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City University of New York

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EFFECTS OF DISSOLVED ELASTOMER ON KINETICS OF LOW CONVERSION POLYMERIZATION

by

SIRISOMA WANIGATUNGA

A dissertation submitted to the graduate faculty in chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, the City University of New York.

1985

This manuscript has been read and accepted for the graduate faculty in chemistry in satisfaction of the dissertation requirment for the Degree of Doctor of Philosophy.

9-18-84 — George Odian

Date — Chairman of Examining Committe

9/18/84 — [signature]

Date — Executive Officer

Arthur Woodward

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City University of New York

ACKNOWLEDGEMENTS

I am grateful to my parents Mr.and Mrs.M.Wanigatunga for their constant encouragement and support for my education including this work.

I am more than grateful to Dr.George Odian for his valuble guidence and support without which this work should have been impossible.

My sincere thanks to Dr.Nan Loh Yang, Dr.Arther.E.Woodward and Dr.Fred Naider for their help in understanding of polymer science.I also like to thank Dr.David.C.Locke for his advice especially during my first two years of graduate school.

I gratefully acknowledge the support given to me for graduate study by the College of Staten Island in the form of teaching assistantships.

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A. INTRODUCTION

A.1 General

Increasing attention is being paid to the manufacture of polymeric blends and alloys(1,2). Blends are prepared by physically mixing different polymers whereas alloys are prepared by generating chemical links between polymers. A typical alloy,the toughened plastic,is prepared by polymerising the monomer in the presence of a dissolved rubber. An example is the preparation of toughened polystyrene by polymerising styrene in the presence of dissolved polybutadiene. Polymerization causes grafting between the two polymers and hence the chemically bound polymers constitute an alloy which has better properties than either of the original polymers. The toughened polystyrene,for instance,has higher impact strength than pure polystyrene toward a falling load,and this is due to the presence of the rubber which can absorb higher amounts of dissipated energy.

In addition to high impact polystyrene, one could visualise an infinite number of polymeric alloys based on different combinations of polymers. By choosing the right combinations many useful alloys with desired properties could be obtained.

How would the dissolution of a polymer affect the kinetics and mechanism of monomer polymerization? The question is important not only in understanding the fundamentals of polymerization but also in better designing reactor vessels and other equipment used to prepare such alloys. In a typical alloying system,for instance, in the preparation of high impact polystyrene, styrene(St) is polymerised in the presence of 5-10 percent dissolved rubber. Benzoyl peroxide(BPO) is used as the initiator and the polymerization is carried to very high conversions. The system remains homogeneous until a particular conversion dependent on the rubber concentration is reached and then becomes heterogeneous.

One can visualize the following effects of the dissolved polymer:

1. Chain transfer onto dissolved rubber or any kind of a reaction between the two polymers
2. Grafting onto rubber
3. Crosslinking of the rubber
4. Increasing medium viscosity
5. Making medium a poorer solvent
6. Chain entanglement
7. Phase separation

A.2 Scope of the Problem

The effects of these factors on various stages could be different. In the absence of polydiene, styrene polymerization constitutes three stages(3,4).

Figure 1 shows that stage 1 involves a constant rate with conversion, stage two an increasing rate with conversion and stage three having a constant rate with conversion. Investigation of the above effects in all three stages is challenging but difficult due to the phase separation at higher coversion.

A.3 Problem

We have investigated effects 1-6 above in stage 1 of the polymerization under homogeneous conditions. A complete understanding of stage 1 is necessary before attempting to investigate more complex stages 2 and 3. All the kinetic studies carried out using the styrene-rubber systems were limited to this region but even here the effects of rubber have not been fully understood yet. We selected a suitable rubber concentration to make the system homogeneous so that complications due to phase separation could be avoided.

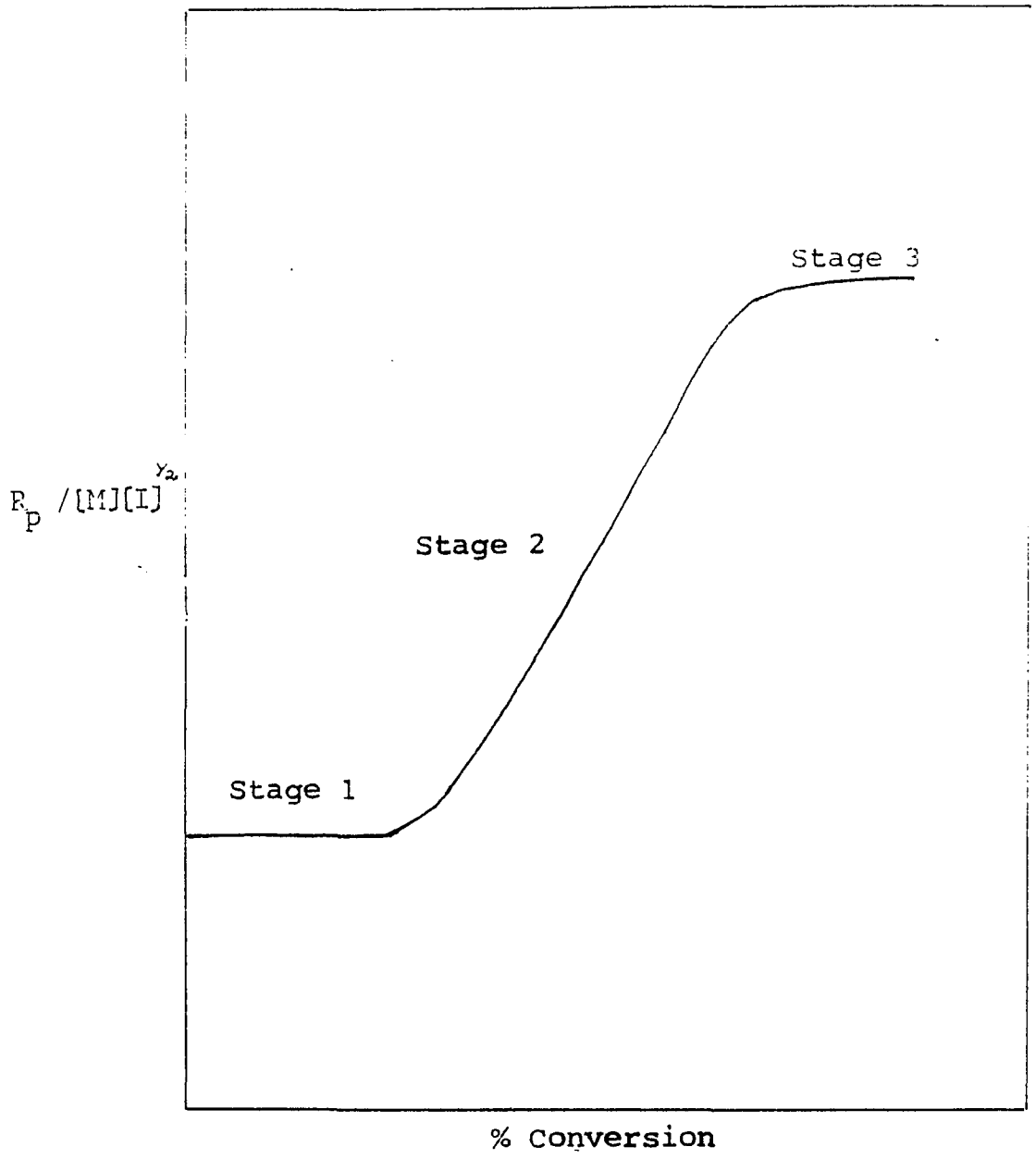


Fig. 1 Effect of Conversion on Polymerization Rate

A.4 Background

Cameron,G.G.et al(5,6,7) investigated stage one of benzoyl peroxide initiated styrene polymerization in toluene with dissolved polydienes. The system was kept homogeneous. The resultant crude product mixture was first extracted with methyl ethyl ketone to remove homopolystyrene. The remainder was then extracted with petroleum ether to remove unreacted rubber. The extractions were repeated until no more polymer was detected in the extracts. The extracted polymers were checked to be pure using IR. The remainder of the mixture was then dissolved in toluene and reprecipitated. This precipitate was assumed to be the graft polymer. The fraction which did not dissolve in any of the solvents was assumed to be the crosslinked mass. Using the weights of homo and graft polystyrenes the rates of polymerizations were calculated and the rates were investigated with different monomer and initiator concentrations.

They used the following reaction scheme to explain the reaction mechanism.

$$I_2 \xrightarrow{k_d} 2I^{\cdot}$$

$$I^{\cdot} + M \xrightarrow{k_{i1}} IM^{\cdot}$$

$$I^{\cdot} + R \xrightarrow{k_{i2}} R^{\cdot}$$

$$R^{\cdot} + M \xrightarrow{k_{i3}} RM^{\cdot}$$

$$IM^{\cdot} + M \xrightarrow{k_p} IM_2^{\cdot} \xrightarrow{k_p} IM_n^{\cdot}$$

$$RM^{\cdot} + M \xrightarrow{k_p} RM_2^{\cdot} \xrightarrow{k_p} RM_n^{\cdot}$$

$$IM_n^{\cdot} + IM_m^{\cdot} \xrightarrow{k_t} IM_{n+m}I \qquad \text{homopolymer}$$

$$RM_n^{\cdot} + IM_m^{\cdot} \xrightarrow{k_t} RM_{n+m}I \qquad \text{graft polymer}$$

$$RM_n^{\cdot} + RM_m^{\cdot} \xrightarrow{k_t} RM_{n+m}R \qquad \text{cross linked mass}$$

where

$[I]$ = (1.24 - 12.07) 10**-3 moles/l

$[M]$ = (0.75 - 5.03) moles/l

$[R]$ = (0.25 - 0.50) monomer moles/l

Using this scheme they derived the following expression for the rate of consumption of styrene, R_p.

$$R_p = k\,[M]\left(2fk_d[I]/k_t\right)^{1/2}$$

This expression agreed with their observations that

$$R_p \propto [M] \quad \text{and} \quad R_p \propto [I]^{1/2}$$

They did not investigate the effects of rubber on rate constants and other transfer constants. They observed that $1/M_n$ of homo polystyrene is directly proportional to $[M]$. Even though the plot of $1/M_n$ versus $[I]^{1/2}$ is claimed to be linear, some non-linearity is apparent in that the slope of the graph increases with increasing initiator concentration. This could be due to some changes in the rate constants: k_t, k_p, k_d or f with increasing initiator concentration or it may be

that the transfer to rubber increased with increasing initiator concentration and this caused the effect.

A.4.1 Chain Transfer

In Cameron's Scheme the following chain transfer step was omitted.

$IM_n^{\cdot} + R$ --------- $IM_n + R^{\cdot}$

The authors did not investigate the variation of M_n of homopolystyrene with rubber concentration to determine whether tranfer to rubber is present,instead they used an indirect argument based on other experimental evidence to support absence of transfer.

Their experimental evidence was that graft polymer and the crosslinked mass was not produced when azo-bis-isobutyronitrile(AIBN) was used as the initiator but they were produced when benzoyl peroxide was used. similar observations have been made by previous workers(20). Also when polydienes were heated in the presence of these two initiators crosslinking took place only when benzoyl peroxide was used(20). These observations have been attributed to the inability of azo-bis-isobutyronitrile to abstract hydrogens from hydrocarbons. There is evidence to support this contention,for instance, when

azo-bis-isobutyronitrile is heated with toluene, the initiator does not abstract hydrogens from toluene(20). We did not find any explanation for this effect in the literature. Either the steric effects due to three surrounding methyl groups or the less electronegative nitrogen atom in azo-bis-isobutyronitrile may be responsible.

The following argument was used by Cameron to conclude that chain transfer is absent. For the graft polymer to be formed the rubber radicals have to be formed. Rubber radicals could be formed only through abstraction of hydrogens by the initiator or the growing polystyrene radicals. Since the graft polymer is not formed with azo-bis-isobutyronitrile both these mechanisms are absent, i.e.,there is no chain transfer onto rubber. Since transfer is absent when azo-bis-isobutyronitrile is used, it will be absent when benzoyl peroxide is used. This is reasonable considering the fact that in both it is the polystyryl radical which is involved in transfer.

But isn't it possible that in both cases chain tranfer is present but grafting does not take place due to the inactivity of the resulting polyallylic radical? A study carried out by Scanlan(8) shows that polystyrene did in fact transfer onto a model compound of rubber, namely

dihydromyrecene(DHM), as shown in Figure 2.

