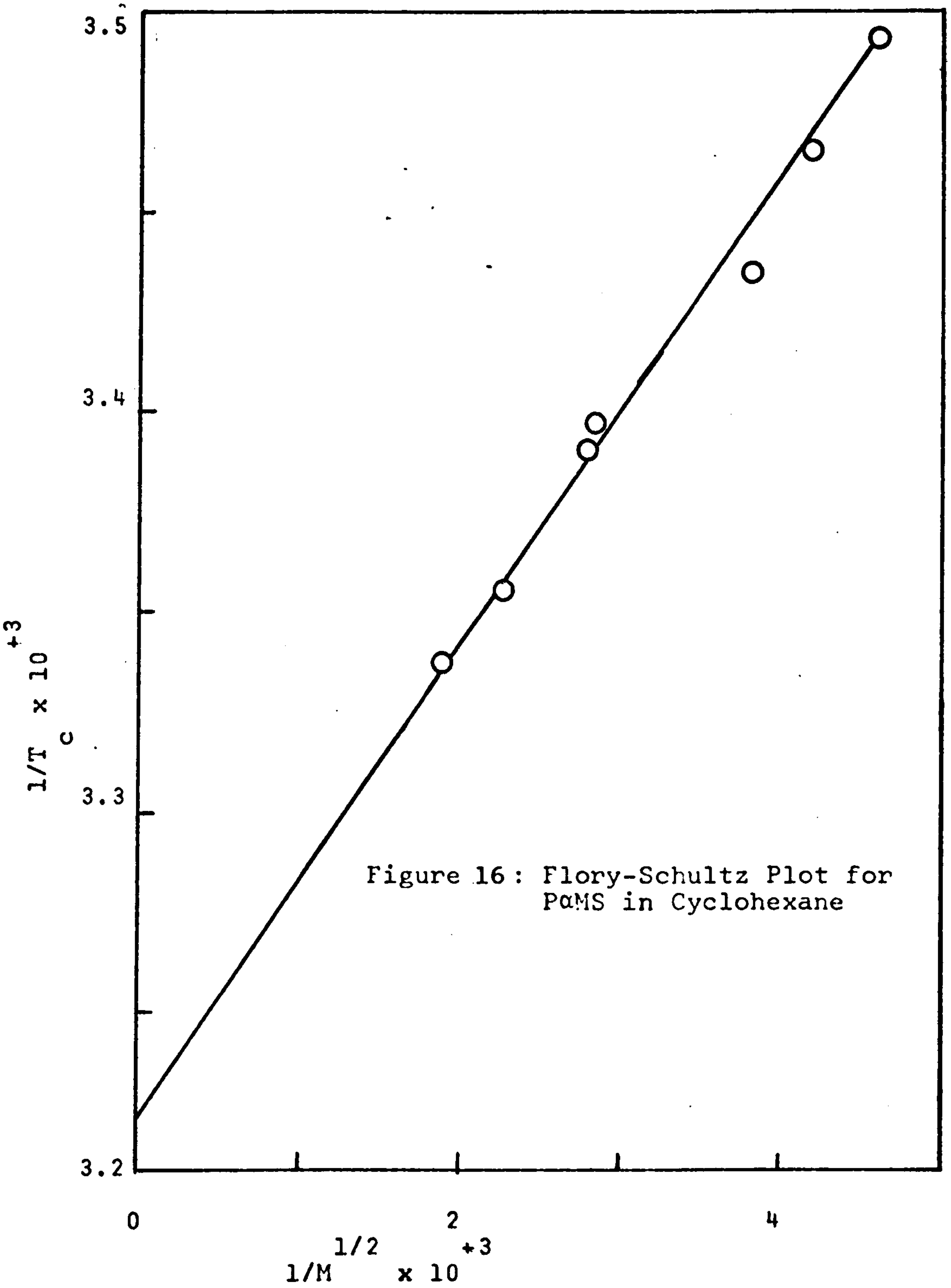

Figure 16 : Flory-Schultz Plot for PαMS in Cyclohexane

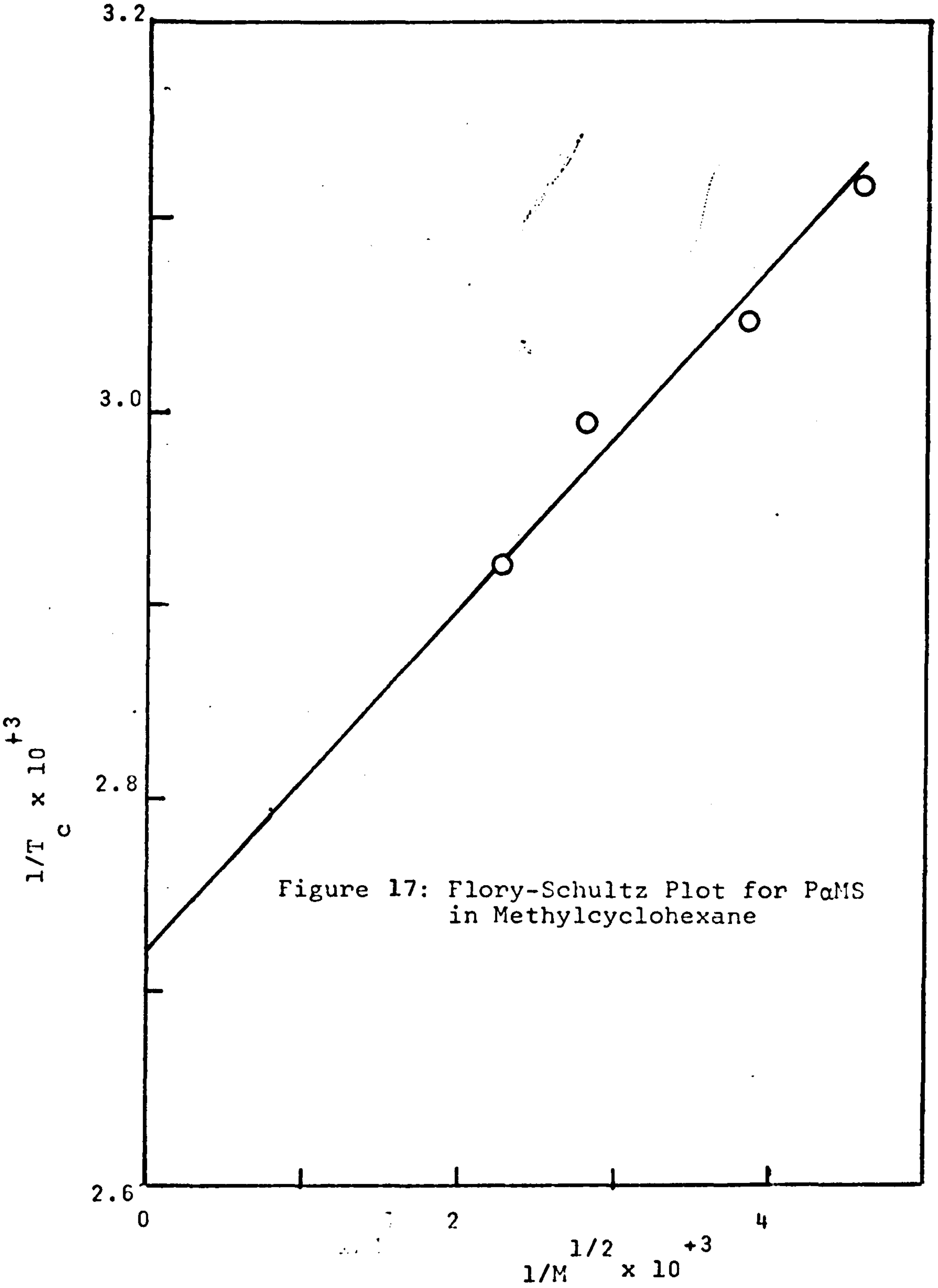

Figure 17: Flory-Schultz Plot for PαMS in Methylcyclohexane

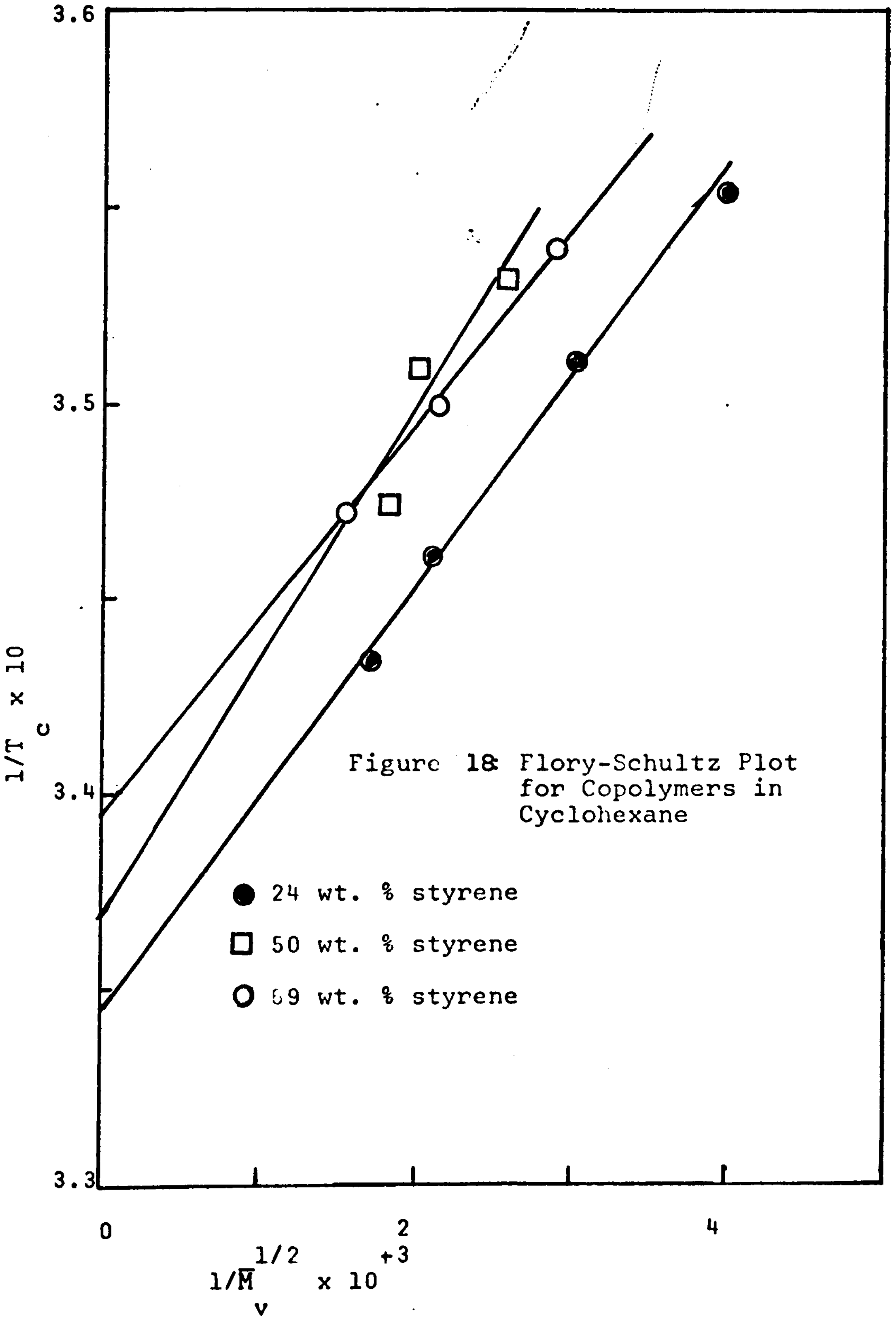

Figure 18: Flory-Schultz Plot for Copolymers in Cyclohexane

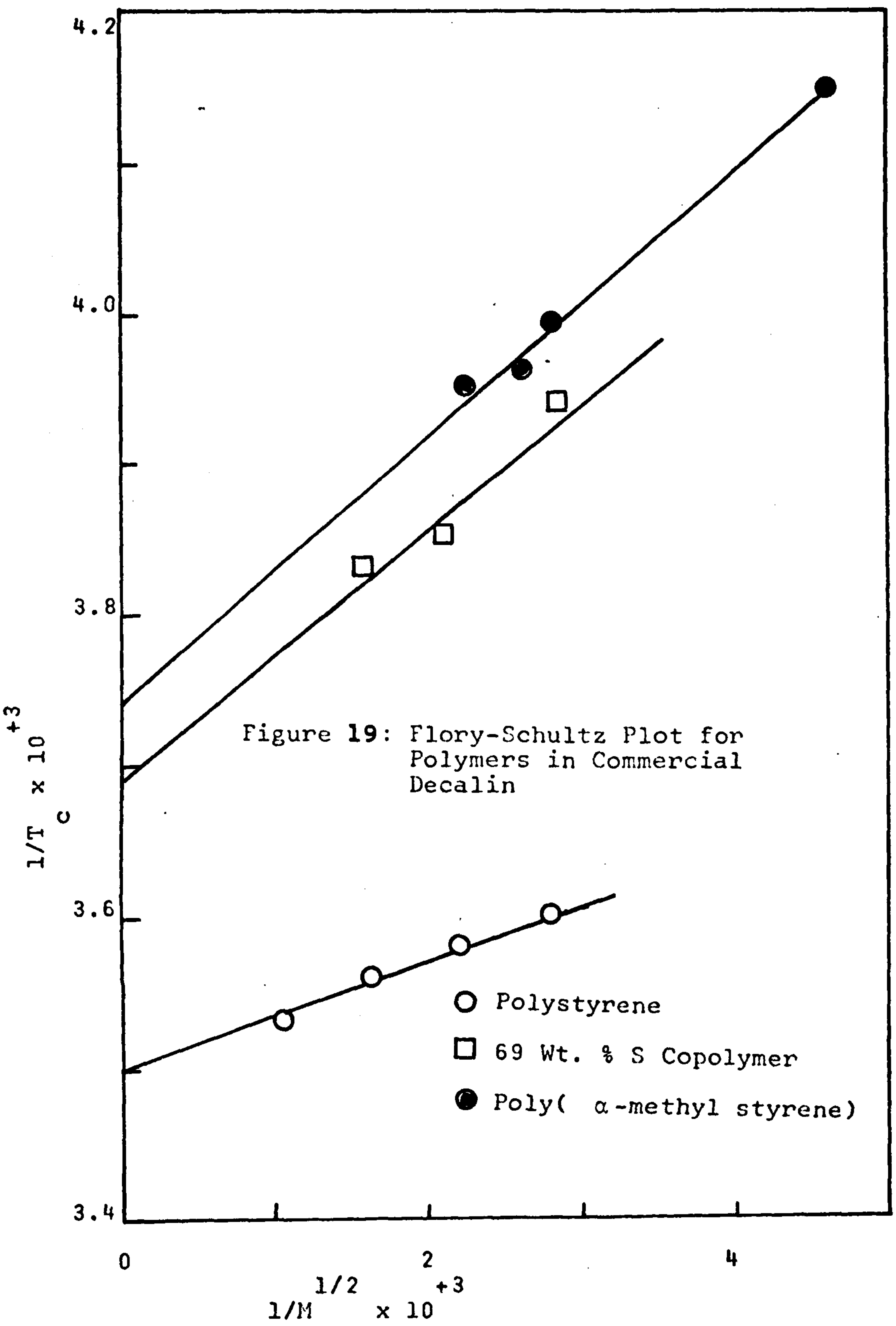

Figure 19: Flory-Schultz Plot for Polymers in Commercial Decalin

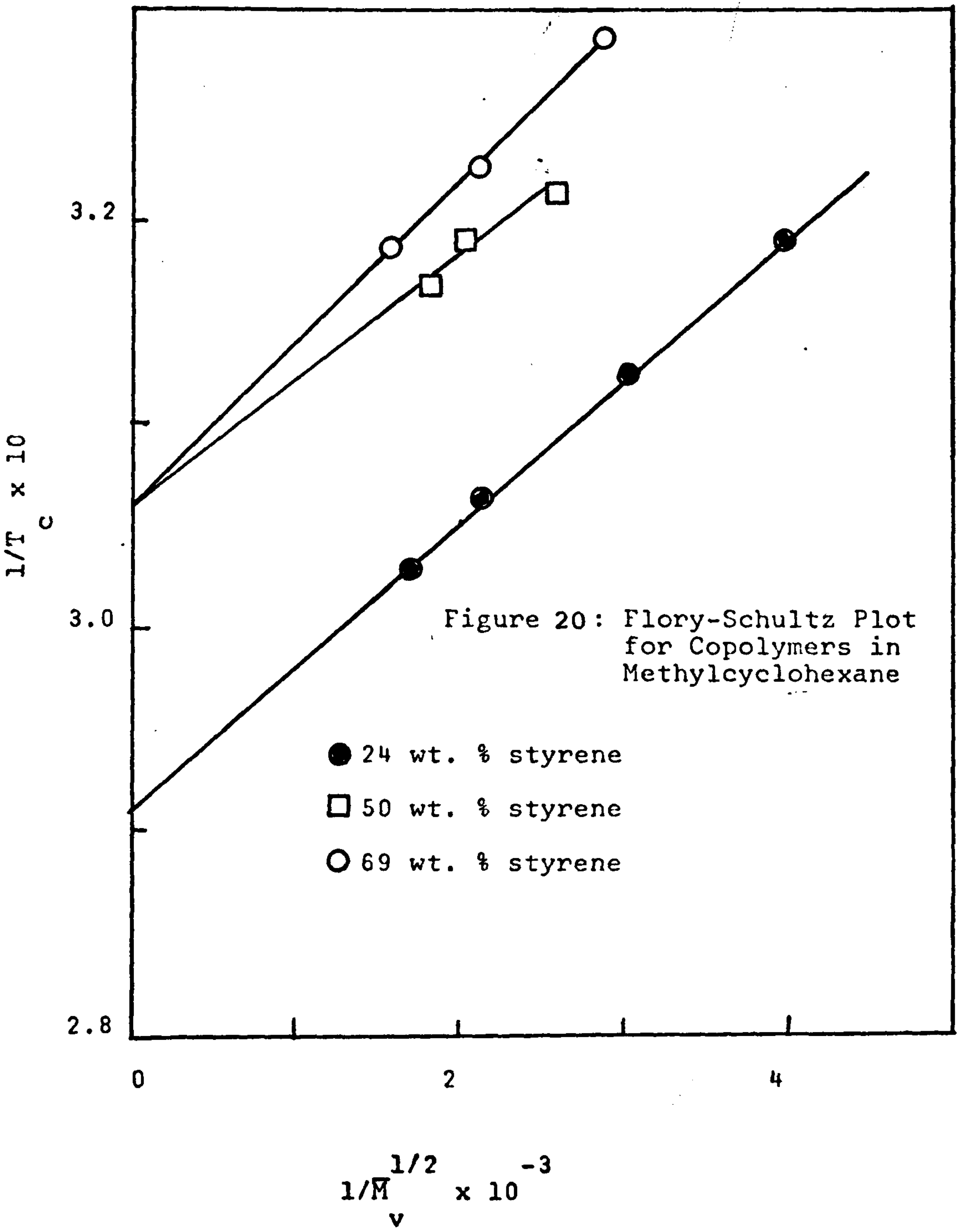

Figure 20: Flory-Schultz Plot for Copolymers in Methylcyclohexane

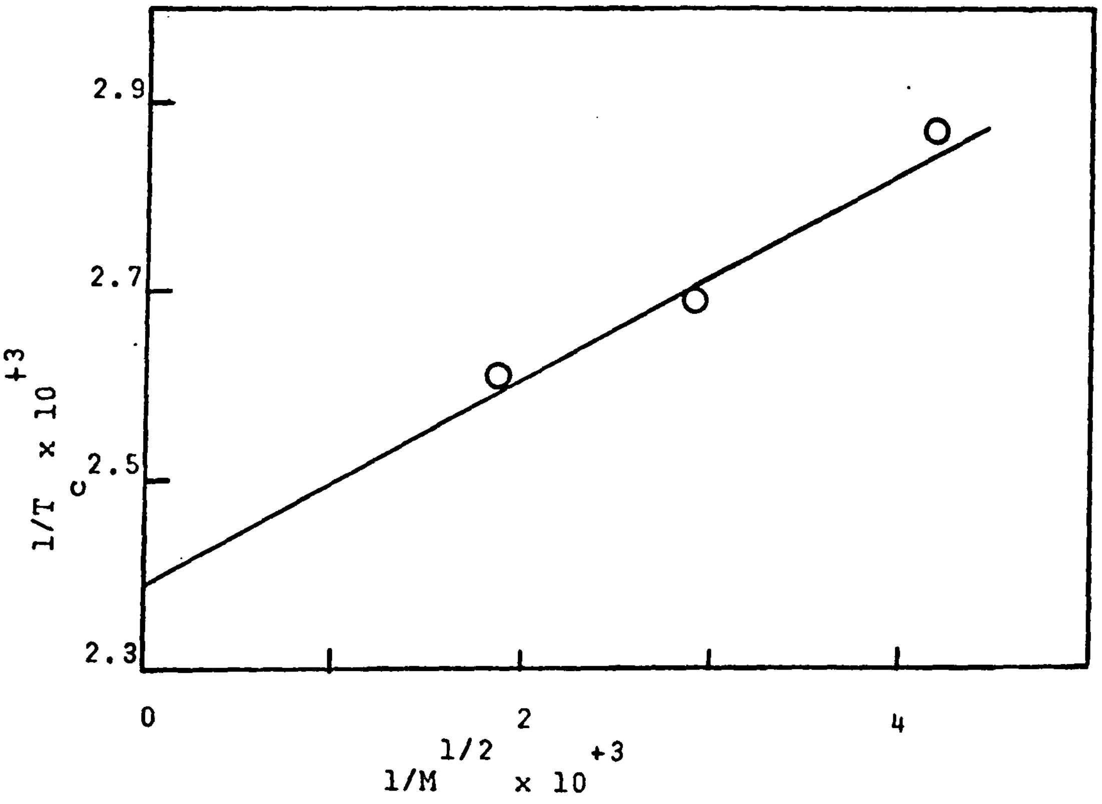

Figure 21: Flory-Schultz plot for PαMS in Diethyl Succinate

B. Synthesis

1. Introduction

The basic idea in producing polymers with narrow molecular weight distributions is to initiate instantaneously all active centers and for the chains to grow without termination. Thus, aside from random fluctuations, all active centers will grow at the same rate and will all be the same size. Number average molecular weights can be computed from

$$(57) \quad \bar{M}_n = \frac{(\text{Grams Monomer Reacted})(\text{Active Centers/Molecule})}{(\text{Moles Active Centers})}$$

The anionic living polymer reaction fulfills these requirements with appropriate initiators. Sodium-biphenyl is an effective initiator for styrene and α-methyl styrene polymerizations.

