

## Zone Fractionation of Cyclohexane-Rich Polystyrene-Cyclohexane Solid Solutions\*

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### Synopsis

Experimental results on the application of zone melting techniques to dilute solutions of polystyrene in cyclohexane under various operating conditions are reported together with observations on static solidification tests on the solutions. The variables investigated were: polymer concentration, number of zones passed, zone length, and zone travel rate. The results showed that at slow zone travel rates (ca. 4.01 cm./hr.) redistribution of solute species occurs in conformity with thermodynamic predictions. In this case, a cyclohexane-rich liquid and a polymer-rich liquid, which coexist at temperatures just above the solidification range, react to form a cyclohexane-rich solid solution upon solidification. The solid solution contained a higher concentration of all polymer species than the cyclohexane-rich liquid, with the ratio of the concentration in the solid to the concentration in the liquid increasing exponentially with molecular weight of the solute. The net result was the accumulation of all solute species toward the head (i.e., first melted and first frozen) end of the zone melted ingot, with the higher molecular weight species enjoying the greatest redistribution in this respect. At moderately faster speeds of zone travel (ca. 4.83 cm./hr.), a reversal in the accumulation trend with molecular weight was found; the higher molecular weight species were carried increasingly to the tail (i.e., the last frozen) end of the sample. Increases in total polymer concentration enhanced this effect. These facts have been interpreted as suggesting that resorption of some of the higher molecular weight species from the polymer-rich phase was not sufficiently fast compared to the rate of freezing, and part of the polymer-rich phase was carried in the moving liquid zone. At significantly faster speeds of zone travel (ca. 9.66 cm./hr.) a decreased redistribution of solute species was found. Increased total polymer concentration reduced the selectivity of fractionation. This effect was interpreted as being the result of the lesser extent to which the resorption reaction in these experiments occurred in relation to the rate of movement of the interphase. Qualitative considerations on the thermodynamic characteristics of the polymer-solvent system most suitable for effective zone fractionation are discussed. The effect of zone fractionation upon the distribution of molecular weight for some of the samples is reported.

### INTRODUCTION

Whenever the ratios of solute concentration in a solid and in a liquid solution phase at equilibrium are different, it is possible to achieve by zone-

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refining techniques a fractionation of the solute along a predetermined direction of the system. In the case of a homologous series of long-chain organic molecules the segregation coefficient  $K$ , defined as the ratio of the volume fractions of similar species in the two different phases, is known to vary as a function of the molecular weight of the species themselves. Therefore, fractionation will result when zone refining methods are applied to molecularly polydisperse high polymer solutions. Measurements of single properties, like intrinsic viscosity or melting point, of paraffins and high polymeric materials subjected to zone fractionation have already been reported.<sup>1</sup> The results showed that some redistribution occurred during zone fractionation; the appropriate averages or extreme values of the property measured varied systematically along the fractionated ingot. In view of contributing to a better understanding of these experiments, it was decided to investigate the effect of zone fractionation on a high polymer dilute solution.

Previous equilibrium studies of these solutions wholly in the liquid region,<sup>2</sup> have shown that two types of systems must be considered with (a) only a single liquid phase region over all temperatures of interest, regardless of the concentration of the polymer in the solvent, and (b) a two-phase liquid region in a range of polymer concentrations. The first situation refers to exothermic polymer solutions with appreciable polymer volume fraction. In this instance there is opportunity for molecular interlocking during phase changes, and as a result, efficient redistribution on freezing of a system, composed of a solvent that is thermodynamically good at temperatures just above the solidification temperature, is rendered difficult, and very low polymer concentrations must be used. For endothermic solution processes (case b), polymer-polymer molecular interactions are reduced to a minimum, and the polydisperse polymer solution can be considered as a family of a series of binary systems where the series parameter is molecular weight and the family parameters are total polymer concentration and molecular weight distribution.

Further consideration of binary systems with miscibility gaps in the liquid region shows that the equilibrium behavior, which is of interest for the experiments under discussion, is the one possessing an upper consolute temperature, separating the regions where only one liquid phase is present from that where two liquid phases coexist. In fact, only in this system the liquid miscibility gap extends to the freezing temperature, thus providing the least possible amount of entrapment of polymer molecules upon freezing. It is, therefore, expected that such a binary solution would more closely approach equilibrium behavior under zone fractionation. In addition, it is well known that in this system, the invariant temperature, at which two liquid and one solid phases coexist, can occur above or below the melting point of the pure solvent. As a result zone melting will induce the solute to be concentrated at the head end (i.e., the first melted and the first frozen) or at the tail end of the ingot, respectively.