This happened with both initiators. On the contrary, if chain transfer is absent with rubber it would be indicative of some polymeric effects of rubber that prevent chain transfer. For instance the viscosity or the medium effect of rubber might be responsible.

A.4.2 Effects of Viscosity and Medium

Also there is confusion about the added rubber on the termination rate constant. Rosen et al(9) investigated styrene polymerization in the presence of dissolved polybutadiene. They compared the rate of styrene polymerization with dissolved rubber to that without rubber and observed that the relative rate decreases with increasing rubber concentration. The decrease was higher for benzoyl peroxide initiated polymerization than for AIBN initiated polymerization. They carried out induction time experiments with 2,2-diphenyl 1-picrylhydracyl(DPPH) to check whether the reductions were due to changes in initiator decomposition constant, k_d , or initiator efficiency, f,and concluded that k_d and f did not change by the introduction of rubber. They attributed the reductions to increase in k_t and concluded that the dissolved polymer makes the medium a poorer solvent for the growing polymer

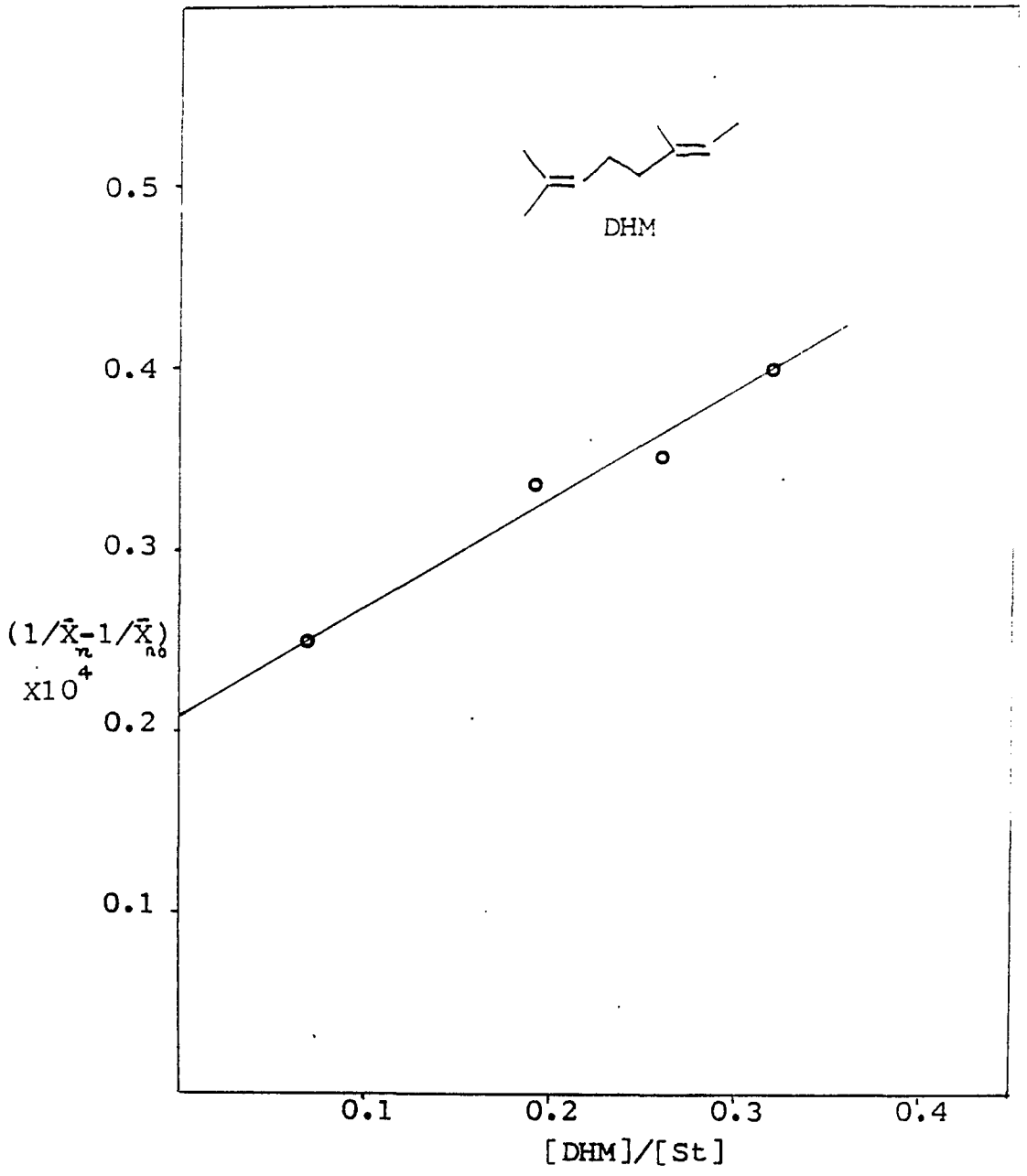


Fig 2 Plot of $(1/\bar{X}_n - 1/\bar{X}_{n0})$ vs [DHM]/[St] for Styrene Polymerization, with dissolved DHM, using BPO at 60°c.

chains,reduces their overall coil dimensions and enhances their rate of diffusion together for termination. They also state that the rate reduction or the increase in k_t is a medium effect rather than a viscosity effect and that there was no correlation between the rate reduction and the viscosity.

On the other hand Brooks et al(10) favor correlation of k_t with viscosity and volume fraction of dissolved polymer rather than with the goodness of the medium. They also used rates for their investigation. Using the rates k_t's were calculated and they were plotted against viscosity of the medium and the volume fraction of the dissolved polymer. They used styrene polymerization but polystyrene was dissolved instead of rubber. They also used methyl methacrylate polymerization with dissolved polystyrene. They did not come to any specific conclusions about the termination process, but suggested that there can be more than one termination constant in the system and also there is a possibility for primary termination.

Even in the absence of a second dissolved polymer,an experimentally verifiable expression for the quantification of the termination rate constant for low conversion polymerization has not been derived in the past. The

termination rate constant was assumed to be a constant in this region. However recent studies with methyl methacrylate polymerization(11,12) have proved otherwise. These studies indicate that k_t is indeed dependent on average chain length of the polymer and the type of solvent.

Many other investigations into the termination in stage 2 of polymerization indicate that the termination constant in vinyl polymerisation is dependent on the viscosity of the medium, the solvent-polymer interactions, the average chain length of the polymer, the excluded volume effect and also on the chain expansion factor(13,14,15,16,17). Therefore we see a necessity to evoke an experimentally verifiable equation to represent vinyl polymerization with and without a dissolved polymer.

A.4.3 Our Approach

In order to investigate the above mentioned effects of dissolved rubber and to quantify those effects, we initiated a molecular weight study of homopolystyrene extracted from the product mixture obtained after polymerization. A molecular weight study would enable us to obtain direct evidence regarding chain transfer and to use an independent experimental method to verify the contradictory observations of Rosen and Cameron who used rates to obtain their results.

(The rates used were the initial rates of styrene consumption. While Rosen et al used dialatometry, Cameron et al used weights of total polymeric mixture obtained after polymerization to calculate the rates. The two methods could lead to different errors and these differences may have caused the differences in their observed rates).

We used polyisoprene as the rubber because previous chain transfer studies had been carried out with a model compound of polyisoprene. Styrene conversion was kept at thirteen percent in order to enhance the effects yet keeping the system homogeneous. Rubber concentration was kept below four per cent so as to keep the system homogeneous. Both benzoyl peroxide and azo-bis-isobutyronitrile were used as initiators in order to isolate the effects of grafting and crosslinking on polymerization.

B EXPERIMENTAL

B.1 Materials

Dry styrene was prepared as follows. Commercially available styrene was washed three times with ten per cent aqueous sodium hydroxide to remove inhibitor, then washed three times with water, predried over anhydrous calcium chloride and dried over calcium hydride for a week. It was then vacuum distilled. Toluene was dried in the same manner

and vacuum distilled. Both styrene and toluene were pure as checked by the Hewlett Packard F and M Scientific 5750 Research Gas Chromatograph using a 5'x1/4" diethyl glycol column and keeping inlet at 250°C and oven at 100°C.

Benzoyl peroxide and azo-bis-isobutyronitrile were purified by recrystallisation from anhydrous methanol(18).

Cis-1,4-polyisoprene(Natsyn 2,200)obtained as a gift from Goodyear Chemical Company contained 98 percent cis-1,4 units. It was purified as follows. Rubber(15g) was cut into small pieces and dissolved in 1500ml of toluene for 45 hours. The solution was ultracentrifuged in a Sorvall super speed RC 2-D Ultracentrifuge at 500 r.p.m. for thirty minutes to remove gel. The supernatant solution was filtered with a standard filter paper under vacuum. The filtrate was then added dropwise into 3750ml of absolute ethanol containing 0.2 per cent antioxidant. The precipitated rubber was washed with absolute ethanol,blotted with filter paper and dried under vacuum at room temperature for 24 hours(19). The number average molecular weight was determined using a Hewlett Packard Mecrolab Model 501 High Speed Membrane Osmometer with toluene at 30° C. The molecular weights were confirmed using Water Associates Model 200 Gel Permeation Chromatograph with toluene under the following conditions:

Columns used	(500,8.5x10**3,10**5,10**6 A)
Flow rate	1ml/min
Degasser temperature	92°C
Inlet	70°C
Oven	82°C
Syphon	52°C
Refractometer	
Base plate	80°C
Heat exchanger	30°C
Span selector	at 4x

Osmometry gave the following value.

$$M_n = (6.68 + .03)10^{**5}$$

Gel Permeation Chromatography gave

$$M_n = 6.95x10^{**5} \qquad M_w = 9.02x10^{**5}$$

The difference between the two values for M_n is less than 5%.

The model compounds, Trans-Pentene and 2-Methyl-2 Pentene(99 percent pure), were obtained from Aldrich Company and Pfaltz and Bauer inc. respectively. They were found to be pure when checked with Hewlett Packard F and M Scientific 5750 Research Gas Chromatograph with a 5'x1/4" 10 per cent diethyl glycol column with oven at 50°C and inlet at 100°C.

99.5% pure antioxidant, 2246(2,2'-methylene-bis 4-methyl-6-tertiary-butyl phenol), was a gift from American Cynamid Company. It contained less than 0.5% moisture which could not have affected the polymers. It was used in all instances except during the polymerization of styrene, i.e, the solutions used for extractions and methanol used for precipitation contained one per cent antioxident.

Table 1 gives data on molecular weights(m.w), boiling points(b.p) and densities of the reagents we used in our experiments.

TABLE 1. TABLE OF DATA OF REAGENTS

	m.w (g/mole)	b.p (°C)	density (g/cm**3)
Cis-Polyisoprene	7.5x10**5		0.91
Styrene	104.2	145	0.91
Toluene	92.1	110.6	0.87
BPO	242.2	103-106	-
AIBN	164.2	102-103	-
Antioxident 2246	340.5	120-132	1.1
Trans-2-Pentene	70.0	37	0.65
2-Methyl-2-Pentene	86.2	67-68	0.69

B.2 Preparation of Samples for Polymerization

Clean and dry pyrex test tubes of 18x150 mm in dimensions were fused to 24/40 female joints through thick glass tubing of 1/4 inch bore and were dried at 105°C. overnight. The desired amount of rubber was dissolved in 15ml of toluene in a 25ml volumetric flask for 16 hours during which time the mixture was kept in the dark under nitrogen.

Figure 3 is a photograph of the high vacuum line we used. It consists of a mechanical pump(1),a mercury diffusion pump(2),3 liquid nitrogen traps:(4,5,and 6), a Mcleod' guage(7) and 5 male 24/40 joints:(8,9,10,11,and 12) connected to the vacuum line through two way stopcocks.The mechanical pump is connected to the trap through 2 inch thick rubber tubing, the trap is connected to the diffusion pump through the same material. The diffusion pump is connected to the two traps in series with glass ball joints. Then comes the vacuum line which is fused to the other end of the traps. The vacuum line is connected to the Mcleod gauge.