Provided initiation is instantaneous, the keys to making polymers with narrow molecular weight distributions are good mixing and rigorous exclusion of terminating reagents. They can terminate by extracting hydrogen from water or alcohols and by reacting with CO_2. Hence, polymerizations must be conducted in a well stirred reactor from which impurities are excluded.

Different reactors can be used to conduct this reaction. We chose a method based on that of Wenger (57-58) modified to suit our needs and facilities. The apparatus was assembled from standard glassware components (figure 22); the only custom glassware was the ground-glass jointed high-vacuum stopcocks. The advantages of this apparatus are: Glass-blowing skills and tools are not needed; The apparatus can be easily disassembled for cleaning; Glass-jointed devices are more robust than complex, one-piece devices. The main weaknesses with this apparatus are: Joints are sources of leaks, and the stopcock grease can dissolve in the reaction medium.

Several precautions were followed to insure random copolymerization. Preliminary studies indicated that if the comonomers were added to the polymerization vessel more rapidly than they could react, then, upon shortstopping the residual reaction mixture was much higher in α-methyl styrene content than was the comonomer feed. Hence, α-methyl styrene copolymerized much more slowly than does styrene. For this reason the mixed monomers were distilled into the reaction vessel only as fast as they could react. If the monomers had been added more rapidly, molecules whose cores were rich in styrene and whose tails were rich in α-methyl styrene would have been formed. A large reservoir of mixed monomers was used to prevent drift in distillate composition. The apparatus was positioned so condensate fell directly into the

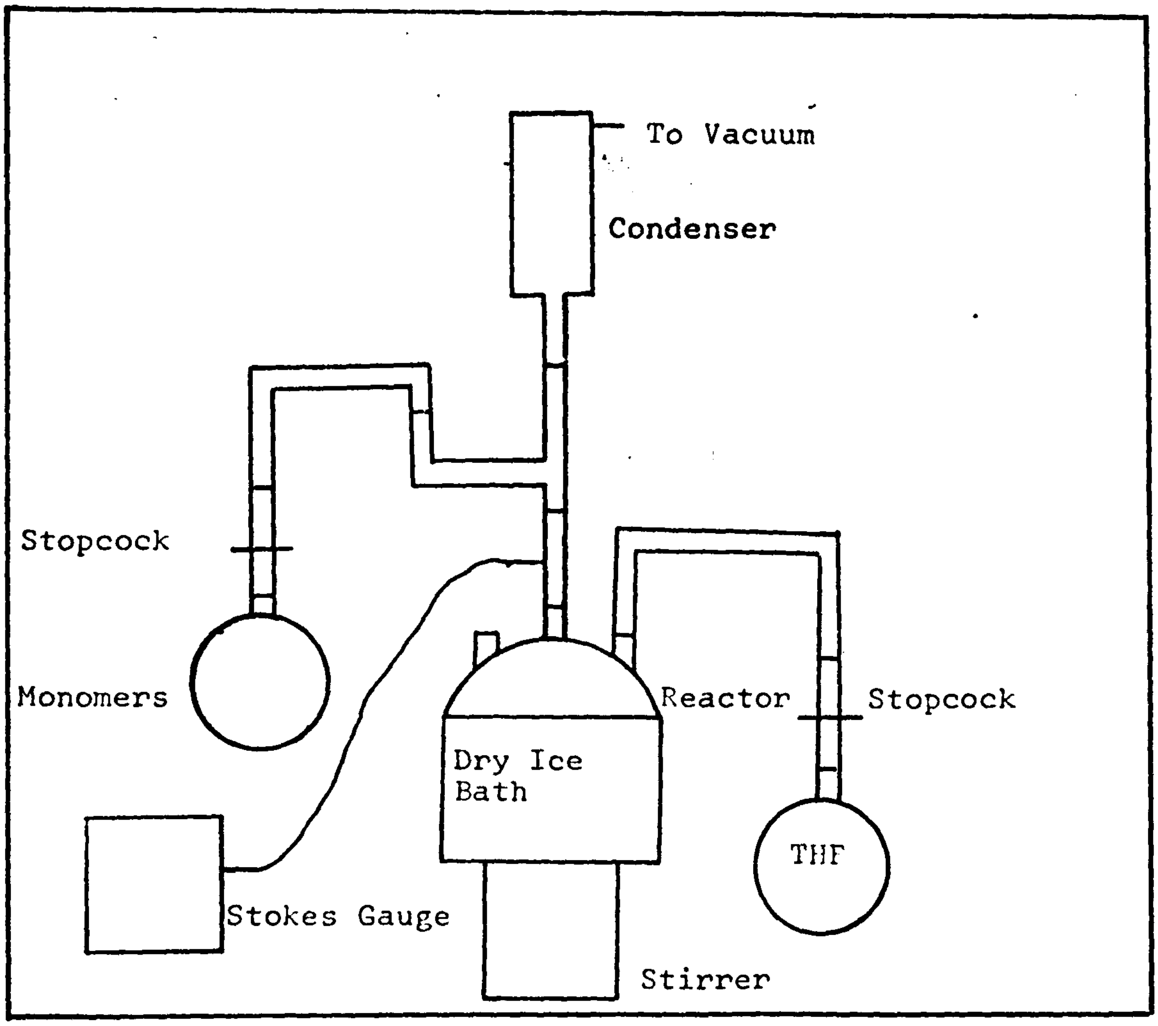

Figure 22: Polymerization Apparatus

reaction medium. If condensate ran directly down the vessel wall, clumps of polymer would form at the interface of the reaction medium and the vapor space. The condenser temperature was kept between -40°C and -30°C to keep the monomers from freezing.

The reaction medium was stirred with a 3/4" x 1/4" Pyrex covered stirring bar. Teflon coated bars reacted with sodium-biphenyl. Stirring was effective except for high concentrations of high molecular weight polymers. When effective stirring ceased, reactions were terminated. Although a high torque stirrer would be desirable, the stirring bars were cheap, easy to clean, disposable and eliminated sources of leaks.

2. Vacuum

Vacuum for the system was supplied by a two-stage mechanical pump and a mercury diffusion pump. Ten millimeter bore high-vacuum stopcocks joined with heavy-wall rubber tubing completed the system which is shown schematically in figure 23.

Fluids were injected into the evacuated reaction system through a silicone rubber septum clamped in a standard 24/40 Teflon port.

Since the reactions were run at pressures from 1.5 to 10. microns, precautions were taken to prevent leaks. Joints were cleaned with potassium hydroxide solutions. A silicone high-vacuum grease was used; because it dissolved in tetrahydrofuran (THF) and aromatic monomers, care was taken to prevent the reaction medium from coming in contact with the stopcock grease. All joints were secured with mechanical clamps. The system pressure was monitored semi-continuously with a Stokes gauge.

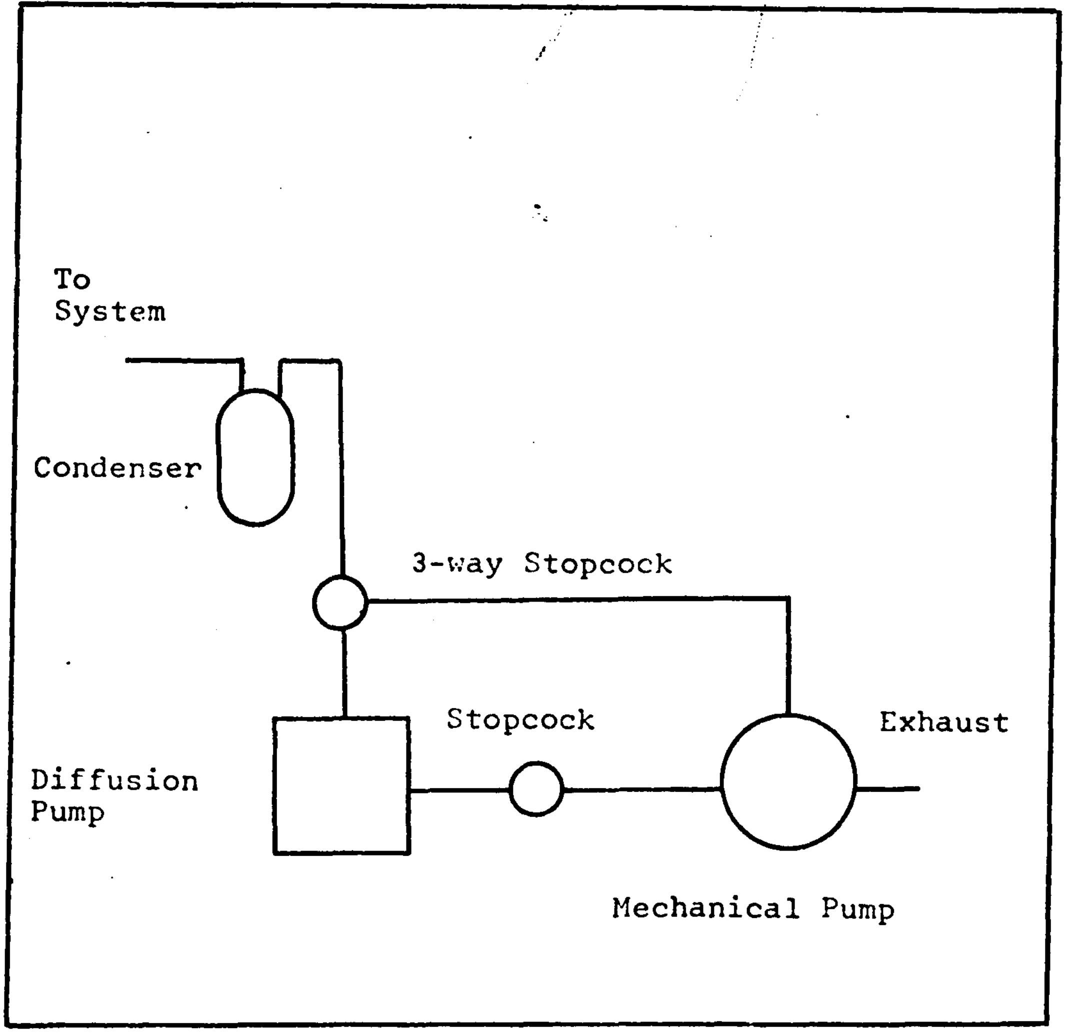

Figure 23: Vacuum System

3. Reagent Preparation

Reagent grade styrene was vacuum-distilled prior to use and stored in a freezer. α-methyl styrene was distilled at atmospheric pressure under nitrogen and stored at room temperature.

For copolymerizations, about 150 gms of mixed monomers were tared into a 250 cc flat bottomed flask together with 20 to 40 gms of barium oxide - a powerful dessicant. The vessel was sealed with a high-vacuum stopcock with standard taper joints and purged with nitrogen to remove oxygen.

Pure tetrahydrofuran (THF) was provided for reactions by distillation from solutions of sodium-naphthalene or sodium-biphenyl. The sodium compounds destroyed any harmful impurities in the THF.