Deviations from thermodynamic equilibrium may be essentially due to

two effects: (a) finite diffusion rates in the liquid (these deviations will induce less net segregation between the liquid and solid than thermodynamics would predict); (b) slow rates of the three-phase reaction. Two cases can be distinguished here, according to the relation between the invariant temperature and the melting point of the pure solvent. When the invariant temperature is above the melting point of the pure solvent, a polymer-rich liquid phase will remain after solidification. The remaining polymer may either be entrapped in the freezing solid thus enhancing the thermodynamic tendency for the heavier molecules to be retained by the solid or carried along in the liquid by the advancing interphase, thus producing an opposite result. Similar reasoning shows that opposite effects can be expected whenever the invariant temperature is below the melting point of the pure solvent.

## EXPERIMENTAL PROCEDURE

### Materials

In summary, to be able to anticipate the results of zone melting a polymer solution with a suitable miscibility gap in the liquid region, it is necessary to know for each species either the relative concentrations of solute in the liquid and in the solid, or the invariant temperatures relative to the melting temperature of the pure solvent.

Three samples of atactic polystyrene were examined, one with a broad distribution of molecular weight and two with narrow distribution. The broadly distributed material (Dow Chemical Co.) had a weight-average molecular weight of 243,000 as determined by the ultracentrifuge sedimentation-velocity method<sup>4</sup> with a Spinco Model E ultracentrifuge, and a ratio of weight-average to number-average molecular weight of 2.055.<sup>5</sup> The two narrowly distributed polymers (Dow Chemical Co.) had weight-average molecular weights of 82,000 and 267,000. The former had a weight-average to number-average molecular weight ratio of 1.05, whereas the same ratio for the latter was found to be 1.08.<sup>5</sup>

Cyclohexane was selected as a solvent on the basis of the arguments discussed in the previous section. Solutions of the desired concentrations were prepared by dissolving the polystyrene samples in the cyclohexane at temperatures near the boiling point of the solvent (81°C.).

### Experimental Methods

The thermodynamic tendency for partition of the polystyrene molecules across the freezing interface of the cyclohexane-polystyrene solutions was ascertained by means of a series of static tests. Test tubes 20 mm. O.D. by 150 mm. long were supported with their lower third in an ice water bath and filled approximately for two-thirds of their length. After periods of 120 or 160 min., the supernatant liquid was decanted, and the solid remaining was allowed to melt. The melted solution was recovered after

being heated into the temperature range above the critical temperature. The molecular weight distributions of the various fractions were determined with sedimentation velocity experiments.<sup>4,6</sup> Runs were made in cyclohexane at the  $\theta$ -temperature, 35°C., at concentrations between 0.10 and 0.20 g./100 cc., and at 59,780 rpm with a double-sector cell. Boundary curves were measured by projecting them onto coordinate paper. Diffusion corrections were made by extrapolating against  $1/t$  to infinite time. Corrections for concentration at this level of concentration were found to be unnecessary. Because there was no detectable differences between the 120 and the 160 min. samples, longer times of treatment were not considered necessary. Visual observation of the liquid in contact with the solid during a static freezing experiment clearly established the presence of two liquid phases. The determination of the invariant temperature and its relation to the melting point of cyclohexane was achieved through the determination of cooling curves. By means of special techniques a precision of about 0.1°C. was obtained.

Carefully controlled movement of a molten zone through a solid ingot of a cyclohexane-rich polystyrene-cyclohexane solution was achieved in toroid-shaped samples contained in Teflon tubes set on a merry-go-round which slowly carried the samples past radiant heaters in a 62 cm. square

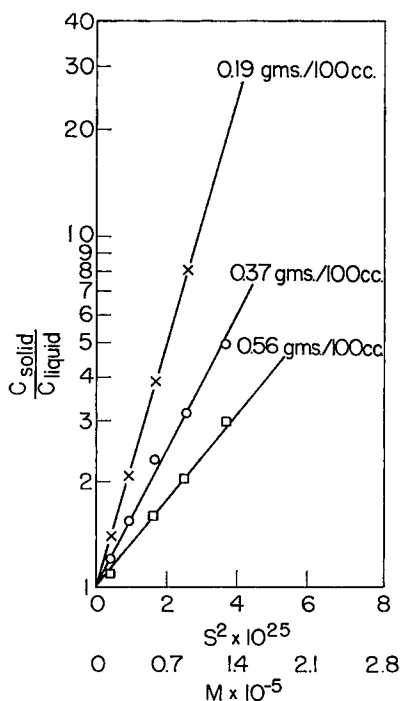


Fig. 1. Ratio of solute concentrations in the solid and liquid vs. molecular weight, and sedimentation coefficient. Determined by static tests on amorphous broadly distributed polystyrene in cyclohexane at 35°C.