The vacuum line is a 3/2 inch O.D.,approximately four feet long glass tubing.Three pairs of 24/40 male joints are fused to it through stopcocks and they are placed 8 inches

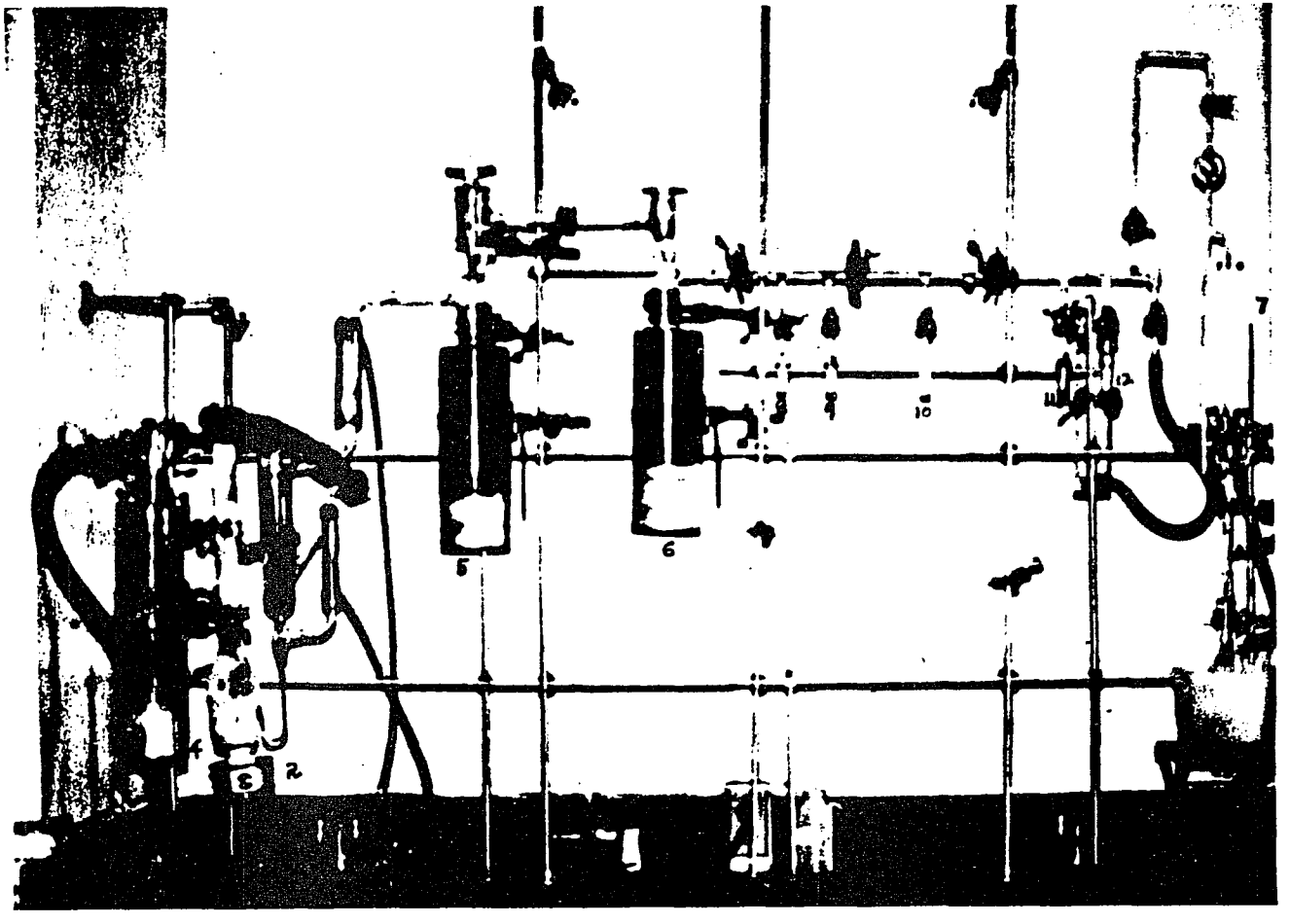


Figure 3 High Vacuum System

apart from each other. Each individual joint in a pair is seperated from the other by 3 inches. In this way five samples can be frozen and thawed at one time using three dewar flasks of liquid nitrogen for freezing.The sixth stopcock(13) could be used to release air in to the system after use. The vacuum was 0.5x10**(-6)mm Hg in all experiments as checked by Mcleod gauge.

After dissolution of rubber for 16 hours,the desired amount of styrene and initiator in toluene were added and the solution was made up to 25 ml and futher stirred for one hour. During this time the vacuum was brought to 0.5x10**(-6) as follows: First liquid nitrogen was poured into the three traps and the water line to cool the upper part of the mercury diffusion pump was opened. Then the mechanical pump was started. After fifteen minutes the mercury diffusion pump was started. At the end of the hour the vacuum was checked using the Mcleod gauge.

15ml of the reaction mixture was now added to the reaction tubes connected to the female joints quickly and they were hooked up to the vacuum. The reaction mixture was then subjected to 5 freezing and thawing cycles so as to make sure that air bubbles in the viscous mixture are completely removed. Usually 5 reaction tubes were used at a

time. The vacuum was checked using the gauge. Then the tubes were sealed under vacuum. Sealed tubes were then covered with aluminium foil and kept in a water bath, previously set at 60°C, for 20 hours. The rubber solutions were always covered with aluminium foil so as to prevent light activated oxidation. After 20 hours the contents were poured into 250ml of methanol cooled with solid carbon dioxide.The precipitated polymer was roughly dried, dissolved in 30ml of toluene and reprecipitated as above.The purified product was collected in a sintered crucible and dried under vacuum for one day.

B.3 Fractionation of the Mixture

The product obtained contains four components,namely free homopolystyrene, unreacted rubber, graft polymer and the crosslinked mass. Several authors have suggested various methods for fractionation of such mixtures (20,21,22,23,24,25). Gel permeation chromatography seems to be a good method but we did not try it because of the possibility of the crosslinked mass clogging the GPC columns. We used the method of Cameron et al(5) with slight modifications. The mixture was cut into thin slices and placed in weighed soxlet thimbles. The polystyrene was extracted by allowing the thimble to stand in cold methyl ethyl ketone under nitrogen for three days. The ketone

extracts were then evaporated to 15ml and polystyrene precipitated in 250ml of methanol cooled with dry ice. The precipitate was washed, collected in a sintered crucible and dried under vacuum for 48 hours at room temperature.

The soxlet thimble now containing the other three components was dried under vacuum, immersed in light petroleum and allowed to stand in the dark under nitrogen for 3 days. The extract containing unreacted rubber was evaporated under vacuum and reprecipitated in 250ml of methanol cooled by dry ice. The precipitate was then washed and collected in a sintered crucible and dried under vacuum for 48 hours at room temperature.

B.4 Testing for the presence of grafting and crosslinking

In order to check grafting and crosslinking,one test sample per each series of experiments was extracted alternatively with methyl ethyl ketone and petroleum ether until no more polymer was detected(usually it took 5 extractions). The remaining mass was dissolved in 30ml of toluene under nitrogen for one day and reprecipitated. The small amount of polymer precipitated was considered to be the graft polymer. The precipitate was dried under vacuum for three days at room temperature.

In experiments where benzoyl peroxide was used as the initiator, some gel material remained undissolved in toluene. This fraction was absent in AIBN initiated polymerizations. The same observation has been made in the past by several authors on the styrene-polybutadiene system and the methyl methacrylate/natural rubber system(5,20,21). This fraction is considered to be the crosslinked mass. Whether the crosslinking is between the rubber molecules only or incorporates polystyrene molecules is not yet known.

B.5 Characterization of Homopolystyrene

The purity of the polystyrene fractions were tested with Beckman IR 4260 Research Infrared Spectrometer using a KBr disk; The spectrum is given in figure 4. It is apparent that the extracted homopolystyrene is well separated from other components in the mixture.

The molecular weights of homopolystyrenes in AIBN polymerizations were determined using Water Associates model 200 Gel Permeation Chromatograph with dimethyl formamide as the solvent. Following conditions were used.

Columns	(500,8.5x10**3,1x10**5,1x10**6 A)
Oven	88°C
Syphon	71°C

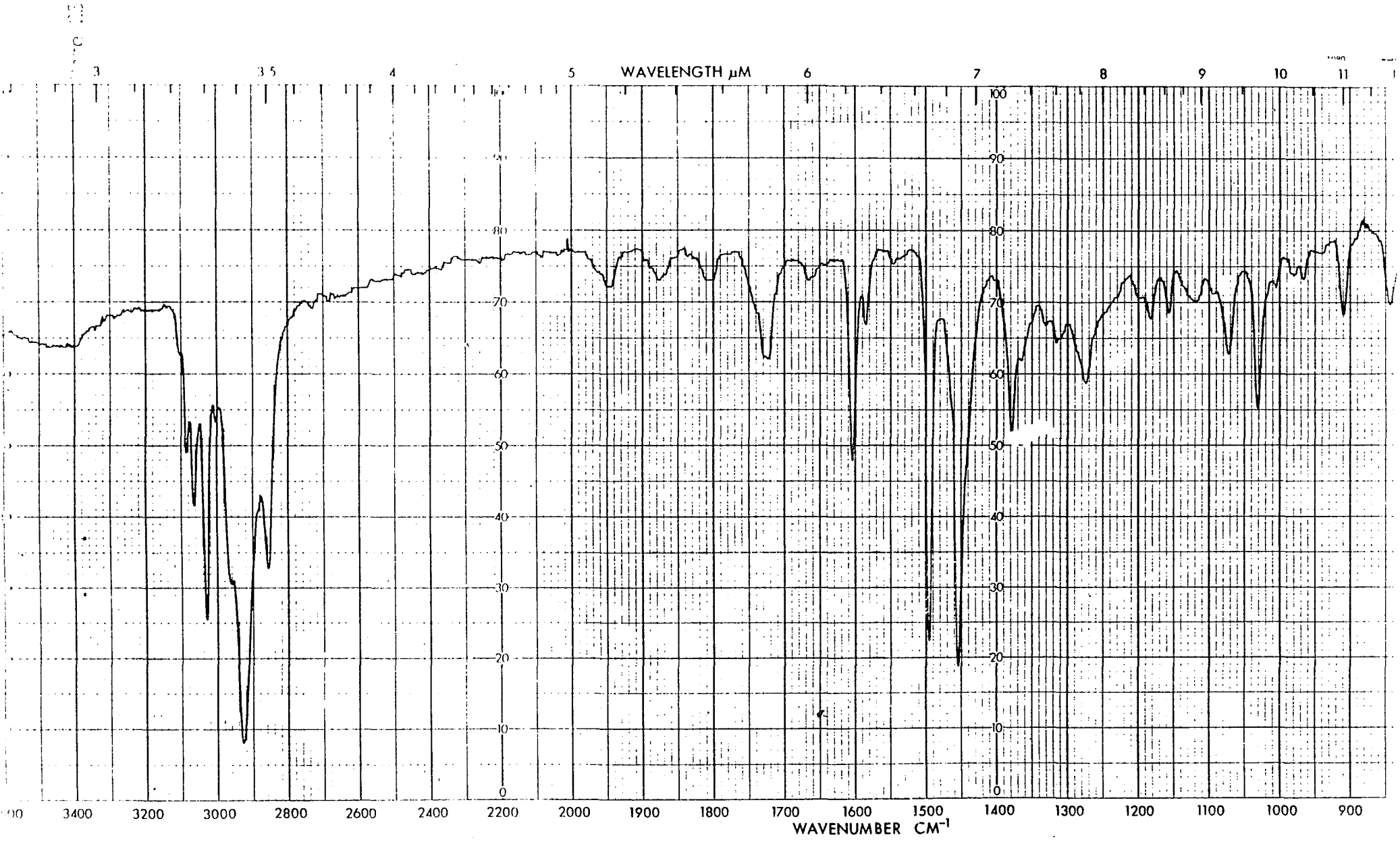


Fig 4 IR Spectrum of extracted Homopolystyrene taken on KBr disk at 27 c.

Degasser	104 °C
Inlet	82 °C
Refractometer	
Base plate	80 °C
Heat exchanger	80 °C

The molecular weights of polystyrenes prepared using benzoyl peroxide were determined using a Hewlett Packard Mecrolab model 501 High Speed Membrane Osmometer with toluene as the solvent.

Both the GPC and the osmometer were checked for their accuracy and precision. Molecular weights could be determined with less than a maximum of 5 percent error. In case of osmometry, the data were also treated using linear regression and the confidence limits calculated statistically (see Appendix 1).