The initiator was prepared by reacting biphenyl with excess sodium in THF. Several days were allowed for the reaction to go to completion. The solution was then stored in a freezer to inhibit the evaporation of THF. A major difficulty with this technique was that the exact concentration of sodium-biphenyl was unknown.

4. Procedure

A copolymerization procedure will be described in detail. This technique can also be used to synthesize polystyrene and poly(α-methyl styrene). A variation useful for producing poly(α-methyl styrene) will also be described.

The apparatus was assembled the day prior to the run and evacuated with the mechanical pump. This permitted the early detection and elimination of leaks. The day the reaction was run the system was evacuated with the diffusion pump for 1/2 hour. The stopcock on the monomer vessel was opened briefly; this flooded the system with nitrogen and evacuated the monomer vessel. The system was then flamed to remove adsorbed water and carbon dioxide and allowed to cool. The condenser was cooled to dry ice temperature after which a small amount of THF was distilled into the system to remove any traces of impurities in the condenser or glassware. The reactor was cooled to $-78^{o}C$, and 200 to 400 gms of THF were distilled in from the sodium-biphenyl solution in 2 to 3 hours. Care was taken during the distillation to prevent the THF from bumping.

After the THF distillation was completed, 3 to 4 drops of monomer were distilled into the reactor. A small quantity of initiator (0.1 to 0.3 ml) was added to the reactor by syringe to deactivate any terminating agents in the solution. If all the impurities were destroyed, the solution remained pale red - characteristic of styrene and α-methyl styrene anions. The main charge of initiator (0.5 to 10. ml) was added next, and the reaction medium became blue - the characteristic color of sodium-biphenyl. Twenty to thirty grams of monomers were distilled into the reactor at a rate of 1 to 2 drops per minute for about 6 hours. During the distillation, the condenser was kept at -30°C to -40°C to prevent the monomer from freezing. The reaction was terminated by adding 5 cc of methanol by syringe.

A modified form of this procedure can be used to make poly (α-methyl styrene). At room temperature the stable anionic form of α-methyl styrene is a tetramer. Hence, if the required quantities into the reaction vessel and the mixture was warmed up to room temperature, initiator could be added without forming high polymer. Small quantities of initiator were added to destroy impurities followed by the main charge of initiator. When the solution was then cooled to -78°C, the polymerization proceeded. This technique can be used with sodium naphthalene which does not instantaneously initiate polymerizations at -78°C but does at room temperature (57). Several of our poly (α-methyl styrene) samples were made by this technique with sodium-biphenyl.

5. Recovery

The polymers were recovered by precipitation from THF solution by adding the polymer solution dropwise to methanol in a Waring blender. The polymer precipitate was filtered from the suspension, washed with methanol and vacuum dried overnight.

C. Copolymer Composition

Compositions of copolymers were calculated via a material balance around the reaction vessels. The quantity of mixed monomer distilled was determined by weighing. The final mixed monomer composition and the residue of mixed monomers in the reaction vessel were measured by gas chromatography. The composition of liquid in the cold trap was also obtained by gas chromatography. From these data copolymer compositions could easily be calculated. Conversions were generally over 95 percent.

Two solutions had to be analyzed; a simple mixture of styrene and α-methyl styrene and a THF solution containing less than 1 percent monomers. A Hewlett Packard Model 700 Gas Chromatograph containing a Carbowax packed column and a thermal conductivity cell was used. A carrier gas flow of 60 cc/min. of helium was used with oven, detector and injection port temperatures of 95°C, 230°C and 190°C respectively. Two microliters were used for the mixed monomer analysis and a five microliters were used for the polymer solution analysis. Replicate measurements were made, and the instrument was calibrated on the day of use. Good separations were obtained. Monomer compositions could be measured to within ± 0.15 percent, and residues as small as 0.01 percent could be detected. Overall compositions could be measured to within about ± 2 percent. Typical calibration curves are shown in Figures 24 and 25.

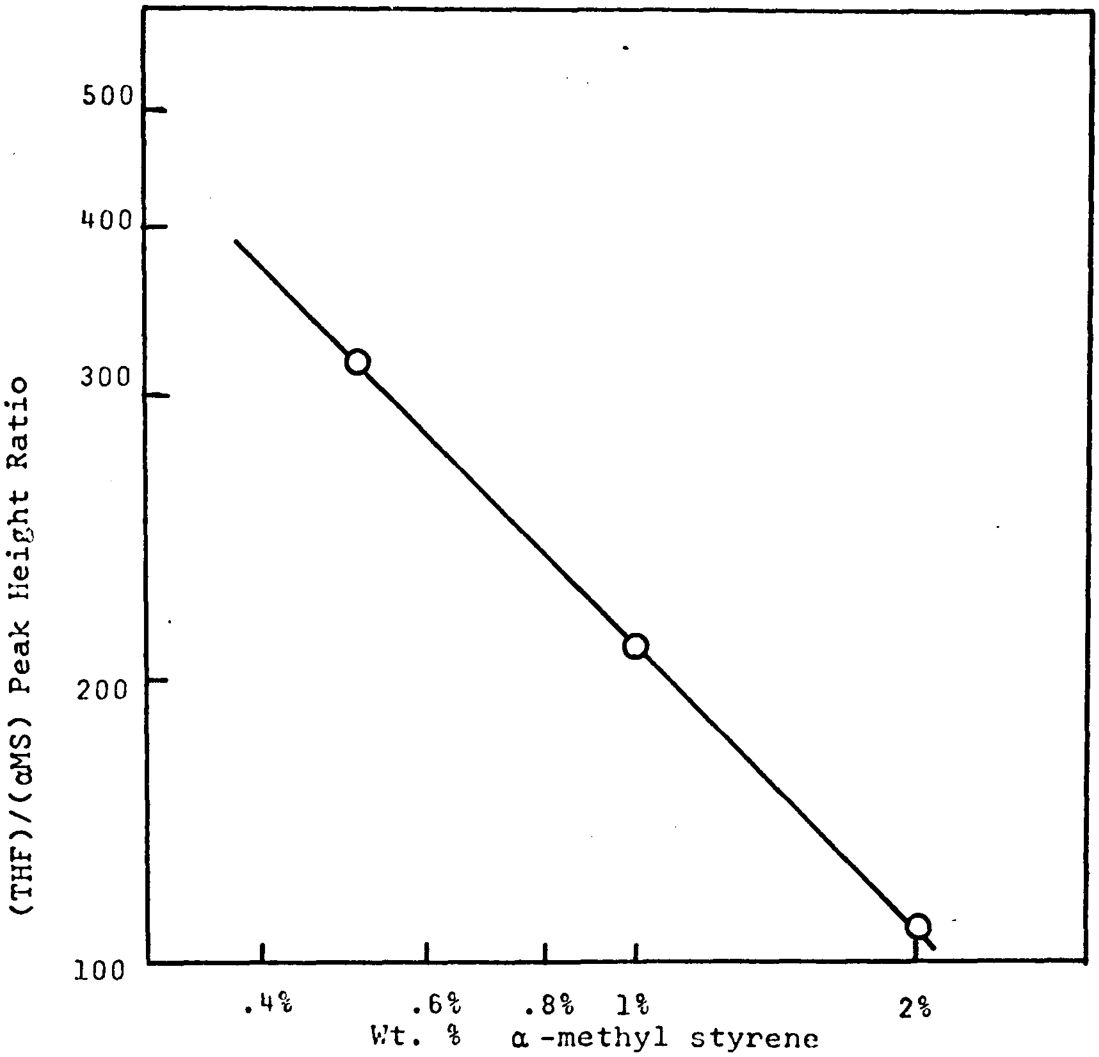

Figure 24.: Chromatograph Calibration Chart

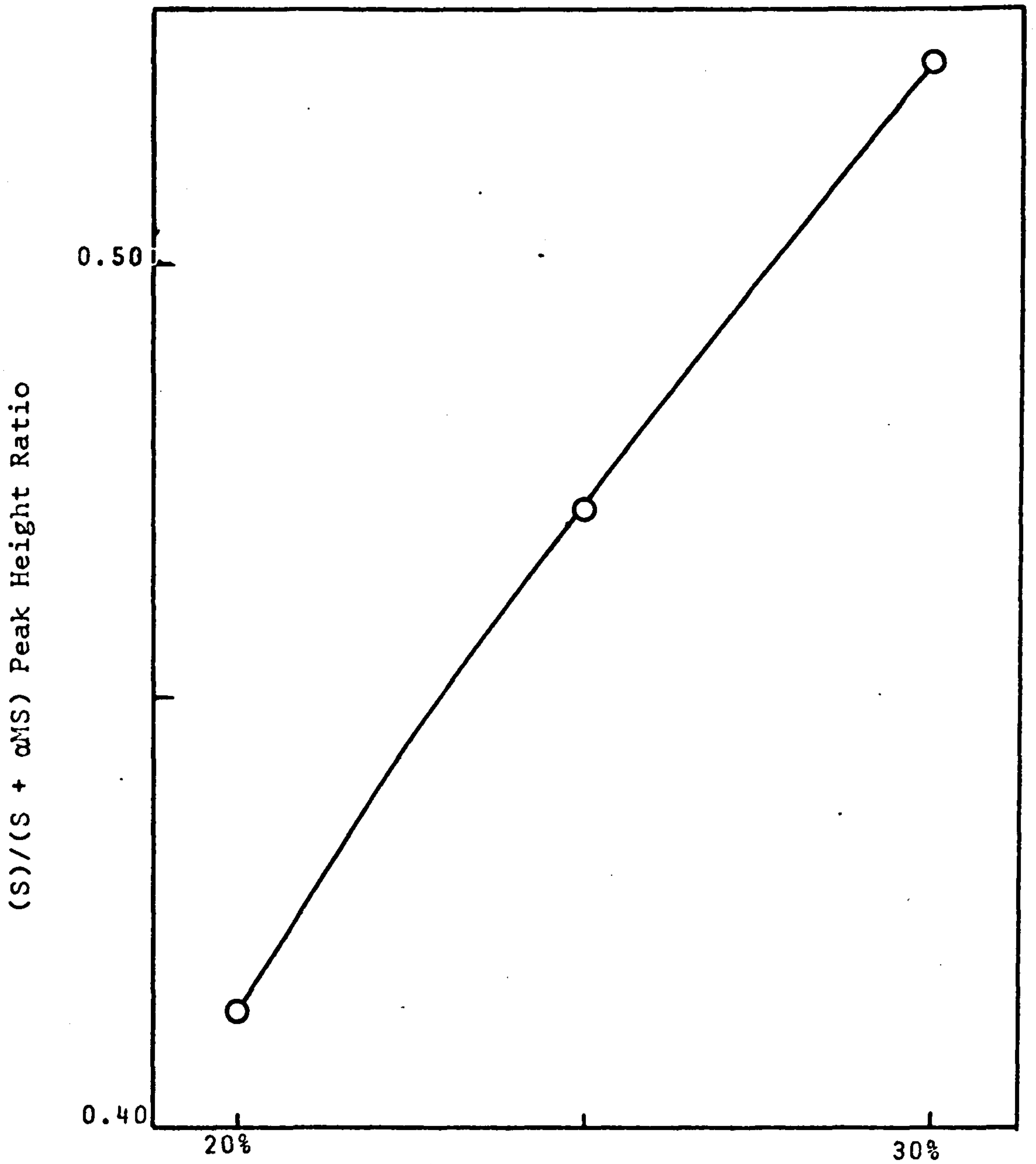

Figure 25: Gas Chromatograph Calibration Chart

D. High-Speed Osmometry

Number average molecular weights and second virial coefficients were determined with a Mechrolab Model 501 High Speed Osmometer in toluene at 37°C with an S&S 08 membrane. Osmometry may be characterized as being a standard but by no means a routine laboratory procedure.