box, maintained at  $-30^{\circ}\text{C}$ . by a refrigerating unit. Molten zones of 4.44 or 6.35 cm. lengths were passed at the rate of 9.66, 4.83, or 4.01 cm./hr. through 96.6 cm. long by 1.15 cm. diameter samples of initial total polymer concentrations ranging from 0.18 to 1.30 g./100 cc. Matter transport<sup>7</sup> was prevented by completely filling the sample containers. Samples were recovered from the zone-melted ingots by cutting them with a high speed saw into short sections which were allowed to melt. Selected sections were examined for the presence of polymer by adding a few drops of the solution maintained above the critical temperature to an excess of methanol. Intrinsic viscosities were determined with an Ubbelohde viscometer directly in the cyclohexane used for zone melting in the single-phase region at temperatures above any critical temperature. Molecular weight distributions were determined as described above.

### RESULTS AND DISCUSSION

The static test data are plotted as the ratio of the solute concentration in the solid to its concentration in the liquid versus the solute's molecular weight, as a function of concentration and of molecular weight distribution in Figures 1 and 2, respectively. In all cases examined, the lines through the experimental points have an intercept on the ordinate of 1.0 and a posi-

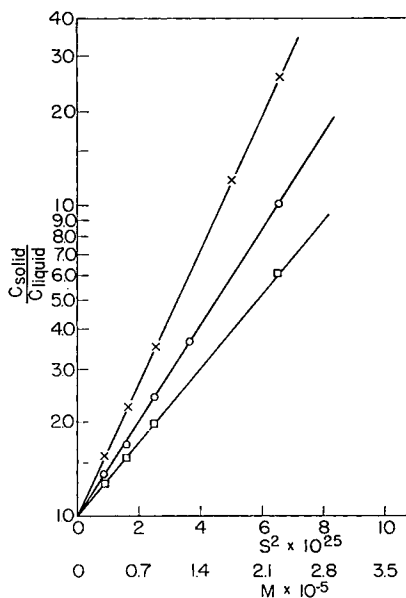


Fig. 2. Ratio of solute concentrations in the solid and liquid vs. molecular weight and sedimentation coefficient. Determined by static tests on mixtures of two amorphous narrowly distributed polystyrenes (MW = 82,000 and 267,000) in cyclohexane at  $35^{\circ}\text{C}$ ., initial concentration 0.50 g./100 cc.: (X) 82,000/267,000 = 2:1 parts by weight; (O) 82,000/267,000 = 1:1 parts by weight; ( $\square$ ) 82,000/267,000 = 1:2 parts by weight.

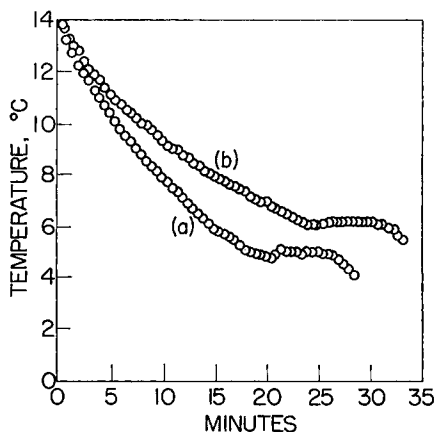


Fig. 3. Cooling curves for cyclohexane-rich polystyrene-cyclohexane solutions: (a) pure cyclohexane (b) cyclohexane with polystyrene (MW = 297,000); concentration = 1.8 g./100 cc.

tive slope. From these figures it is clear that increases in polymer concentration in the solution and in the proportion of high molecular weight material shift the solid-to-liquid concentration ratio for any species to lower values. On the basis of this evidence, it was not considered likely that entrapment played an increasingly important role with an increase of solution concentration and high molecular weight polymer. To improve the definition of the invariant temperature from cooling curve experiments, the latter were performed on solutions of the narrowly distributed polystyrene in cyclohexane. As shown in Figure 3, the material with a molecular weight of 267,000 produced an isothermal reaction at a temperature approximately one degree above the melting point of the pure solvent, indicating that the ratio of solute concentration in the solid to that in the liquid was  $> 1.0$ . The results of the zone-melting experiments can be conveniently grouped in two categories: (1) the effects of the number of zones passed and of the zone length, and (2) the effects of total polymer concentration and of zone travel rate.