B.6 Experimental Conditions

Table 2 shows the experimental conditions we used for styrene polymerizations. The initiator concentrations were varied in series a, d, g, q, r, and t. The rubber concentrations were varied in series b and c.

Table 2 Experimental Conditions for Styrene Polymerization with Dissolved Rubber

Series	PIP Conc. (monomer m/l)	Initiater Conc. (x10**3 m/l)	Monomer Conc. (m/l)
a	0.25	1.23	1.72
	0.25	2.66	1.72
	0.25	4.40	1.72
	0.25	6.64	1.72
	0.25	19.50	1.72
	0.25	24.93	1.72
	0.25	34.85	1.72
	0.25	39.93	1.72
b (BPO)	0.10	1.32	1.75
	0.20	1.32	1.75
	0.30	1.32	1.75
	0.40	1.32	1.75
c (AIBN)	0.10	1.25	1.75
	0.20	1.25	1.75
	0.30	1.25	1.75
	0.40	1.25	1.75
d (AIBN)	0.25	1.25	1.75
	0.25	4.40	1.75
	0.25	9.64	1.75
	0.25	19.50	1.75
g (AIBN)	-	1.25	1.75
	-	4.40	1.75
	-	9.64	1.75
	-	19.50	1.75
q (AIBN)	0.15	1.25	1.75
	0.15	4.40	1.75
	0.15	9.64	1.75
	0.15	19.50	1.75
r (AIBN)	0.35	1.25	1.75
	0.35	4.40	1.75
	0.35	9.64	1.75
	0.35	19.50	1.75
t (BPO)	-	1.23	1.72
	-	4.40	1.72
	-	9.64	1.72
	-	24.93	1.72

Table 3 shows the conditions we used for styrene polymerizations with dissolved model compounds. While Trans Pentene was used in series m, 2-Methyl-2-Pentene was used in series o.

Table 3. Experimental Conditions for Styrene Polymerization with Dissolved Model Compounds

Series	Model Conc. (m/l)	Initiator Conc. (x10**3 m/l)	Monomer Conc. (m/l)
m (BPO)	-	1.32	1.75
(Trans Pentene)	0.10	1.32	1.75
	0.20	1.32	1.75
	0.30	1.32	1.75
	0.40	1.32	1.75
o (BPO)	-	1.32	1.75
(2-Methyl	0.10	1.32	1.75
-2-Pentene)	0.20	1.32	1.75
	0.30	1.32	1.75
	0.40	1.32	1.75

C RESULTS AND DISCUSSION

C.1 Chain Transfer

The presence of chain transfer to rubber could be checked by investigating the variation of the M_n of homopolystyrene with rubber concentration. If the system is assumed to be following normal kinetics, M_n of polystyrene will be given by the classical equation:

$$1/M_n = T_o[I]^{1/2} + T_1 + T_2 \text{ ------- } 1$$

where $T_o = (2fk_d k_t)^{1/2}/M\, k_p [M]$

$T_1 = k_{Tol}[\text{toluene}]/M_o[M] + k_I[I]/M_o[M] + k_m/M_o$

$T_2 = k_{tr}[R]/M_o[M]$

k_d = Dissociation constant of the initiator

f = Initiator efficiency

k_t = Termination rate constant

M_o = Molecular weight of monomeric unit of polystyrene

k_{Tol} = Transfer constant to solvent

k_I = Transfer constant to initiator

k_m = Transfer constant to monomer

k_{tr} = Transfer constant to rubber

$[M]$ = Monomer concentration

$[I]$ = Initiator concentration

[R] = Rubber concentration

If chain transfer is present, $1/M_n$ in equation 1 should increase with rubber concentration. The b series of experiments were used to verify this matter. The results are shown in figure 5. It is apparent that $1/M_n$ did not vary with rubber concentration. Before deciding that chain transfer is absent, we have to be satisfied that there are no other mechanisms by which $1/M_n$ was kept constant. One such mechanism is that the chain transfer was present, but the increase of the transfer term, T_x, was counterbalanced by a decrease in other terms of the equation1. The T_o term, for instance, could have decreased due to a decrease in any one of the constants, k_t, k_d or f, or due to an increase in k_p.

Previous literature indicates that k_t is indeed affected by the introduction of rubber. Ludowico and Rosen(9) investigated the effects of polybutadiene on the rate of polymerization of styrene under homogeneous conditions at fairly high initiator concentrations. They found that the rate of polymerization decreases with increasing rubber concentration. To determine whether the decrease in rate was due to a decrease in k_d and/or f they carried out classical induction time experiments with 2,2-diphenyl-1-picryl hydrazyl(DPPH). Results showed that, the constants, k_d and f were unaffected by the introduction of

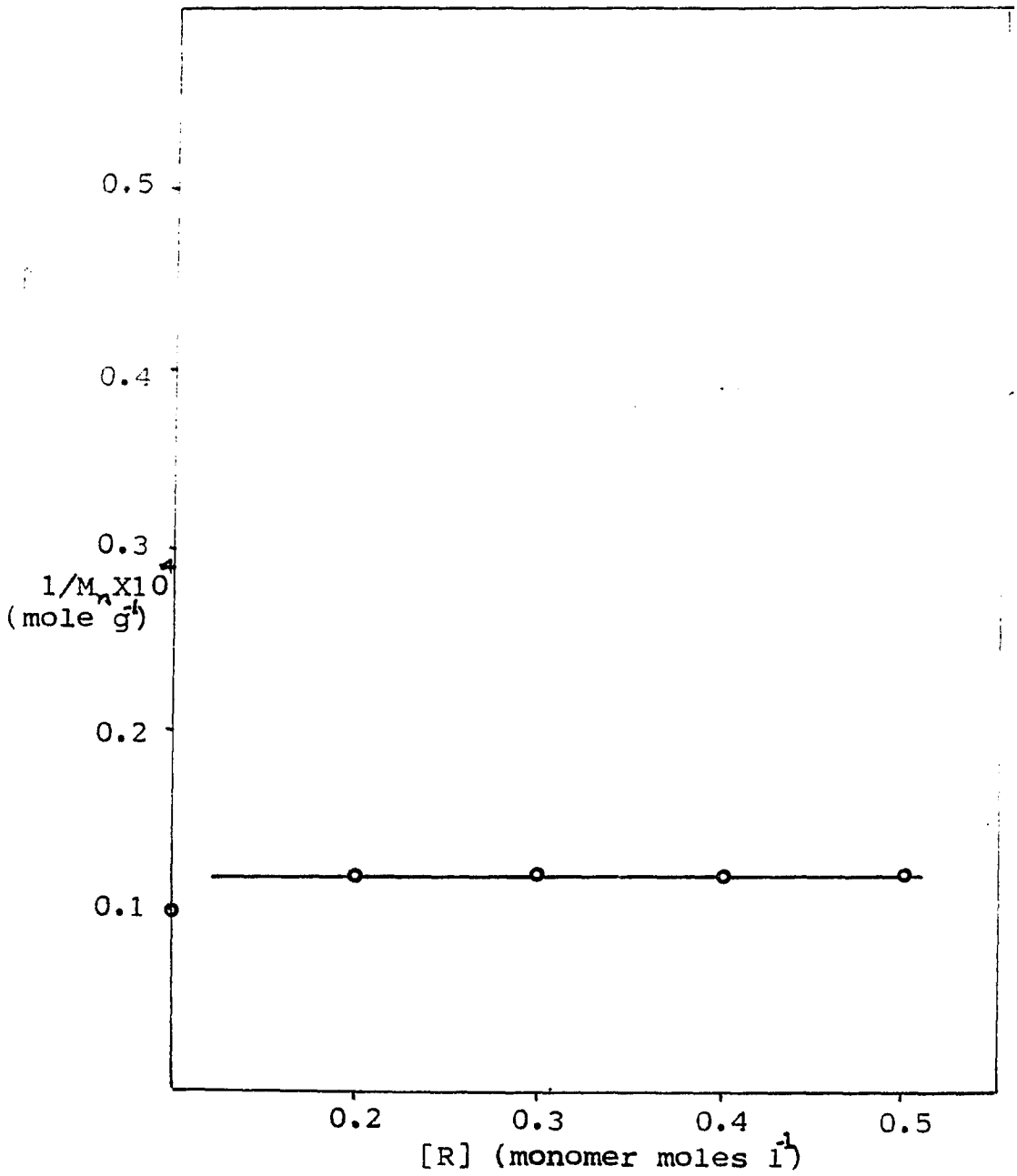


Fig 5 Plot of $1/M_n$ vs [R] for Styrene Polymerization with dissolved PIP using BPO. [St] = 1.746 moles l^{-1}, [BPO] = 1.25 X 10 moles l^{-1}.

rubber and that it was the increase in k_t that caused the decrease in rate.

Effects of rubber concentration on k_p have not been reported in the past. However many previous investigations(15,16,17) into the high conversion region of styrene polymerization, without any dissolved rubber, indicate that k_p is not significantly affected by the conversion. Therefore we can assume that k_p would not be affected here too.

The observation that k_t increases with increasing rubber concentration contradicts the observations of Cameron et al. Both Cameron and Rosen used rate of polymerization to investigate k_t, but the methods used to measure the rates were different. Cameron weighed the polymeric mixtures obtained after polymerization and plotted the weight against reaction times. From these graphs, rates of polymerizations were calculated. Rosen used dilatometry to obtain rates. Weighing of polymers can give errors that are not found in dilatometry and these errors may have caused the discrepancy between the two sets of results.

We used the a and t series of experiments (see Table 2) to investigate the effects of rubber on k_t and other transfer constants. Figure 6 shows the variation of $1/M_n$ with [I]**0.5. It is apparent that $1/M_n$ varies linearly with [I]**0.5 in the presence of rubber, and the two graphs, one in the absense of rubber and the other in the presence of rubber, almost overlap. Using regression analysis the intercepts and the slopes of the graphs were obtained, and using them, T_o and $(T_1 + T_2)$ were calculated. Using fig 5, a value for $T_o[I] + T_1 + T_2$ was obtained.

Table 4 lists these values. $(T_o[I] + T_1)$ was obtained from a separate experiment done in the absence of rubber. It is apparent that introduction of rubber did not change T_o. Subtraction of the T_1 term from $(T_1 + T_2)$ shows also that $T_2 = 0$. Table 4 also shows that the two sets of experiments, one with changing initiator concentration and the other with changing rubber concentration, lead to the same conclusion that introduction of rubber did not change T_o and that $T_2 = 0$. Therefore we could conclude that k_t was unaffected by the introduction of rubber and that the chain transfer is absent.