1. Assembly

In assembling the osmometer several precautions were followed. The osmometer chamber was kept clean, and the solvent lines were filled only with hot, filtered, degassed solvent. The osmometer head was tightened evenly to insure a tight membrane seal. At times the capillary tube was cleaned. On reassembly, solvent was forced through the Teflon line (which connected the solvent cup on the elevator with the capillary tube) while the glass capillary tube was inserted into the Teflon line. This procedure prevented the formation of microscopic bubbles at the junction of the capillary tube and Teflon line that are supposed to slow the osmotic equilibria measurements. The optics were carefully adjusted. The membranes, which were conditioned according to the procedure recommended by Arro Laboratories, were the source of many difficulties. They often contained pinholes or creases that caused leaks or were too stiff to seal properly. It took as long as a week after the membrane was installed until the osmometer operated properly. During this period, the osmometer head was tightened occasionally. The osmometer was always checked with a sample of known molecular weight after assembly.

2. Operation

Best results were obtained when the polymers were dissolved in distilled, filtered, degassed reaction grade toluene. The solutions were made up in 8 dram polyethylene capped vials according to the following:

1. Dissolve about 0.5 gms of polymer in 50 cc of toluene.
2. The solution was filtered to give solution D.
3. Dilute 20.0 ml of D with 20.0 ml of toluene to give B.
4. Combine 10.0 ml of B with 10.0 ml of D to give C.
5. Dilute 10.0 ml of B with 10.0 ml of toluene to give A.

A 10.0 ml sample of D was evaporated to dryness to obtain solution concentrations.

The following procedure was followed in osmometer operation. The osmometer was first zeroed with solvent several times. The solutions were added in increasing order of concentration - A, B, C and D. At least two replicates of each solution were run with a precision of ± 0.015 cm. The solutions were kept at about $39^{\circ}C$ before they were put in the osmometer. From 10 to 40 minutes were required to attain equilibrium. Longer times were needed when concentrations were changed than when replicates were run. It was found that flushing the solution chamber with four sample tube heights of solution removed any traces of previous solutions for concentrations A and B whereas five sample tube heights were needed for samples C and D.

After the run was completed the solution chamber was flushed with concentrations C, B, A and solvent; the osmometer was allowed to equilibrate at several intermediate concentrations. This was done to reduce membrane shock from rapid changes in concentration. It was also useful to add the solutions by syringe and to drain the solution chamber slowly.

Aside from scatter and occasional spurious points the major difficulties encountered in osmometer operation were end-point drift and low magnitude oscillations in osmometer output. Draining the solvent chamber slowly tended to reduce oscillations.

3. Data Treatment

Two different methods can be used to treat osmotic pressure data. One can plot Π/c versus c to obtain SVC's and $\bar{M}_n$ based on the virial equation for osmotic pressure with third and higher order terms neglected

$$\Pi/RT = (c/\bar{M}_n + A_2c^2) \tag{58}$$

One can also plot $(\pi/c)^{1/2}$ versus c which is based on the observation that the third virial coefficient, A_3, is given by

$$A_3 = \frac{1}{4} \bar{M}_n A_2^2$$

In general, linear plots described our data. A sample curve is shown in figure 26.

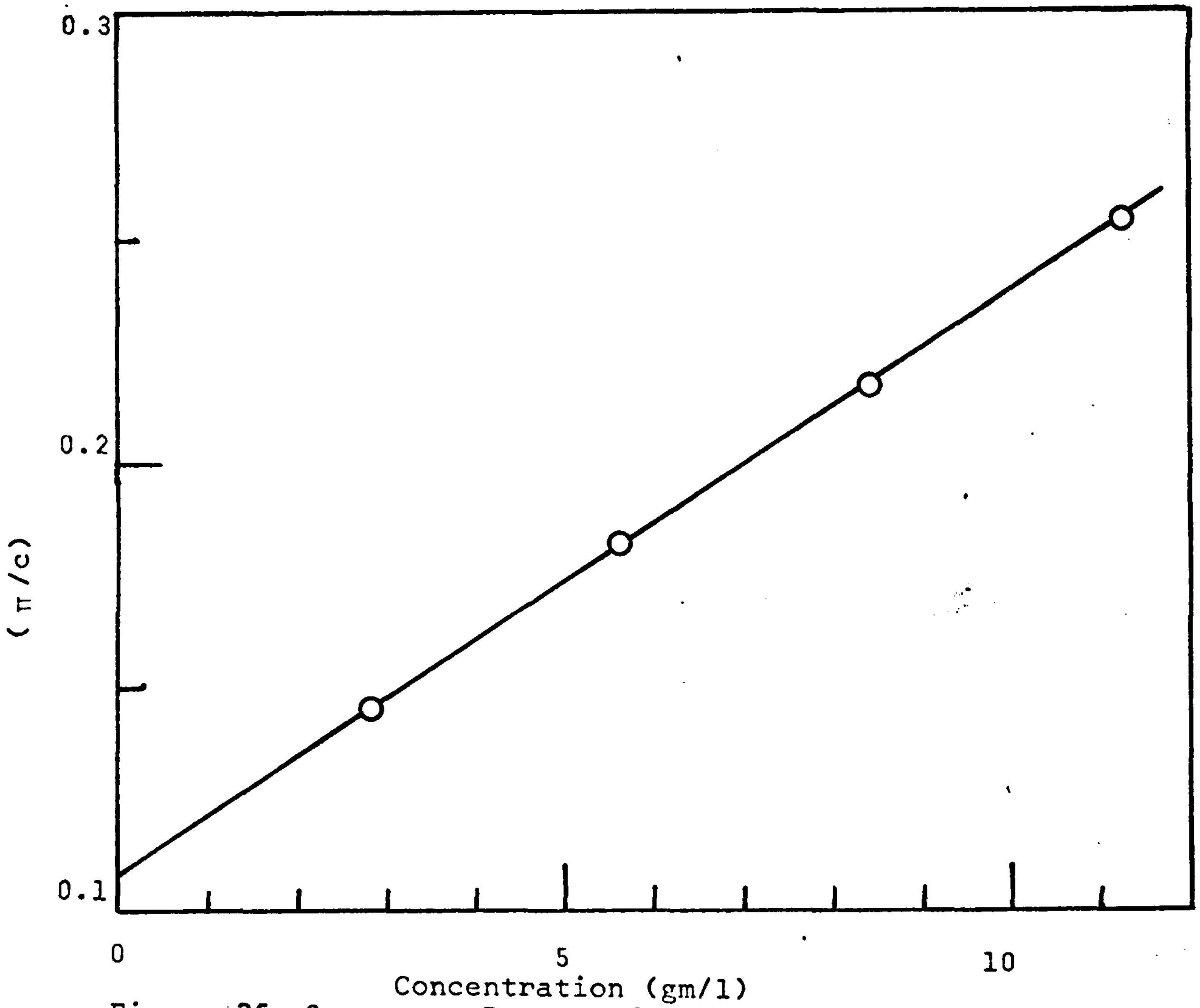

Figure 26: Osmometry Results for Sample IV-5 in Toluene at 37°C

E. Phase Equilibria Measurements

Phase equilibria were determined by cloud points after Schultz and Flory (33). Between four and six solutions of a given polymer sample were prepared in either Teflon lined screw cap test tubes or ground glass stoppered test tubes. The former were preferred since they were disposable and sealed tightly. The polymers were dissolved by heating in an oven overnight at a temperature higher than their critical temperature. Phase separation was detected by clouding of the polymer solution as the temperature was lowered below the polymer solution critical temperature. The temperature at which a scale held behind the test tube could no longer be read established the precipitation temperature. Cloud points could be detected to within $\pm$ 0.15 C and cooling rates of $1^{\circ}C$ to $3^{\circ}C$ per hour were used. A typical phase diagram is presented in Figure 27 .

Water baths were used for temperatures from $3^{\circ}C$ to $60^{\circ}C$, and silicone oil baths were used at higher temperatures. An acetone bath cooled by a pumped, externally chilled water-methanol mixture was used at temperatures below $3^{\circ}C$.