#### Effects of the Number of Zones Passed and of Zone Length

A sample of the system amorphous polystyrene-cyclohexane was examined over the fraction of its length, not subject to the effect of normal freezing, in order to determine the locations where changes in the concentrations of the species present were most significant for 5 and 6 zones passed (this variable being arbitrarily chosen). Table I shows that the value of the sedimentation coefficient,  $s$ , corresponding to the maximum value of the apparent distribution function for each segment, changed more in the cases of 1.56 and 2.92 zone lengths than in either of the other pairs of successive segments investigated. (Here,  $a$  is the segment location in zone lengths from head end.) Because of this fact, the comparison of

TABLE I  
Sedimentation-Velocity Data for the First Four Segments of a  
Polystyrene-Cyclohexane Ingot with an Initial Concentration of  
2.25 g./100 cc. Zone-Melted with Five 6.35 cm. Zones Passed at  
4.83 cm./hr.

Sedimentation coefficient $s \times 10^{12}$	Product of apparent distribution function and sample concn. $\times 10^{-10}$ , gm./100 cc.			
	$a = 0.20$ , segment concn. = 1.48 g./100 cc.	$a = 1.56$ , segment concn. = 2.08 g./100 cc.	$a = 2.92$ , segment concn. = 2.27 g./100 cc.	$a = 4.28$ , segment concn. = 1.92 g./100 cc.
0.1		0.11		
0.2		0.14		
0.3		0.34		
0.4		0.78	1.86	3.58
0.5		1.35	3.97	4.15
0.6	0.01	1.87	7.33	6.53
0.7	2.09	2.87	5.20	6.22
0.8	3.17	3.85	3.41	0.77
0.9	3.31	4.20	1.01	
1.0	2.57	3.05		
1.1	2.13	2.65		
1.2	1.17	1.66		
1.3	0.14	1.35		
1.4		1.15		
1.5		0.82		
1.6		0.63		
1.7		0.46		
1.8		0.22		

all concentrations of the solute in various positions along the zone melted sample was made at these positions.

Representative molecular weight distribution curves for a zone travel rate of 4.83 cm./hr. are shown in Figure 4, where the apparent distribution function  $g(s)$  is defined by the equation:<sup>3</sup>

$$w_i = g(s) K^2/2S_i$$

and  $w_i$  and  $K'$  are the weight polymer fractions and a constant, respectively. Since in the presentation and discussion of the results only the ratios of weight fractions or of concentrations are used, a knowledge of the absolute value of the constant  $K'$  is not required.

Detailed data taken from a series of similar curves for experiments with various zone lengths and numbers of zones passed are presented in Table II. An increase in the number of passes or in the zone length resulted in increasing the difference between the weight-average molecular weight averages. Also noted is a trend for the ratio of breadths at  $1/2$  peak heights to decrease with increasing number of passes.

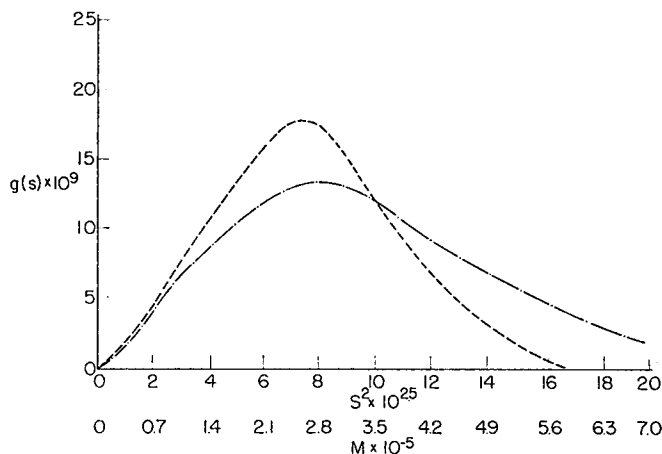


Fig. 4. Molecular weight distribution curves of segments from a sample of amorphous broadly distributed polystyrenes in cyclohexane zone-melted at 4.83 cm./hr. (initial concentration 0.75 g./100 cc.; 6 passes of 4.44 cm. zone in 96.6 cm. sample; sedimentation velocity experiment performed at 35°C. in cyclohexane): (---)  $1.56 \pm 0.20$  zone lengths from head end; (-.-.)  $2.92 \pm 0.20$  zone lengths from head end.