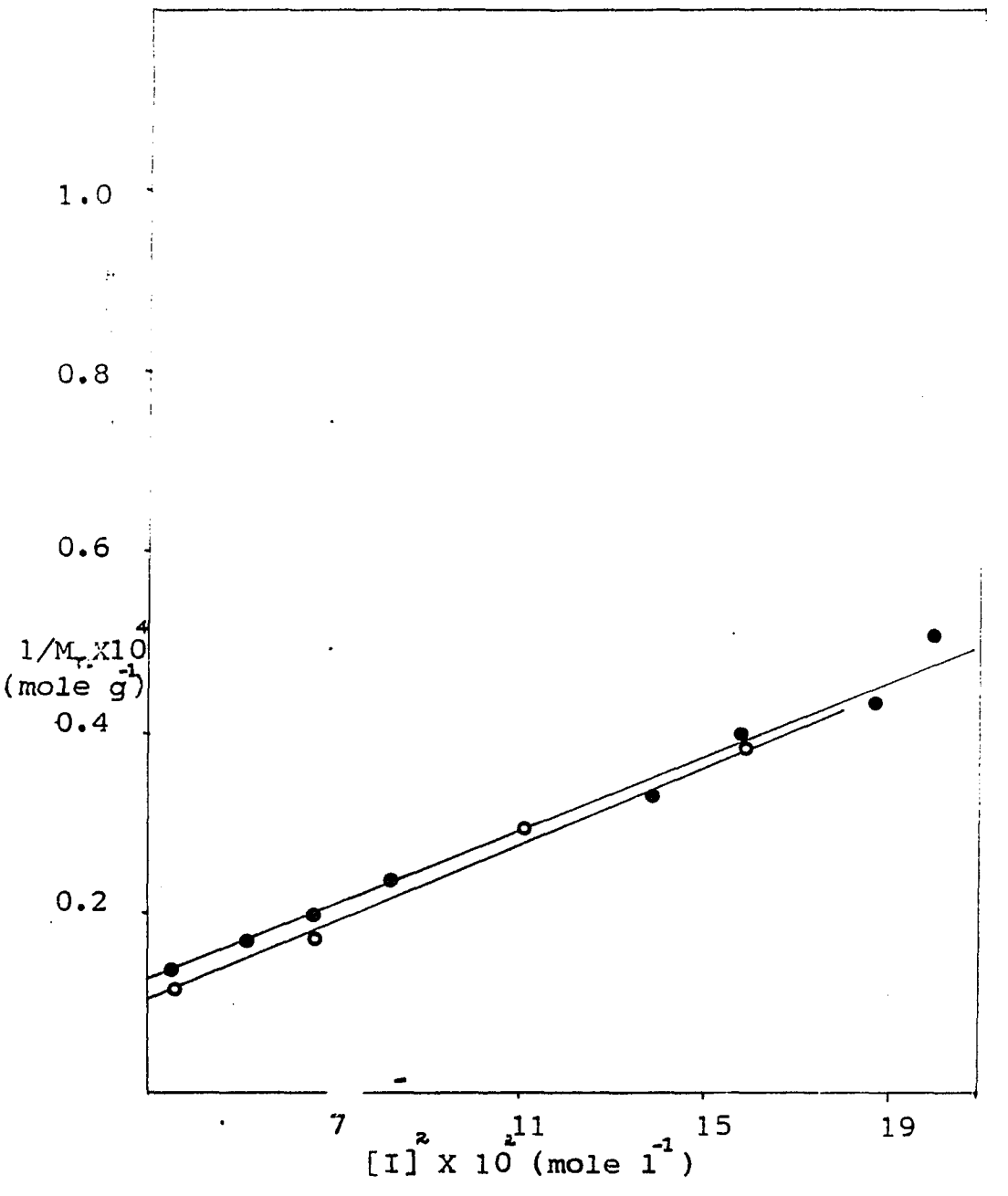


Fig 6 Plots of $1/M_n$ vs $I^{\frac{1}{2}}$ for Styrene Polymerization using BPO at 60°c.
o without PIP, ● with PIP, [St] = 1.715 moles l^{-1}, [PIP] = 0.25 monomer moles l^{-1}.

Table 4 Effects of Dissolved PIP on Termination and Transfer Constants in Styrene Polymerization using BPO at 60°C.

	without PIP	with PIP
T_o (mole$^{\frac{1}{2}}$ g^{-1} l$^{\frac{1}{2}}$)	0.02X10**2	(0.02+0.00)10*2
T_1 (mole g^{-1})	(0.03-0.04)10**4	-
$T_1 + T_2$ (mole g^{-1})	-	(0.06+0.01)10**4
$T_o[I]^{\frac{1}{2}} + T_1 + T_2$ (mole g^{-1})		(0.12+0.00)10**4
$T_o[I]^{\frac{1}{2}} + T_1$ (mole g^{-1})	(0.11+0.00)10*4	

Similar experiments were carried out using AIBN instead of BPO so as to isolate any effects due to grafting and crosslinking on k_t and chain transfer. Previously it has been reported that grafting and crosslinking are absent with AIBN while they are present with BPO(5,6,7) (We confirmed this fact by isolating, in BPO initiated polymerization only, two other fractions in addition to homopolystyrene and unreacted rubber). The reason for the difference between the initiators is not clear. But there is some evidence to support the fact that AIBN does not abstract hydrogens from hydrocarbons. For instance, when AIBN is heated with natural rubber the rubber does not crosslink(20). Also when AIBN is heated with toluene the initiator does not abstract

any hydrogens(20). It is possible that the nitrogen in AIBN is not electronegative enough or that the radical is sterically hindered so that the abstraction of hydrogens is prevented.

Figure 7 obtained from AIBN initiated experiments is a plot of $1/M_n$ versus [R]. It shows that $1/M_n$ does not vary with rubber concentration. Figure 8, obtained from the d and g series of experiments, show that $1/M_n$ varies linearly with [I]**0.5. The two graphs, obtained both in the presence and absence of rubber, almost overlap. Using linear regression, the constants were again calculated. Table 5 lists them. T_o, i.e., $(= (2fkk_d)^{1/2}/M_o\ k_p[M])$, did not change by the introduction of rubber and therefore k_t was unaffected by the introduction of rubber. Also $T_2 = 0$ and therefore chain transfer to rubber is absent.

Table 5 Effects of Dissolved PIP on Termination and Transfer Constants in Styrene Polymerization using AIBN at 60°C.

	with out PIP	with PIP
T_o (mole$^{1/2}$ g^{-1} l^{-1})	(0.04+0.00)10**2	(0.04+0.00)10**2
T_1 (mole g^{-1})	(0.01+0.01)10**4	-
$T_1 + T_2$ (mole g^{-1})	-	(0.04+0.02)10**4
T_o [I]$^{1/2} + T_1 + T_2$ (mole g^{-1})	-	(0.16+0.00)10**4
T_o [I]$^{1/2} + T_1$ (mole g^{-1})	(0.15+0.00)10**4	-

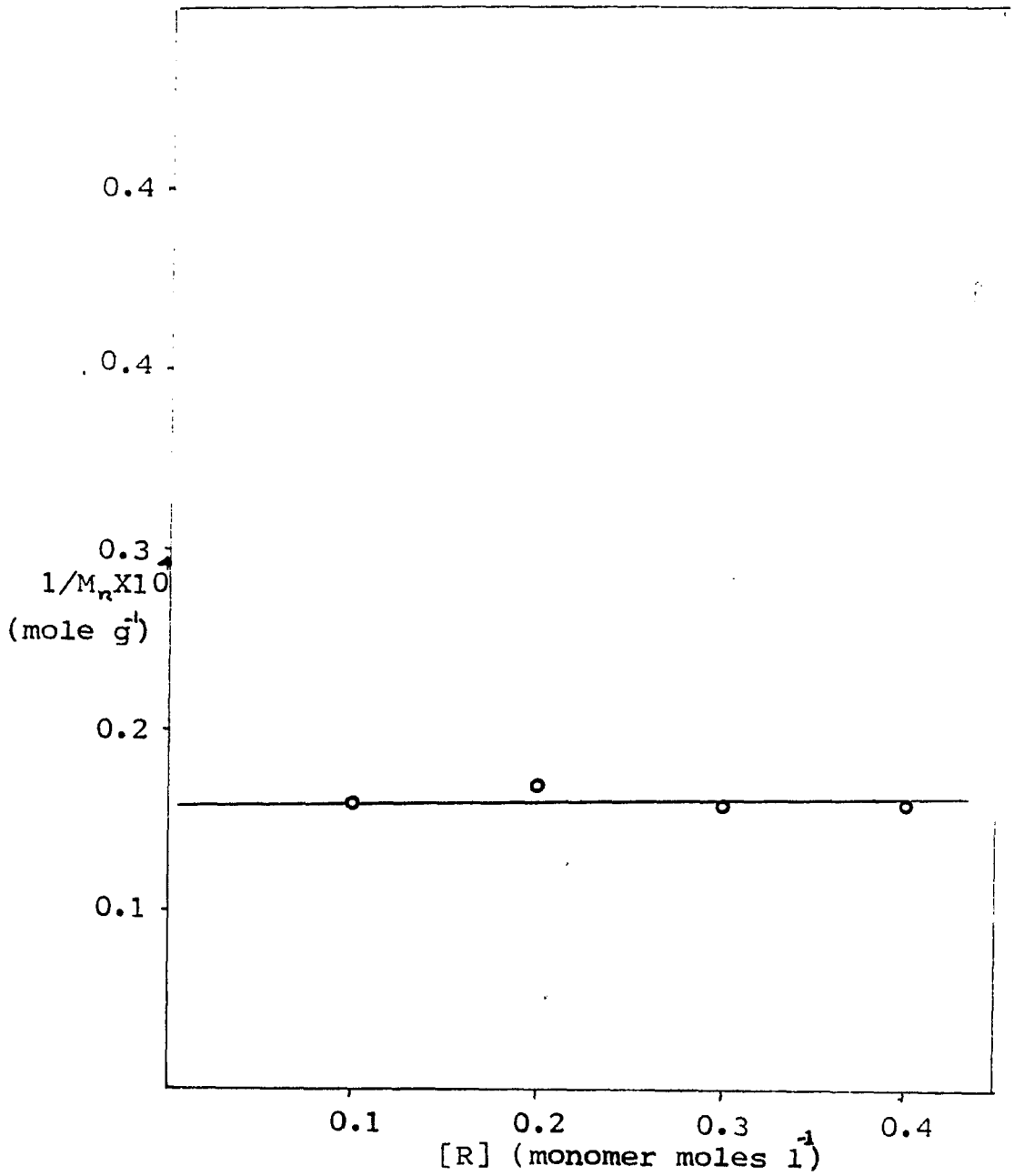


Fig 7 Plot of $1/M_n$ vs [R] for Styrene Polymerization with dissolved PIP using AIBN.
[St] = 1.746 moles l^{-1}, [AIBN] = 1.25 X 10 moles l^{-1}.

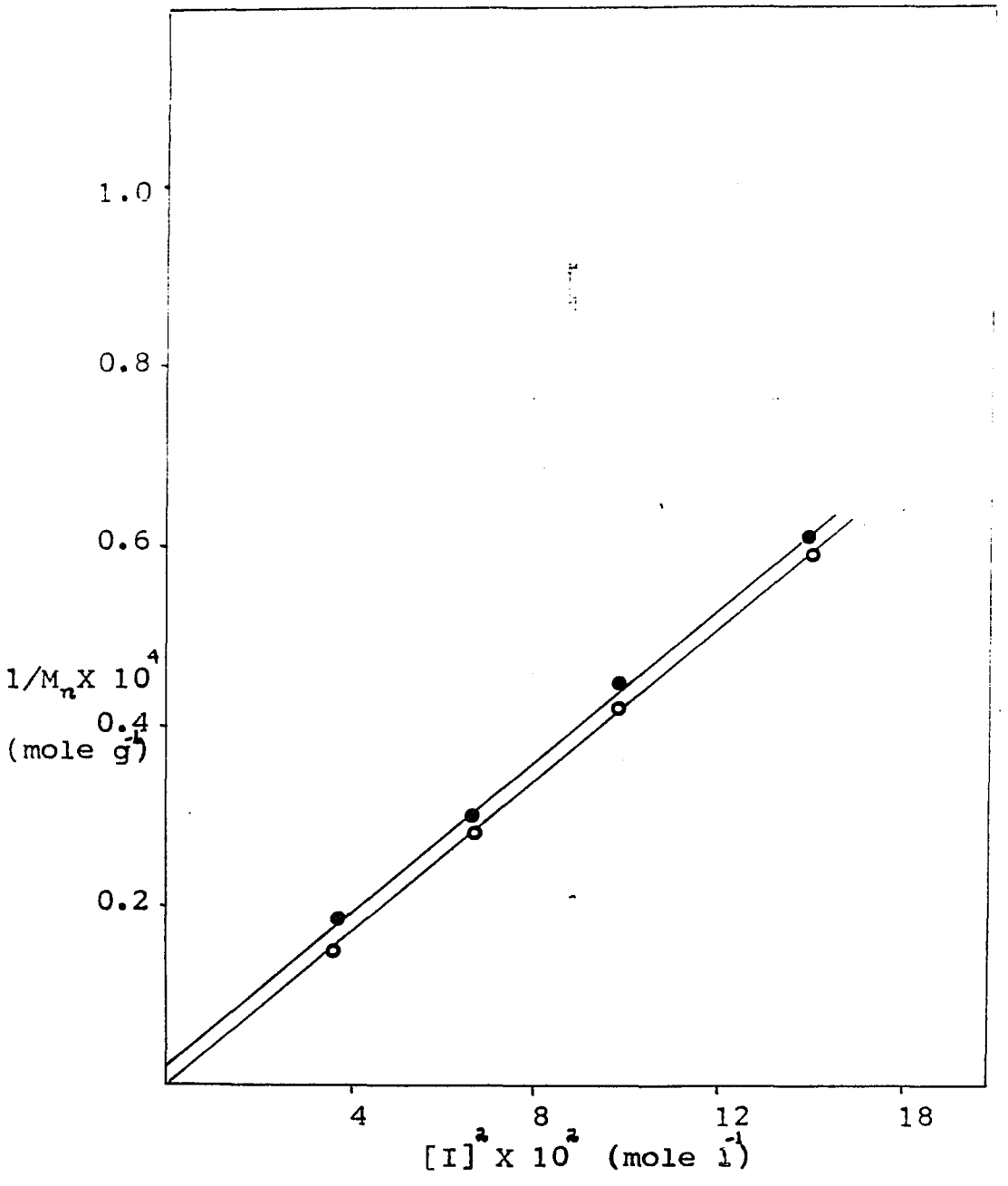
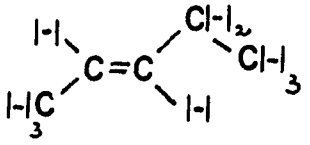
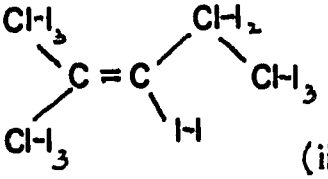


Fig 8 Plots of $1/M_n$ vs $.I^{\frac{1}{2}}$ for Styrene Polymerization using AIBN at 60° c.
o without PIP, ● with PIP, [St] = 1.746 moles l^{-1}, [PIP] = 0.25 monomer moles l^{-1}.