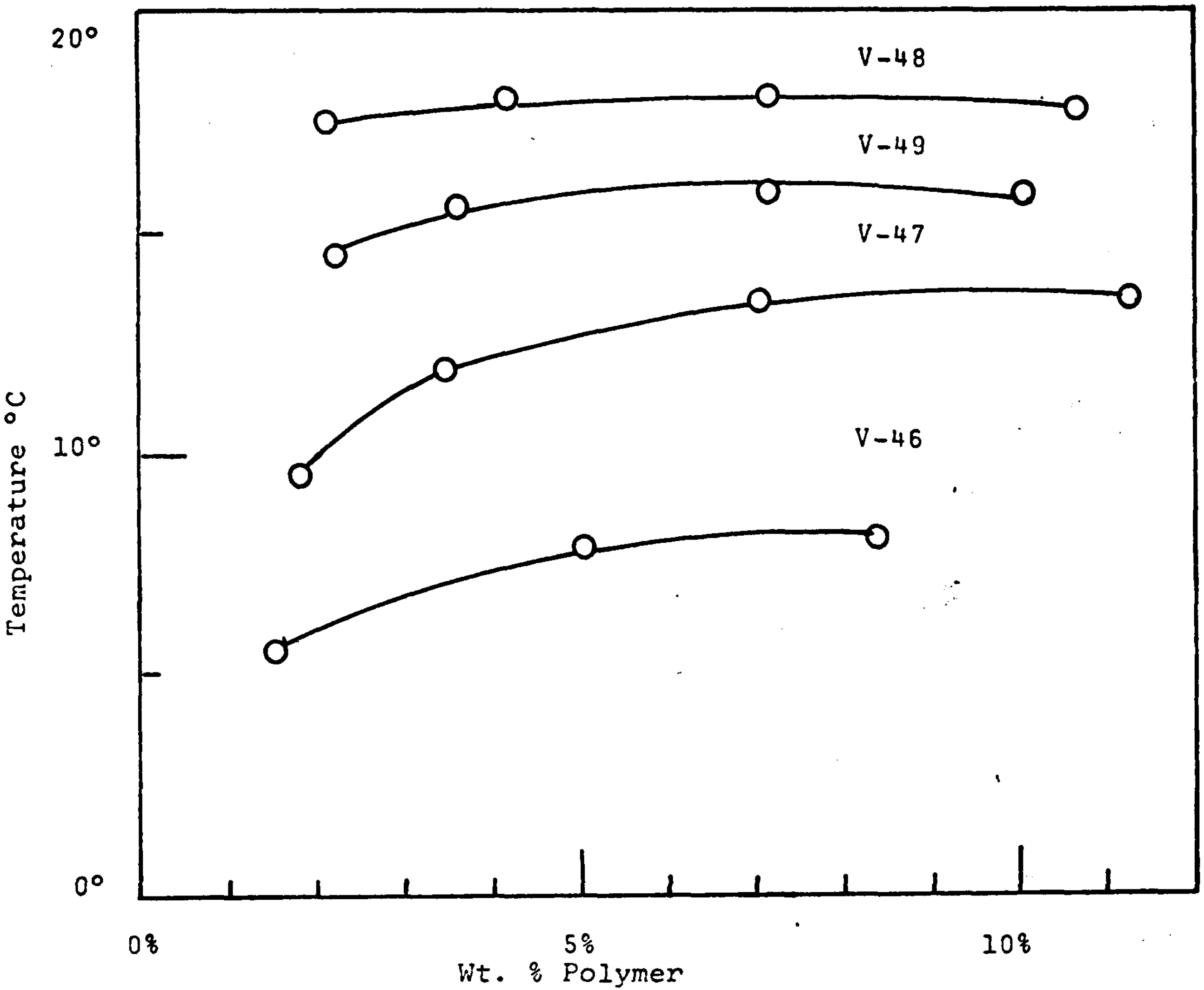

Figure 27: Phase Equilibria in Cyclohexane

[illegible] High-Pressure Osmometry

1. Construction

A high-pressure osmometer, similar to that of Daoust and Flory (73) was constructed at the City College. The osmometer was constructed from type 316 stainless steel and consisted of three parts; a head-A, a mid-section-B, and a base-C. The base contained the solvent chamber and a place for the plate which supports the membrane. The mid-section clamped the membrane firmly in place over the plate. The head contained a stirrer and formed a solution chamber when clamped in place. Viton O-Rings sealed the osmometer faces and a gland and packing nut with Teflon braid packing sealed the stirrer shaft. A valve incorporated into the head provided a solution reference level. As suggested by Daoust and Flory, a stirrer driven by a 2.8 rpm high torque motor was inserted in the solution chamber to prevent dilution of the solution near the membrane. The membrane plate was pitched to minimize membrane ballooning. A 10 inch long 1mm capillary tube with a 10/30 standard taper joint was used to monitor the movement of solvent. The ground-glass joint on the capillary tube was gasketed with a Teflon sleeve and secured with rubber bands.

The O-Ring grooves in the osmometer faces were cut too deeply to permit effective O-Ring seals. To correct this problem twisted Teflon tape, which deformed to fill the bottom of the O-Ring grooves, was used to reduce groove depth to give the O-Rings adequate compression. A 10 mil Teflon gasket was placed under the plate to aid in sealing the solvent chamber. This combination proved to be effective.

Leaks developed in some of the silver solder joints and a pin hole leak was detected in the solvent chamber. The Teflon gasket on the 10-30 jointed capillary tube leaked slightly. This was corrected by using a small amount of silicone high vacuum grease. To prevent contamination of the solvent, the solvent chamber was purged after each run. The existence of these leaks, which were unexpected, indicated that the osmometer had to be carefully leak tested prior to use.

Pressures below 20 psig were measured with mercury or water manometers. Pressures above 20 psig were measured with a Statham* Gold Cell transducer with a pressure adapter containing a 50 psig diaphragm. The transducer was powered

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* Statham Instruments, Inc., Los Angeles, California

by a Hewlett Packard model 6215A power supply. The transducer was calibrated with a dead-weight tester., A calibration chart for the appropriate pressure range is shown in Figure 28.

2. Osmometer Assembly

The solvent chamber in the base was filled with toluene after which the Teflon gasket and plate were inserted. Care was taken to insure the elimination of all bubbles from the solvent chamber. The membrane-conditioning schedule is described in Table 22. The final membrane treatment was done in the osmometer. Distortion occurs in the final step, which shrinks the membrane onto the plate and holds it firmly in place. The osmometer cavity above the plate was filled with 50 cc of 75 percent toluene - 25 percent acetone mixture. A 600W membrane was placed over the plate and held in place with a weight. Since the membranes were invisible in this solution, the weight prevented them from drifting about. The membrane was then carefully clamped in place with part B. Excess toluene-acetone solution was removed from the solution chamber, which was then filled with toluene. The solvent chamber was purged with toluene to remove any traces of acetone. Several hours were needed for the membrane to completely condition.

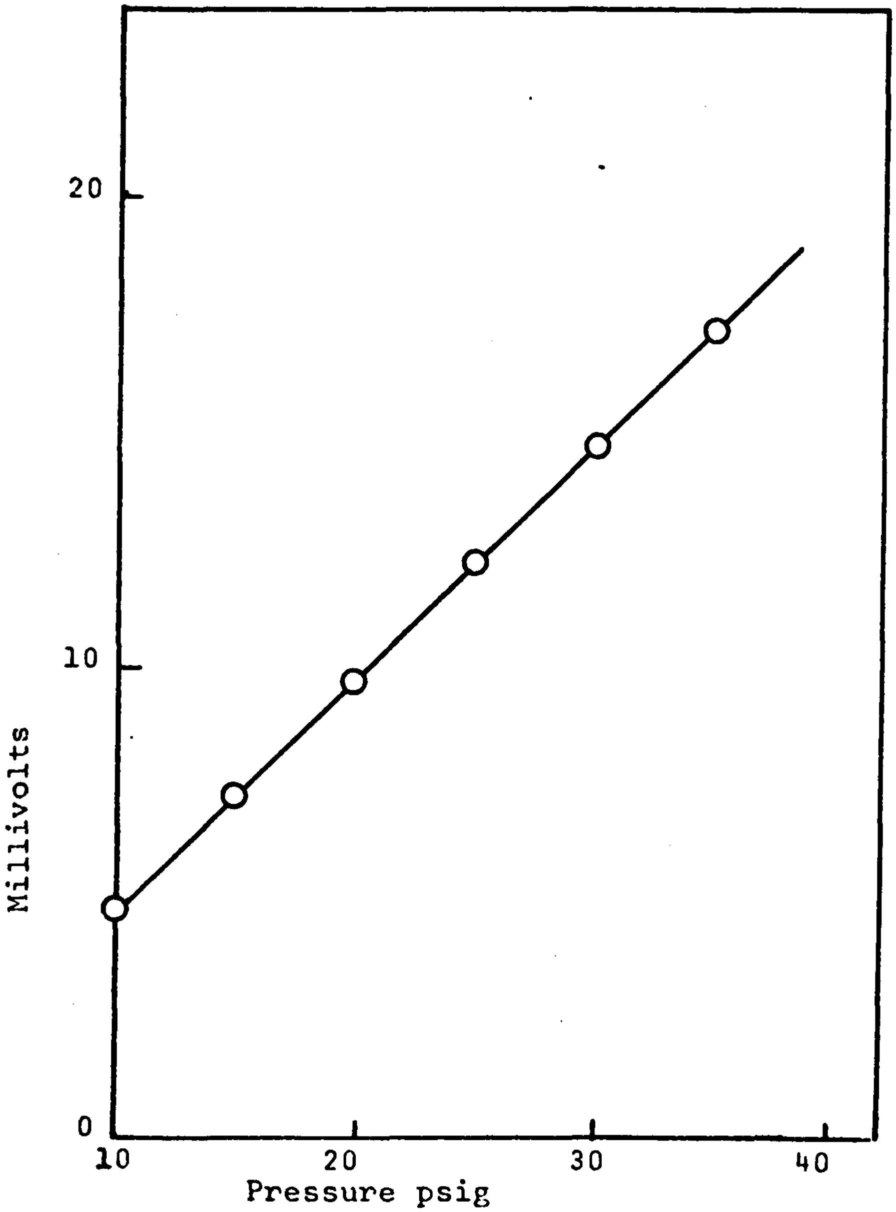

Figure 28: Transducer Calibration

The osmometer was then leak tested. A Teflon gasket was placed in the solution chamber under the lip of the head to prevent the membrane from being cut. The solution chamber was filled with toluene and the head was clamped in place. The capillary tube was then inserted in place and held there with rubber bands. The osmometer was thermostatted and a pressure equal to the head of liquid in the solvent chamber was applied. No motion in the capillary was noted when the two pressures were equal.

3. Operation

About 10 cc of solution were placed in the solution chamber. A Teflon gasket was inserted in the solution chamber to keep the membrane from being torn. The head was then clamped in place, and the capillary tube was inserted in place and secured with rubber bands. The osmometer was then placed in a thermostatted bath. The stirrer was attached and activated and the solution chamber was pressurized. It required one to two hours for the system to come to thermal equilibrium and for all membrane distortions to be eliminated. During this time pressures were applied to the solution to minimize motions of the solvent level. After this, the pressure was adjusted to give zero motion to the capillary level. Equilibrium was obtained when no motion in the capillary was observed for about one hour. The level of fluid in the capillary was measured with a cathetometer.

After equilibrium was attained, the osmometer was removed from the water bath and opened. A sample of polymer solution was evaporated to dryness to determine the solution concentration. The solution chamber was then cleaned. To clean the head, a 30 cc syringe was used to force toluene through the solution level valve and through the pressure port.

Table 22. Treatment Procedure for Type 600W Membranes*

50 Percent Water 50 Percent Alcohol 2 Hours	100 Percent Alcohol 8 Hours	50 Percent Alcohol 50 Percent Acetone 4 Hours
100 Percent Acetone 4 Hours	75 Percent Acetone 25 Percent Toluene 4 Hours	50 Percent Acetone 50 Percent Toluene 4 Hours
25 Percent Acetone 75 Percent Toluene 4 Hours	100 Percent Toluene 4 Hours	

* Arro Laboratories, Joliet, Illinois

4. Data Treatment

The Flory-Huggins constant was calculated from values of the osmotic pressure using

$$\chi = (1/v_2^2)\ ((-\Pi v_1^o/RT) - \ln(1-v_2) - (1-v_1^o/v_2^o)v_2) \qquad (60)$$

The osmotic pressure must be corrected for the head of fluid on the solvent.

Densities are required to calculate volume fractions. There is disagreement in the literature as to the density of polystyrene; some values are given in Table 23. Density is essentially constant at molecular weights greater than 30,000 (69). In any event, a change in polystyrene density from 1.04 to 1.08 gm/cm^3 reduces the Flory-Huggins parameter by only 3 percent. We measured the density of hot pressed pellets of polystyrene, poly (α-methyl styrene) and copolymer V-36 and obtained values of 1.06, 1.08 and 1.07 gm/cm^3 ± 1 percent respectively; these values were used in our calculations of χ.

Table 23. Density of Polystyrene

Source	T °C	ρ; gm/cm^3
M. Gordon and I. MacNab (70)	20	1.053
	40	1.048
G. S. Martin, S. S. Rogers and L. Mandelkern (71)	20	1.048
	37	1.041
	60	1.036
Polymer Handbook (67) and "Styrene" (68)	ambient	1.04-1.06
Flory and Schultz (33), Bawn et al. (65)	25	1.083
NBS PS 705	ambient	1.077
Partial Specific Volume (66)		
D. Goldwasser et al.	ambient	1.06

G. Solution Behavior in the Region of Molecular Overlap

Studies of the behavior of polymer solutions in the concentration region where molecular overlap occurs (1 percent or 2 percent to 10 percent by volume polymer) have been reported by only three groups of investigators. Daoust and Flory (73) found that χ for polyisobutylene dissolved in benzene and pentane, two poor solvents, varied smoothly with composition. Krigbaum and Carpenter (49) observed similar behavior for cyclohexane solutions of polystyrene. A modest minima in χ was observed for polyisobutylene dissolved in cyclohexane, a good solvent, by Daoust and Flory (73), but they suggested that this phenomena was caused by experimental error.