(i)

Now the following question arises. Why is that the chain transfer is absent in rubber when it is present in the model compound? In order to confirm that there is chain tranfer to model compounds we used two models which were different from that used previously. The models we used were trans pentene(i) and 2-methyl-2-pentene (ii).



(ii)

While the former models polybutadiene the latter models polyisoprene. The m and o series of experiments(see table 3) with models i and ii gave the results in figure 9.

There is chain transfer to 2-methyl-2-pentene. At the highest concentration of this model (i.e.,0.4 moles/l) the change in molecular weight is 18 per cent; indicating that the change is not an experimental error. Trans pentene, on the other hand,did not show chain transfer. It may be that the 2-methyl-2-pentene containing more allylic hydrogens has a higher probability for attack by polystyrene radicals.

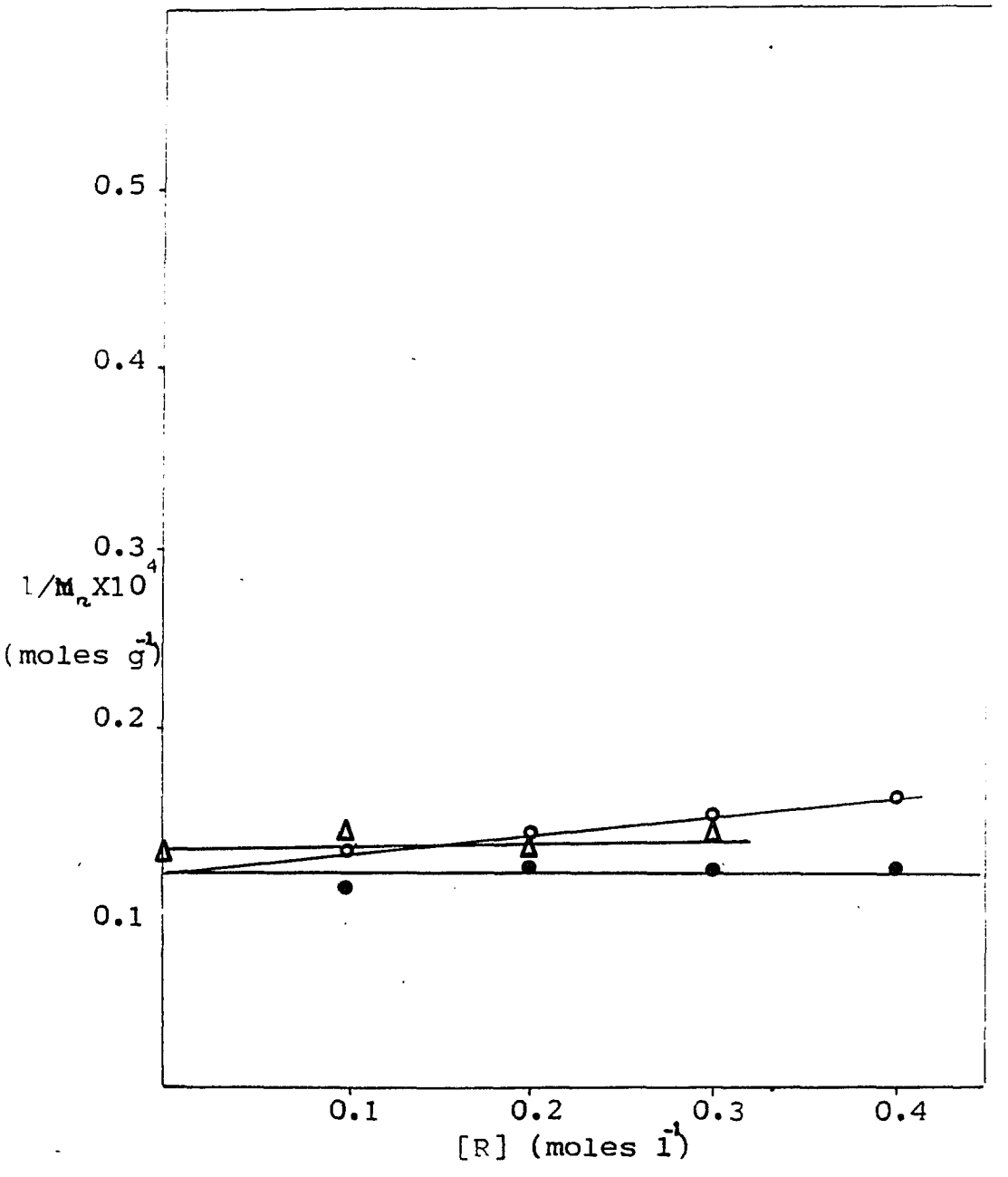


Fig 9 Plots of $1/M_n$ vs [R] for Styrene Polymerization at 60°c with Dissolved Models.
Δ Trans Pentene, o Methyl Pentene, ● PIP,
[BPO] = 1.321 X 10**3 moles l^{-1}, [St] = 1.746 moles l^{-1}.

We now conclude that there is no chain transfer onto polyisoprene even though there is chain transfer onto its model. Considering the small change in the molecular weight of extracted polystyrene, however, the amount of transfer cannot be very large. In view of the similarity of the bonds involved in rubber and its model, the absence of transfer to rubber cannot be due to a chemical phenomenon. Two possible physical phenomena could be the following.

a) The high molecular weight rubber increases the viscosity of the medium and now the polystyrene radicals and rubber molecules translate very slowly thereby decreasing transfer significantly,(sort of a viscosity effect due to rubber).

or

b) Dissolved rubber makes the medium a poorer solvent and now the more tightly coiled polystyrene radical makes the radical end less available for transfer(sort of a solvent effect).

C.2 Viscosity and Solvent Effects of Rubber

C.2.1 Key parameters of solvent and viscosity effects: γ, $(\frac{1}{2}-\chi)$, c

As indicated above, the absence of chain transfer could be related to a viscosity or a solvent effect of dissolved rubber. As a matter of fact any other polymer or even the homopolymer can cause viscosity and solvent effects in a polymerization. Therefore prior to analyzing the effect of a dissolved polymer, we shall examine the viscosity and solvent effects of the homopolymer formed in the polymerization.

In styrene polymerization without any dissolved rubber, the polymerising medium could be considered as a conventional polymer solution. The viscosity in a polymer solution is explained using the Huggin's equation.

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

where, η_{sp} = specific viscosity

$[\eta]$ = intrinsic viscosity

k' = huggin's constant

c = polymer concentration in gms/cc

however,

$$\eta = (\eta - \eta_0)/\eta_0$$

where η = macroscopic viscosity

η_o = solvent viscosity

Using these two equations and substituting for $[\eta]$ it can be shown that(appendix 2) the macroscopic solution viscosity is a function of

1) Average degree of polymerization; ν

2) Polymer concentration; c

3) Polymer solvent interaction parameter ; χ

(appendix 2 shows that it is more appropriate to use $(1/2-\chi)$ rather than χ itself. Also note

that $\Delta H_{mix} = (\delta_1-\delta_2)\phi_1\phi_2 = RT\chi\phi_2$

where, δ_1 = Solubility parameter of the solvent

δ_2 = Solubility parameter of the polymer

ϕ_1 = Volume fraction of the solvent

ϕ_2 = Volume fraction of the polymer

Therefore use of $(\delta_1-\delta_2)$ or even ΔH_{mix} too is suitable).

4) Molecular weight distribution;

5) Viscosity of the solvent; η_o

Examination of the solvent effect or the segmental diffusions in polymer solutions shows that the segmental diffusion too is dependent on the same variables. Mahabadi and O'Driscoll(17) show that the termination rate constant

due to segmental diffusion in stage 1 of methyl methacrylate polymerization is given by

$$k_s = k_{s.o}(1 + \delta c)$$

where, $k_{s.o}$ = Zero conversion value for k_s

c = Polymer concentration

δ = f(Average degree of polymerization, solvent and chain stiffness)

Therefore we could see that,under the conditions where the molecular weight distribution of the polymer, stiffness of the polymer and the viscosity of the solvent are constant, both theviscosity effect(translational diffusion) and the solvent or medium effect(segmental diffusion) are dependent only on three parameters; γ, (1/2 -χ), and c. These three parameters therefore are the key variables that completely describe the translational and segmental diffusions under the conditions employed in our experiments. i.e., trasnlational and segmental diffusion = f(v, ( ) c).

C.2.2 Quantification of Styrene Termination using Key Parameters

Viscosity and medium effects,i.e.,translational and segmental diffusions could affect the styrene polymerization

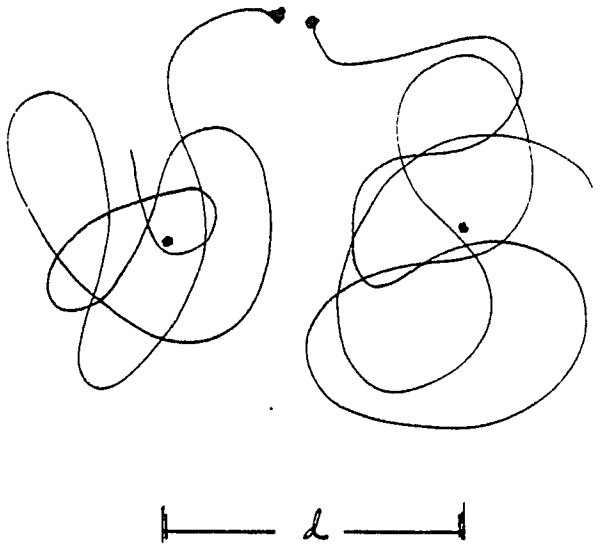
in many ways. They can affect k_t, k_p, f, k_d and other transfer constants. In view of the higher magnitude of k_t their effects on termination would be the highest. Examination of the termination process shows that it could be completely explained using translational and segmental diffusions. The termination process consists of the following three steps(figure 10).

a) translation of the two terminating radicals to a distance, d ,which is the distance between the two centers of gravity of the radical chains at collision.

b) movement of the chain ends until the radical ends meet with each other.

c) the reaction between the radical ends.

It is clear that the first two steps depend on the translational and segmental diffusions, respectively. The third step too can be shown to be dependent on these two diffusions. This third step, reaction between the radical ends, depend on two factors; the length of time the two chains stay at a distance,d, and the probability with which the two radical ends meet one another. The former factor would depend on the translational diffusion of the chains



	Translational	Segmental
k_t^{α}	$\frac{1}{\bar{y}}$	$\bar{y}$
	$\delta_1 - \delta_2$	$\delta_1 - \delta_2$
	$\frac{1}{c}$	c

Fig 10 Termination Process in Free Radical Polymerization

and the latter would depend on how many times the radicals have to collide with the other parts of the two chains before they find each other. This number of collisions would in turn depend on the segmental diffusions of the two chains.