In order to explore the solution behavior in this region, χ was computed for the samples used in the high pressure osmometer and from the dilute solution, high speed osmometry measurements.* The results are tabluated in Appendix A-2 and are summarized in Table 24. Similar values of χ were observed for polystyrene and poly (α-methyl styrene) in

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* The relationship between SVC and the Flory-Huggins parameter χ is given by

$$(1/2 - \chi) = v_1^{o} A_2 / \rho^{2}_{\text{polymer}}$$

where A_2 has units of (mole-cm^3)/(gm)^2

dilute and moderately concentrated solutions. The modest difference in χ for the copolymer sample V-36 was probably caused by errors in the high speed osmometry results for this material. Examination of figure 8 shows that the SVC for sample V-36 is too small when compared to those of the other 50 percent styrene copolymers. A larger value of SVC would yield a smaller value of χ. Hence, χ appears to be a constant in the concentration range from very dilute to 25 percent by volume. Additional data would be needed to verify this observation.

The Flory-Huggins parameters were apparently constant in the concentration range of 0 percent to about 25 percent by volume polymer. Thus, the Flory-Huggins theory appears to represent solution behavior in moderately concentrated solutions and in dilute solutions. This suggests that molecular overlap may not strongly influence solution behavior in good solvents. The molecular interpretation of this finding is not clear. The transition from dilute to concentrated solution behavior may be smooth; the classification of solutions into dilute and concentrated types may be a requirement needed for analytical investigation but may have no real physical basis.

Table 24. Comparison of Solution Behavior in Dilute and Moderately Concentrated Solutions

Sample	χ	
	Dilute Solutions	Moderately Concentrated Solutions
PS III-9	0.418	0.413
PαMS IV-3	0.455	0.454
Copolymer V-36	0.439	0.416

H. Variation of the Flory-Huggins Parameter with Temperature

As originally formulated the enthalpy of mixing term $RT\chi n_1 v_2$ in the Flory-Huggins theory was written as $Bn_1 v_2$ where B equals a constant, characteristic of the differences in mer-solvent, mer-mer and solvent-solvent interaction energies. Hence, (χT) is a constant. This situation can be clarified via the fundamental thermodynamic relationship

$$(61) \qquad \partial(\Delta G_m/T)/\partial T = -\Delta H_m/T^2$$

If this equation is applied to the Flory-Huggins equation

$$(62) \qquad -(\partial(\Delta G_m/T)/\partial T) = Rn_1 v_2 (\partial\chi/\partial T)$$

or with equation

$$(63) \qquad \Delta H_m = -T^2 n_1 v_2 (\partial\chi/\partial T)$$

To maintain the original form of the equation for ΔH_m, it follows that

$$(64) \qquad \partial\chi/\partial T = -\chi/T$$

or equivalently

$$(65) \qquad (\chi T) = \text{constant}$$

I. Unperturbed Dimensions

1. Light Scattering Data

Unperturbed chaim dimensions are usually compared in terms of the ratio R = $(R_{\Theta}/M^{1/2}) / (R_{of}/M^{1/2})$, the ratio of the radius-of-gyration for that of an unperturbed chain to that of a freely-orienting tetrahedyl chain. Literature data for the molecular dimensions of polystyrene, poly-(α-methyl styrene) and poly (p-methyl styrene) are presented in Table 25. Poly (α-methyl styrene) and poly (p-methyl styrene) have about the same values. The greater value of R for poly (p-methyl styrene) compared to polystyrene could be attributed to the greater volume of the paraphenyl group. The greater expansion of poly (α-methyl styrene) compared to polystyrene could be attributed to chain stiffness, mer-volume or a combination of the two. Conversely, the value of R is not particularly sensitive to polymer structure, as it varies only from 1.61 to 2.72 for polymers as different as polypropylene and polyacrylamide, respectively (51,72).

2. Intrinsic Viscosity Studies

Some literature values of K_{Θ} and R computed from are given in Table 26. The values of R computed from light scattering and K_{Θ} correspond for polystyrene but not for poly (α-methyl styrene). No comparison is possible for poly (p-methyl styrene). This discrepancy may be attributable to experimental error or a weakness in the theory correlating intrinsic viscosity with chain dimensions.

3. Experimental Results

Stockmayer-Fixman-Kurata (SFK) plots for poly (α-methyl styrene) and a 24 weight percent styrene copolymer are shown in Figures 29 and 30 and K_Θ's derived from them are presented in Table 26. Some literature values of K_Θ obtained from intrinsic viscosity studies are also tabulated. K_Θ obtained for poly (α-methyl styrene) is in good agreement with literature values. K_Θ for our copolymer is about the same as that for polystyrene and poly (α-methyl styrene).

4. Discussion

SFK plots require values of $\bar{M}_w$, which were not measured. Since the copolymers had $(\bar{M}_v/\bar{M}_n)$ ratios of 1.0 - 1.6, SFK plots were made only for the 24 weight percent styrene copolymer because this copolymer series had the narrowest molecular weight distributions. Intrinsic viscosity molecular weights were used as estimates of $\bar{M}_w$.

The results cited here and those in the literature indicate that unperturbed chain dimensions are not sensitive to chain structure or stiffness, whereas both are more strongly manifested in T_g. The error in measurement is as large as the difference in K_Θ between polystyrene and poly (α-methyl styrene). No useful information could be obtained from this aspect of our work; hence, these studies were discontinued.

Table 25. Molecular Dimensions from Light Scattering Data

Material	Temp. C	Solvent	$(R_{\Theta}/M^{1/2})$ (a)	$(R_{of}/M^{1/2})$ (a,c)	R (b)	Source
PS	34	cyclohexane	690	302	2.28	Polymer Handbook (67)
PS	35	cyclohexane	730	302	2.42	Polymer Handbook
PS	35	cyclohexane	670	302	2.22	Polymer Handbook
PS	35	cyclohexane	705	302	2.33	Polymer Handbook
PS	34.8 15.0	cyclohexane decalin	675	302	2.24	J. C. Berry (54,55)

Molecular Dimensions from Light Scattering Data (continued)

Material	Temp. C	Solvent	$(R_\Theta/M^{1/2})$ (a)	$(R_{of}/M^{1/2})$ (a,b)	R (d)	Source
PpMS	16.4	diethyl succinate	714	284	2.52	G. Tanaka et al. (52)
PpMS (c)	16.4	diethyl succinate	680	284	2.39	G. Tanaka et al. (52)
PαMS	34.5	cyclohexane	711	284	2.50	T. Kato et al. (62)

(a) Angstroms $\cdot 10^{-3}$

(b) $R = (R_\Theta/M^{1/2})/(R_{of}/M^{1/2})$

(c) Corrected for polydispersity

(d) $(R_{of}/M^{1/2}) = 3.08/(\text{Degree of Polymerization})^{1/2}$;(Angstroms)

Table 26. Molecular Dimensions from Intrinsic Viscosities

Material	$K_\Theta \cdot 10^{-5}$	$(R_\Theta/M^{1/2})$ (a,d)	$(R_{of}/M^{1/2})$ (c,d)	R (b)	Solvent	Temp.C	Source
PS	83	661	302	2.19	cyclohexane toluene	SFK plot	Papazian (56)
PS	82	658	302	2.18	cyclohexane	34.0	Krigbaum and Flory (77)
PS	84 ± 2	664	302	2.20	cyclohexane	34.5	Altares et al. (76)
PαMS	73	634	284	2.23	cyclohexane	34.5	T. Kato et al. (62,64)
PαMS	70.6	627	284	2.20	trans-decalin.	9.5	T. Kato et al. (62,64)

Molecular Dimensions from Intrinsic Viscosities (continued)

Material	$K_\Theta \cdot 10^{-5}$	$(R_\Theta/M^{1/2})$ (a,d)	$(R_{of}/M^{1/2})$ (c,d)	R (b)	Solvent	Temp. C	Source
PαMS	74 ± 10	636	284	2.24	benzene + methanol	30	Polymer Handbook (67)
PαMS	72 ± 6	631	284	2.22	cyclo-hexane toluene	SFK plot	Goldwasser and Williams
24 Percent by Weight Styrene S-αMS copolymer	73 ± 6	634	292	2.17	cyclo-hexane toluene	SFK plot	Goldwasser and Williams

(a) Computed from Flory-Fox Equation $K = \Phi(R_\Theta/M^{1/2})^3$, $\Phi = 2.87\,(10)^{21}$

(b) $R = (R_\Theta/M^{1/2})/(R_{of}/M^{1/2})$

(c) $(R_{of}/M^{1/2}) = 3.08/(\text{Degree of Polymerization})^{1/2}$; Angstroms

(d) Angstroms $\cdot 10^{-3}$

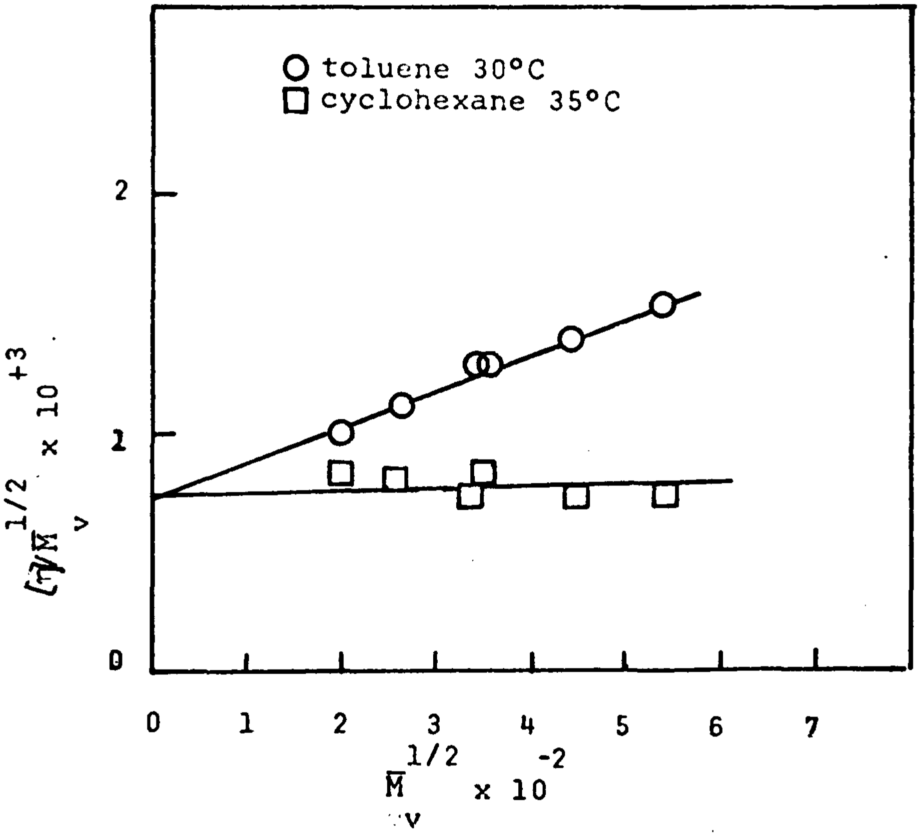

Figure 29: Stockmayer Fixman Kurata Plot for Poly(α -methyl styrene)

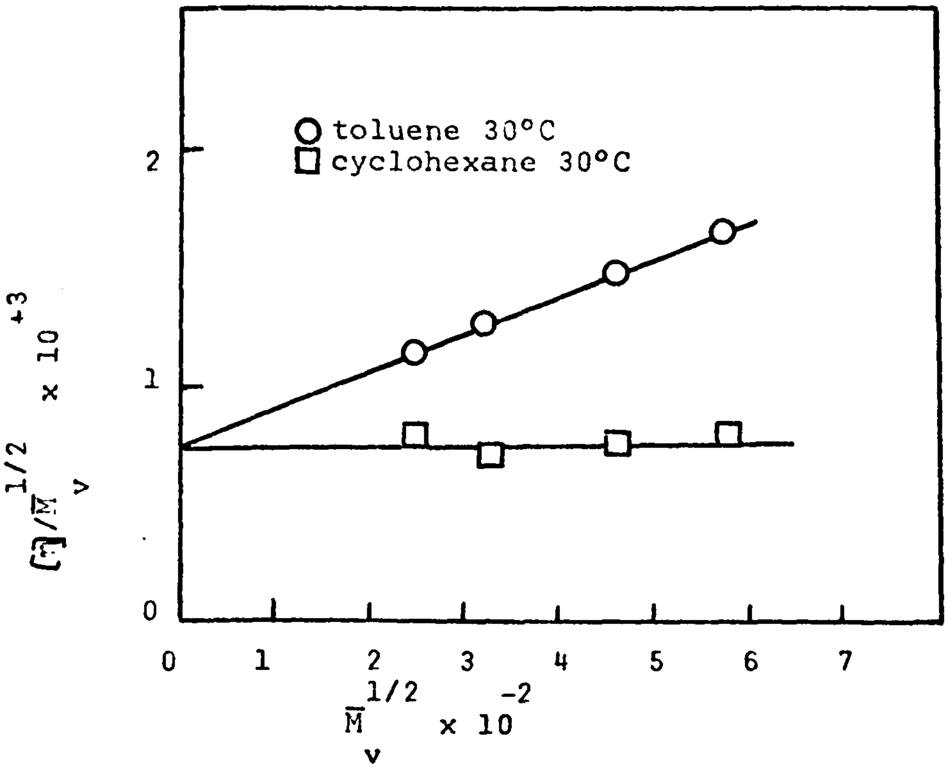

Figure 30 : Stockmayer Fixman Kurata Plot for the 24 Wt. % Styrene Copolymers

REFERENCES

1. P. J. Flory, J. Chem. Phys., 10, 51 (1942); 9, 660 (1941)
2. M. L. Huggins, Ann. N. Y. Acad. Sci., 43, 1 (1942)
3. M. L. Huggins, J. Chem. Phys., 9, 440 (1941)
4. P. J. Flory, R. A. Orwell and A. Vrij., J. Amer. Chem. Soc. 86, 3507 (1964); 86, 3515 (1964)
5. P. J. Flory., J. Amer. Chem. Soc., 87, 1833 (1965)
6. G. Gee and L. Treloar, Trans. Faraday Soc., 38, 147 (1942)
7. G. Gee and W. J. C. Orr, Trans. Faraday Soc., 42, 507, (1946)
8. B. E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64, 2035 (1968); 2053 (1968); 2061 (1968);2066 (1968)
9. I. Priggogine, N. Trappeniers and V. Mathot, Disc. Faraday Soc., 15, 93 (1953)
10. I. Priggogine, N. Trappeniers and V. Mathot, J. Chem. Phys., 21, 559 (1953)
11. I. Prigogine, A. Bellmans and C. Narr-Colin, Disc. Faraday Soc., 26, 751 (1957)
12. L. Tonks, Phys. Rev., 50, 955 (1936)

13. S. H. Maron, J. Polymer Sci., 38, 329 (1959)

14. S. H. Maron and N. Nakajima, J. Polymer Sci., 40, 59 (1959); 42, 327 (1960); 44, 333, (1960); 46, 157, 169 (1960); 47, 587 (1961)

15. S. H. Maron and C. Daniels, J. Macromolecular Sci., Phys., 2, 743 (1968); 2, 769 (1968)

16. W. R. Krigbaum and D. O. Geymer, J. Amer. Chem. Soc., 81, 1859 (1959)

17. J. F. Heil and J. M. Prausnitz, A. I. Ch. E. Jour., 12, 678 (1966)

18. G. M. Wilson, J. Amer. Chem. Soc., 86, 127 (1964)

19. R. V. Orye and J. M. Prausnitz, Ind. and Eng. Chem., 57, 18 (1965)

20. H. Renon and J. M. Prausnitz, A. I. Ch. E. Jour., 14, 135 (1968)

21. J. Hildebrand, J. Amer. Chem. Soc., 38, 1452 (1916)

22. G. Scatchard, Chem. Rev., 8, 321 (1931)

23. J. Hildebrand and R. Scott, The Solubility of Electrolytes. 3rd edition, Reinhold, New York, 1950.

24. E. B. Bagley, T. P. Nelson, J. W. Barlow and S. A. Chen, Ind. and Eng. Chem. Fundamentals, 9, 93 (1970)

25. A. Bundi and D. J. Simkin, A. I. Ch. E. Jour., 3, 473 (1957)

26. R. F. Blanks and J. M. Prausnitz, Ind. and Eng. Chem., Fundamentals, 3, 1 (1964)

27. C. M. Hansen, J. Paint Tech., 39, 104, 505, 511 (1967)

28. W. Gordy, J. Chem. Phys., 8, 170 (1940); 9, 204, 215 (1941)

29. E. R. Liebermann, Official Digest, 34, 30 (1962)

30. H. Burrell, Preprints from ACS Division of Organic Coatings and Plastic Chemistry, 28, 682 (1968)

31. J. D. Crowley, G. S. Teague and J. W. Lowe, J. Paint Tech., 38, 269 (1966), 39, 19 (1967)

32. P. A. Small, J. Appl. Chem., 3, 71 (1953)

33. A. R. Schultz and P. J. Flory, J. Amer. Chem. Soc., 74, 4760 (1952)

34. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953

35. R. Konigsveld and A. J. Staverman, J. Poly. Sci., A-2, 6, 305, 325, 349, 367, 383 (1968)

36. R. Konigsveld, L. A. Leinjens and A. R. Schultz, J. Poly. Sci., A-2, 8, 1261 (1970)

37. T. Kotaka, Y. Murakami and H. Inagaki, J. Phys. Chem., 72, 829 (1968)

38. H. Matsuda, K. Yamano and H. Inagaki, J. Poly. Sci., 7, 609 (1969)

39. G. E. Molau, 'Solution Behavior in Block and Graft Copolymers' in Characterization of Macromelecular Structure, Publication 1573, National Academy of Sciences (1968)

40. W. S. Stockmayer, L. D. Moore Jr., M. Fixman and B. N. Epstein, J. Poly. Sci., 16, 517 (1955)

41. Y. Shimura, J. Poly. Sci., Pt. A-2, 4, 423 (1966)

42. A. Kotera, T. Saito, Y. Wanatabe and M. Oharna, Makromol. Chemie, 87, 195 (1955)

43. B. H. Zimm, J. Chem. Phys., 14, 164 (1946)

44. W. G. McMillan and J. E. Mayer, J. Chem. Phys., 13, 276 (194

45. T. H. Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley Inc., Reading, Mass., 1960

46. J. G. Kirkwood and J. R. Riseman, J. Chem. Phys., 16, 565 (1948)

47. P.J. Flory, J. Chem. Phys., 17, 303 (1949)

48. P. J. Flory and T. J. Fox, J. Amer. Chem. Soc., 73, 1904 (19

49. W. R. Krigbaum and D. K. Carpenter, J. Chem. Phys., 59, 1166 (1955)

50. W. H. Stockmayer and M. L. Fixman, J. Poly. Sci., C, No. 1, 137 (1963)

51. M. Kurata and W. H. Stockmayer, Fortschr. Hochpolymer Forsch., 3, 196 (1963)

52. G. Tanaka, S. Imai and H. Yamakawa, J. Chem. Phys., 52, 2639 (1970)

53. Y. Noguchi, A. Aoki, G. Tanaka and H. Yamakawa, J. Chem. Phys., 57, 2651 (1970)

54. G. C. Berry, J. Amer. Chem. Soc., 44, 4550 (1966)

55. G. C. Berry, J. Chem. Phys., 46, 1338 (1967)

56. L. A. Papazian, Polymer, 12, 399 (1969)

57. F. Wenger, J. Amer. Chem. Soc., 82, 4281 (1960)

58. F. Wenger, Makromol. Chemie, 36, 200 (1960)

59. A. F. Sirrianni, C. J. Worsfold and S. Bywater, Trans. Far. Soc., 55, 2124 (1959)

60. R. W. Lenz, Organic Chemistry of Synthetic High Polymers, Interscience, New York, 1967

61. S. Brownstein, S. Bywater and D. J. Worsfold, Makromol. Chemie, 48, 127 (1961)

62. T. Kato, K. Miyaso, I. Noda, T. Fujimoto and M. Nagasawa, Macromolecules, 3, 777 (1970)

63. A. Nishioka and Y. Kato, Polymer Letters, 1, 633 (1963)

64. K. Noda, M. Mizutani, T. Fujimoto and M. Nagasawa, Macromolecules, 3, 787 (1970)

65. C. E. H. Bawn, R. F. J. Freeman and A. R. Kamalidden, Trans. Far. Soc., 46, 677 (1950)

66. R. F. Boyer, 'Styrene, Physical Properties and Thermal Characteristics', in Encyclopedia of Polymer Science and Technology, Interscience, New York, 1971

67. J. Brandrup and E. H. Immergut, Polymer Handbook, Wiley and Sons, New York, 1964

68. R. H. Boundy, Styrene, Reinhold Co., New York, 1952

69. T. G. Fox and P. J. Flory, J. Appl. Phys., 21, 581 (1950)

70. M. Gordon and I. A. Macnab, Trans. Far. Soc., 49, 31 (1953)

71. G. M. Martin, S. S. Rogers and L. Mandelkern, J. Poly. Sci. 20, 579 (1956)

72. H. Morawetz, Macromolecules in Solution, Interscience Publishers Inc., New York, 1965

73. P. J. Flory and H. Daoust, J. Poly. Sci., 25, 429 (1957)

74. L. M. Kotliar, J. Poly. Sci. 55, 71 (1961)

75. J. M. G. Cowie and S. Bywater, J. Poly. Sci., A-2, 6, 499 (1968)

76. T. Altares Jr., D. P. Wyman and U. R. Allen, J. Poly. Sci. A-2, 2, 4533 (1964)

77. W. R. Krigbaum and P. J. Flory, J. Poly. Sci., 11, 37 (1953)

78. K. L. Hoy, B. A. Price and R. A. Martin, 'Tables of Solubility Parameters', Union Carbide Corp. (1965)

79. C. W. McCall and W. P. Slichter, New Methods of Polymer Characterization, B. Ke - Editor, Interscience Publishers Inc., New York, 1964

80. T. Kotaka, T. Tanaka, H. Ohuma, Y. Murakami and H. Inagaki, Polymer Jour. 1, 245, (1970)

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