Since the diffusions depend only on ν, $(1/2-\chi)$, and c we suggest that the termination process could be completely described by these three parameters. Examination of the effects of these parameters on termination would be the same as examining their effects on the two types of diffusion. figure 10 summarises the effects of the three parameters on the diffusions. As chain length increases the chain translates more slowly and hence an increase in ν causes a decrease in the translational diffusion. However the longer the chain the longer would be its segments and hence an increase in ν causes an increase in segmental diffusion. When the medium becomes poorer, the chains coil up and hence their translation would be higher. Therefore an increase in $(\frac{1}{2}-\chi)$ causes an increase in translational diffusion. The coiling up further causes an increase in the density of the segments and hence the poorer the medium the higher would be the segmental diffusions for termination. An increase in the concentration of the polymer would create more obstacles

for the movement of terminating radicals and hence an increase in c causes a decrease in translational diffusion. However increased concentration would increase the segmental densities of the terminating pair and hence an increase in c causes an increase in segmental diffusion.

We now hypothesize that the termination rate constant in styrene polymerization could be completely described by the equation,

$$k_t = k_{t.o}\, \gamma^{n} (1/2 - \chi)^{m} c^{q}$$

In styrene polymerization, the dependence of k on c is absent, because the rate of polymerization in low conversion region is independent of the conversion, i.e., polymer concentration. Therefore,

$$k_t = k_{t.o}\, \gamma^{n} (1/2 - \chi)^{m} \quad \text{---------} \quad 2$$

C.2.3 Quantification of Viscosity and Medium effects in Styrene Rubber System

Can we use equation 2 to quantitate the termination process in styrene polymerization with dissolved rubber? Here too the termination could be completely described by the translational and segmental diffusions and hence the same three key parameters have to be considered. The concentration again does not affect k_t because, in this system, the rubber concentration did not have an effect on

the molecular weight of the polystyrene produced (figures 5 and 7).

Since the dissolved polymer, the rubber, is different from the polymer generated in the system, it is necessary to examine whether there can be any other variables that should be incorporated into the hypothesis. Two other parameters that can affect translational and segmental diffusions are the molecular weight distribution and the chain stiffness.

Our experiments show that the dissolution of the rubber did not change the molecular weight distribution of the polystyrene produced. Figure 11 shows the GPC diagrams obtained from polystyrene samples prepared under various conditions. The diagrams obtained from samples prepared with dissolved rubber using either AIBN or BPO completely superimpose with the diagrams produced without dissolved rubber.

The stiffness of the polystyrene and cis-1-4-polyisoprene molecules is different and hence it should be taken into consideration in equation 2. However the effects due to stiffness are not significant in our experiments. At constant initiator concentration, the molecular weight of polystyrene produced with 4% w/v rubber (4% is the maximum concentration of rubber and the maximum conversion of polystyrene was 13%) differed only by 8% from

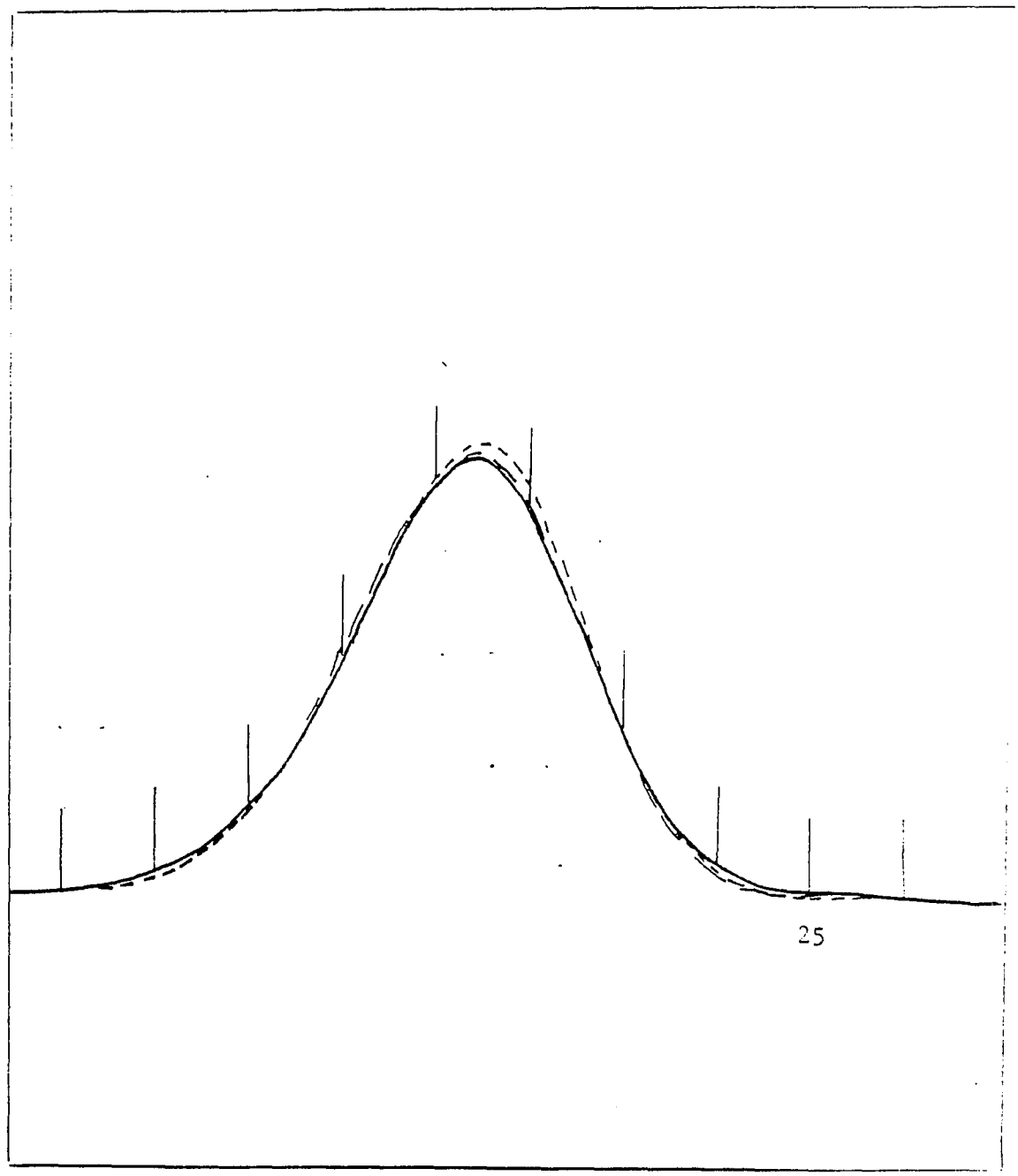


Fig 11 GPC Diagrams of homopolystyrenes
---- without PIP, ---- with PIP (BPO initiated),
---- with PIP (AIBN initiated).

the molecular weight of polystyrene produced in the absence of rubber. Also see figures 6 and 9. The graphs of $1/M_n$ vs $[I]^{1/2}$ with and without rubber almost superimpose, indicating that the molecular weights are not significantly affected by the difference in stiffness of the two polymers under the conditions used. Ours were dilute solution studies with low rubber concentrations. At higher rubber concentrations and at higher styrene conversions the stiffness may have to be included in equation 2.

Therefore equation 2 could be applied to low conversion styrene polymerization with dissolved rubber. We can now combine this hypothesis with equation 1 to obtain an experimentally verifiable expression.

We defined before that

$$1/M_n = T_0 [I]^{1/2} + T_1 + T_2 \text{ --------- } 1$$

The terms T_1 and T_2 are small compared to $T_0 [I]^{1/2}$ term and hence

$$1/M_n = (2fk_d k_t [I])^{1/2}/M_0 k_p [M] \text{ --------- } 3$$

but $M_n = 2\nu M_0$ ---------- 4

and $k_t = k_{t0} \nu^n (1/2 - \chi)^m$ --------- 2

Combination of these equations give(appendix 3)

$$-\log[I] = (2+n)\log\nu - 2\log k_p[M]/(8fk_d k_{t0})^{1/2} + m/2 \log(1/2-\chi) \text{ --- } 6$$

According to equation 6 , a plot of -log[I] versus log ν should yield a straight line and the slope would give a measure of n. The intercept would give a measure of $(1/2 - \chi)$.

Figure 12 shows the graphs obtained using this equation for styrene polymerization with varying concentrations of dissolved rubber. The points fall on good straight lines. We see that the styrene polymerization without rubber is different from that in the presence of rubber and that the AIBN initiated system with dissolved rubber is different from that initiated by BPO. Also the change in rubber concentration seems to have an effect on the system.

It seems that this method of treating data is more powerful than the classical method of plotting $1/M_n$ vs either $[I]^{1/2}$ or [R]. This method seems to bring up " subtle changes that did not surface in the classical treatment of the system.

Table 6 gives the various n and intercept values calculated from the graphs in figure 12 for styrene-rubber system. (The values were rechecked using linear regression). Before giving any interpretation of n and the intercepts, we shall clarify their significance using some other systems.

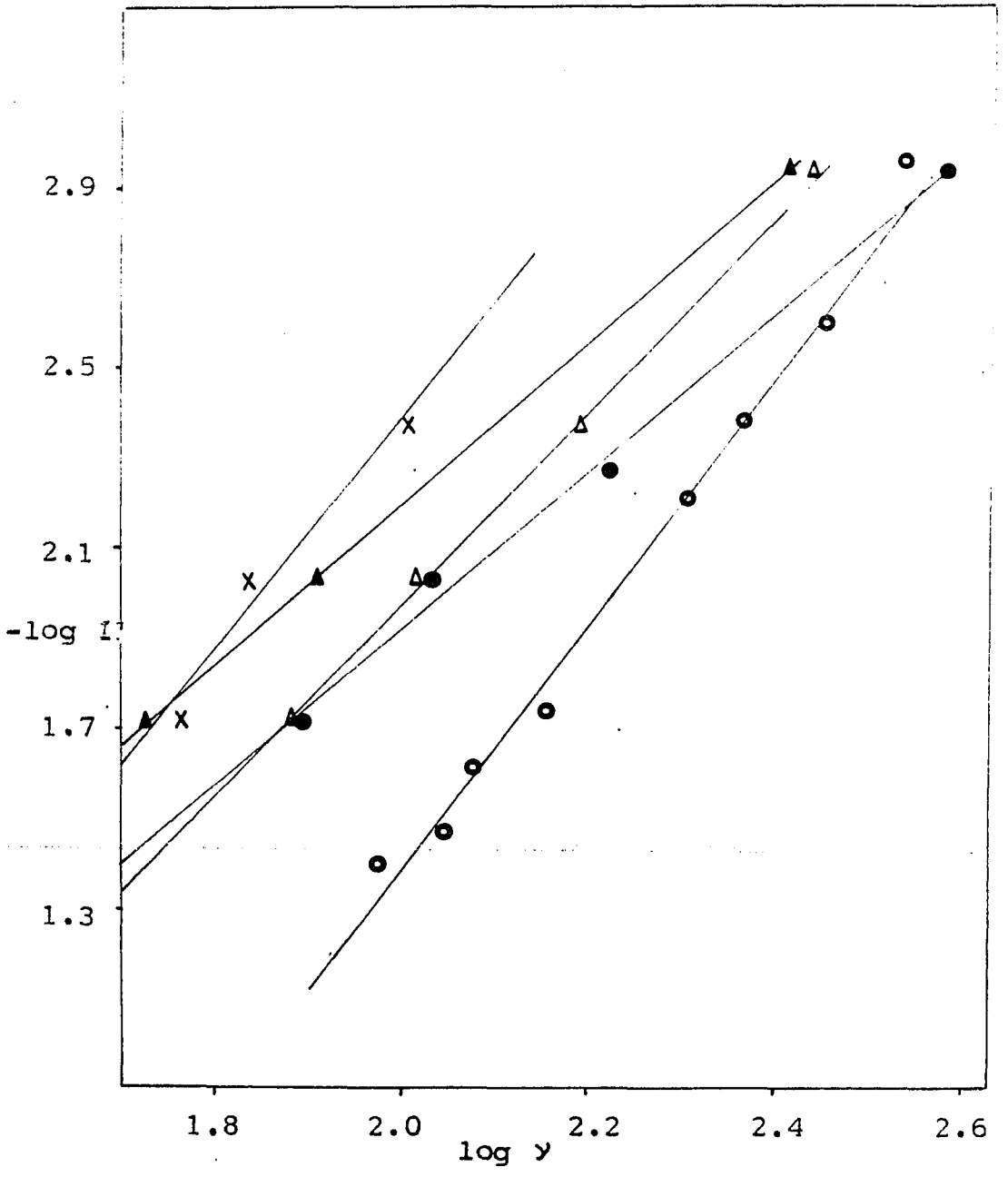


Fig 12 Plots of -log I vs log y for Styrene Polymerization using AIBN at 60°c.
● without PIP, X 1.8 percent PIP, Δ 3 percent PIP,
▲ 4.2 percent PIP, o 3 percent PIP with BPO.

Table 6 Effects of dissolved PIP on n and intercept in Styrene Polymerization using AIBN at 60°C.

PIP,%	n	intercept
0	-0.30	-1.47
1.8	+0.58	-2.80
3.0	+0.10	-2.24
4.2	-0.31	-1.20
3.0(BPO)	+0.73	-4.41

C.2.4 Significance of n and Intercept

Brooks et al(10) polymerised styrene and methyl methacrylate in the presence of dissolved polystyrene and investigated the changes in rate of polymerization against viscosity and volume fraction of the dissolved polymer. They used the rates to calculate the termination rate constants and these constants were plotted with viscosity and volume fraction of the dissolved polystyrene. They did not come to any specific conclusion regarding the termination process but suggested that the system might have more than one termination reaction and probably a primary termination too.However differentiation between these

suggestions was not possible using only rate data.

We used their rates in the low conversion region to test our hypothesis. Applying equation 2 to the equation for rate of polymerization:

$$R_p = k_p [M] (f k_d [I]/k_t)^{1/2}$$

We obtain(appendix 4)

$$\log R_p = (1+n)/(2+n)\log[I] + m/(n+2)\log(1/2 - \chi) + \text{constant} \quad ---- 7$$

Table 7 Effects of dissolved PS on n and intercept in Styrene Polymerization with AIBN at 60°C.

PS,%	n	intercept
0	-0.04	3.62
3.27	0.00	3.62
12.17	-0.18	3.74
20.00	-0.18	3.73

A plot of Log R_p versus Log [I] therefore would give n and an intercept which depends on $(1/2 - \chi)$. Table 7 gives the various values obtained from such plots. In the absence of any dissolved polystyrene and also at 3.27 percent dissolved polystyrene n equals 0 indicating that the termination rate is independent of chain length.However at 12 and 20 percent dissolved polymer n has a negative value.

The termination rate constant is inversely proportional to chain length and this indicates that the translational diffusion is controlling the system.

Table 8 Effects of dissolved PS on n and intercept in methyl methacrylate Polymerization with AIBN at 60°C.

PS,%	n	intercept
0	0	2.93
4.7	0.04	3.03
9.1	0.33	3.09
14.0	0.17	3.13
19.0	-0.11	3.27

Table 8 shows n obtained in a similar manner from low conversion rate data for methyl methacrylate polymerization in the presence of dissolved polystyrene(10). Contrary to the previous observation, n is positive here up to a certain percent of dissolved polymer. This indicates that the termination rate constant is increasing with average chain length and therefore the segmental diffusion is controlling the system. When the percent of dissolved polymer is increased to 19, n is negative and now the translational diffusion becomes appreciable.

In view of the above n could be considered as a parameter indicating whether the system is diffusion controlled and if so whether the diffusion is translational or segmental. Also n quantitates the effect of chain length on termination rate constant and hence could be used to quantitate the effect of chain length on low conversion polymerization.

The intercept ($1/2-\chi$) could be considered as a measure of the polymer solvent interaction. Therefore the intercept in styrene-polystyrene system(table 7) gives an idea about the interaction between the solvent and the dissolved polystyrene. The intercept did not change with increasing concentration of the dissolved polymer. This is not surprising since the dissolved polymer is the same as the growing polymer and hence additional interactions have not been produced.

On the contrary, when polystyrene is dissolved in methyl methacrylate polymerising system, the intercept increases with increasing polystyrene. Is it possible that the interaction between the solvent and the growing polymer is changed by the introduction of the second polymer? The solvent, in this case methyl methacrylate,is not changed by the dissolved polymer. Also the solvent is in excess as compared to the dissolved polymer and hence a change in the

interaction between the growing polymer and the solvent is not possible.

A more probable explanation would be that the growing polymer interacts with the dissolved polymer. If this is correct, the polymer-polymer interaction should not increase with increasing dissolved polymer when the dissolved polymer is same as the growing polymer. In agreement with this, table 7 shows that the intercept did not increase with increasing dissolved polymer when polystyrene is dissolved in styrene(table 7). There should not be any new polymer-polymer interactions and hence the intercept shows no change with increasing dissolved polystyrene.

Therefore in a multicomponent polmerization, the intercept could be considered as a parameter that takes into account the polymer-solvent as well as polymer-polymer interactions.

C.2.5 Interpretation of n and Intercept in Styrene-Rubber System

Table 6 gives the n values obtained for the styrene polymerization with dissolved rubber. At 1.8 percent rubber, n is positive and hence the system is segmental diffusion controlled. As the rubber concentration is

increased to 4.2 percent n becomes negative and now the system is translational diffusion controlled.

Now the problem about the chain transfer can be addressed. We observed earlier that while there was no chain transfer onto rubber there was chain transfer on to its model compound. The two possible explanations suggested were that,

a)Rubber increases the viscosity of the medium bringing about diffusion control,lowering the transfer rate.

or,

b)Rubber makes the medium a poorer solvent which causes segmental diffusion control and now the coiled up polystyryl radicals make their radical ends less available for tranfer.

The chain transfer experiments were carried out at 3 percent rubber concentration and since n is positive, the system is segmental diffusion controlled at this concentration. Therefore it seems that it is the solvent effect,not the viscosity effect, which is controlling the system. Therefore we can conclude that the rubber makes the medium a poorer solvent and brings about segmental diffusion control. The coiled up polystyryl radicals make their radical ends less available for chain transfer.

Table 6 shows that the n value for the BPO initiated system is greater than that for the AIBN initiated system at the same rubber concentration. Both values are positive.Only the former system undergoes grafting and crosslinking and therefore, we could conclude that, the grafting and crooslinking increase the segmental diffusions in the system. They cause a medium effect rather than a viscosity effect.

Table 6 also shows that the intercept in the polystyrene-rubber system increase with increasing rubber concentration. Parallel to the conclusion in the Methyl methacrylate-Polystyrene system polymer-polymer interactions could be operative in this system and the increase in the intercept is due to the increase in these interactions.

C.3 Chain Entanglements

Chain entanglements in a polymerization cause a broadening of the molecular weight distribution of the resultant polymer(17). Figure 11 shows the GPC diagrams for polystyrenes obtained under different conditions. The molecular weight distribution obtained with dissolved rubber is almost the same as the one obtained without dissolved rubber. Also the polystyrene prepared using BPO has the same distribution as the one prepared using AIBN. This

indicates that the grafting and crosslinking do not have an effect on the molecular weight distribution. We could conclude therefore that the rubber, the graft polymer and the crosslinked mass were not involved in any chain entanglements.

D CONCLUSIONS

a) The parameters, n and $(1/2 - \chi)$ of equation 1 completely quantify the viscosity and solvent effects of the diisolved polymer. While n indicates whether the translational or segmental diffusion is controlling in the system, the intercept indicates whether any polymer-polymer interactions are present in addition to the polymer-solvent interactions.

b) Upto 3 percent rubber, the system is segmental diffusion controlled. Thereafter it becomes translational diffusion controlled.

c) Chain transfer to rubber is absent even though it is present with the model compound for rubber. This is due to the fact that the rubber makes the medium a poorer solvent and now the coiled up polystyrene chains make the radical chain ends less available for chain transfer.

d) Translational and segmental diffusions would be different for different types of dissolved polymer; for instance, in styrene polymerization, dissolution of rubber causes more segmental diffusion than the dissolution of polystyrene.

e) Grafting and crosslinking increase segmental diffusion rather than increasing translational diffusion.

f) There are no chain entanglements among polystyrene, rubber, graft polymer and the crosslinked mass.

APPENDICES

Appendix 1

Statistical Treatment of Osmometric Data [1]

$$M_n = RT/(\pi/C)_0 = RT/\text{intercept}$$

$$S_{M_n} = \{[\partial M_n/\partial RT/M_n]^2 S^2_{\text{intercept}}\}^{1/2}$$

Where

S_{M_n} - Standard error of M_n

$S_{\text{intercept}}$ - Standard error of intercept

$$S_{M_n} = \frac{M_n^2}{RT} S_{\text{intercept}} = \frac{S_{\text{intercept}} \times M_n}{\text{intercept}}$$

$$95\% \text{ Confidence Limits} = \pm 2S_{M_n} = \frac{2S_{\text{intercept}} \times M_n \times 100}{\text{intercept} \times M_n}$$

$$95\% \text{ Confidence Limits} = \frac{2S_{\text{intercept}} \times 100}{\text{intercept}}$$

Appendix 2

Viscosity Effect/Translational Diffusion

$$\eta = f(\gamma,(1/2-\chi),c,p,\eta_o)$$

$$\eta_{sp/c} = [\eta] + k[\eta]^2 c \quad \text{- Huggins Equation}$$

$$\eta_{sp} = (\eta-\eta_o)/\eta_o$$

$$[\eta] = KM_v^a = KM_v^{1/2}\alpha^3 = K(M_n p)^{1/2}\alpha^3 = (M_o \gamma p)^{1/2}\alpha^3$$

$$K = f(\gamma)$$

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

Segmental Diffusion

$$k_s = f(\gamma,(1/2-\chi),C)$$

$$k_s = k_{so}(1+\delta c)$$

where δ is a function of solvent character and molecular weight.

Note

$$\Delta H_{mix} = (\delta_1-\delta_2)^2\phi_1\phi_2 = RT\chi\phi_2$$

Appendix 3

$$k_t = k_{to} \nu^n (1/2-\chi)^m$$

$$-\text{Log } I = (2+n)\log\nu - 2\log \frac{k_p[M]}{(8fk_dk_{to})^{1/2}} - \frac{m}{2}\log(1/2-\chi)$$

Derivation of Above Equation

$$\frac{1}{M_n} = \frac{1}{M_o} \frac{[k_t 2fk_d]^{1/2}[I]^{1/2}}{k_p[M]}$$

$$\nu = \frac{M_n}{2M_o} = \frac{k_p[M]}{2(2fk_d)^{1/2}[I_2]^{1/2}} \frac{1}{(k_{to})^{1/2}\nu^{1/2}(1/2-\chi)^{m/2}}$$

$$\nu^{1+n/2} = \frac{k_p[M]}{(8fk_dk_{to})^{1/2}} \frac{1}{[I_2]^{1/2}(1/2-\chi)^{m/2}}$$

$$\frac{2+n}{2}\log\nu = \log \frac{k_p[M]}{(8fk_dk_{to})^{1/2}} - \frac{1}{2}\log I - m/2 \log(1/2-\chi)$$

Appendix -

$$R_p = k_p[M]\left(\frac{fk_dI}{k_t}\right)^{1/2}$$

Substituting for k_t using equation 2,

$$R_p = k_p[M]\left(\frac{fk_dI}{k_{to}}\right)^{1/2} \frac{1}{\nu^{n/2}\left(\frac{1}{2} - \varkappa\right)^{n/2}} \qquad \text{--------} \qquad A$$

$$\text{But} \quad \nu = \frac{k_p[M]}{2(fk_dI)^{1/2}k_t} = \frac{k_p[M]}{2(fk_dI)^{1/2}k_{to}^{1/2}\nu^{n/2}\left(\frac{1}{2} - \varkappa\right)^{n/2}} \qquad \text{-----} \qquad =$$

$$\text{and} \quad \nu^{1+n/2} = \frac{k_p[M]}{2(fk_dIk_{to})^{1/2}(1/2-\varkappa)^{m/2}}$$

$$\text{and} \quad \nu = (k_p[M]^{2/n+2}2^{-2/n+2}(fk_dIk_{to})^{-1/2+n}(1/2-\varkappa)^{m/2\ n/n+2}$$

Substituting for ν in A

$$R_p = [k_p^{(1\ -\ 2/2+n)}2^{(2/n+2\ -\ 1)}(fk_dk_{to})^{(1/2+n\ -\ 1/2)}]M^{2/2+n}I^{1+n/2+n}(1/2-\varkappa)^{m/n+2}$$

$$\log R_p = \log(\text{const}) + \frac{1+n}{2+n}\log I + \frac{m}{n+2}\log(1/2 - \varkappa)$$

(at constant[M]

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