### Effects of Total Polymer Concentration and Zone Travel Rate

Zone melting of a mixture of the two narrowly distributed amorphous polystyrenes dissolved in cyclohexane at a zone travel rate of 4.83 cm./hr. produced an accumulation of the low molecular weight species at the head end of the ingot, and of the high molecular weight species at the tail end, as indicated by intrinsic viscosity data shown in Figure 5. This result is contrary to theoretical expectations.<sup>3</sup> The results of zone melting of broadly distributed polystyrene are summarized in Figures 6 and 7 for various number of zones passed, initial concentrations, and rate of advance of the zones. The data show that smaller molecules had their concentration ratios  $>1$ , while for larger molecules the ratios were  $<1$ , in accord with the results found with the two narrowly distributed polystyrenes. As expected, the slopes of the curves increase with the number of zones passed, indicating increased redistribution. As a result of this fact, the cross-over from values of the ratio greater than unity to values less than unity occurred at lower molecular weights with increased extent of zone melting.

An increase in the initial concentration produced also a shift of the concentration ratios for the various species. The number of species with concentration ratios  $>1$  were reduced and those with concentration ratios  $<1$  were increased with increased polymer concentration when the zone travel rate was 4.83 cm./hr.

In the case where the rate of zone travel was reduced to 4.01 cm./hr., the concentration ratio was always  $\geq 1.0$ . Because the slower rates should more nearly approximate the thermodynamically controlled behavior,



TABLE II  
Amorphous Polystyrene Zone-Melted in Cyclohexane at a Zone Travel Rate of 4.83 cm./hr.

Sample <sup>a</sup>	Initial concn., g./100 cc.	Final concn., g./100 cc.	No. of zones passed	Zone length, cm.	$\bar{M}_w$ ( $\pm 5\%$ )	$\bar{M}_{ws} - \bar{M}_{w3}$	Breadth at $\frac{1}{2}$ peak height (ph)	Breadth at $\frac{1}{2}$ ph) <sub>3</sub> (Breadth at $\frac{1}{2}$ ph) <sub>5</sub>
V <sub>2-3</sub>	0.75	0.97	5	4.44	225,000	24,000	315,000	0.74
V <sub>2-5</sub>	0.75	0.86	5	4.44	249,000		424,000	
T <sub>4-3</sub>	0.75	1.16	6	4.44	244,000		273,000	
T <sub>4-5</sub>	0.75	1.13	6	4.44	276,000		382,000	0.72
V <sub>1-3</sub>	0.75	1.14	5	6.35	181,000		203,000	
V <sub>1-5</sub>	0.75	1.11	5	6.35	215,000		287,000	0.71
T <sub>3-3</sub>	0.75	1.00	6	6.35	268,000		294,000	
T <sub>3-5</sub>	0.75	0.96	6	6.35	326,000		441,000	0.67
U <sub>2-3</sub>	0.18	0.21	5	4.44	218,000		210,000	
U <sub>2-5</sub>	0.18	0.21	5	4.44	243,000		277,000	0.74
U <sub>1-3</sub>	0.18	0.22	5	6.35	287,000		221,000	
U <sub>1-5</sub>	0.18	0.22	5	6.35	319,000		343,000	0.64
U <sub>3-3</sub>	0.18	0.23	6	6.35	201,000		238,000	
U <sub>3-5</sub>	0.18	0.19	6	6.35	—		—	—

<sup>a</sup> Samples labeled "—3" refer to segments taken 1.56  $\pm$  0.20 zone lengths from the head end; samples labeled "—5" refer to segments taken 2.92  $\pm$  0.20 zone lengths from the head end.

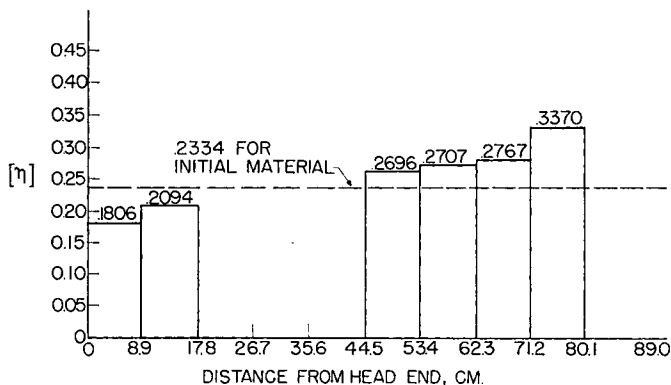


Fig. 5. Intrinsic viscosity vs. sample position after zone melting a mixture of two amorphous narrowly distributed polystyrenes (MW = 82,000 and 267,000) in cyclohexane at 4.83 cm./hr. Initial concentration: 3.17 g./100 cc.; 6 passes of 10.16 cm. zone in 96.6 cm. sample. Viscosities measured at 34.2°C. Numbers refer to viscosity values.

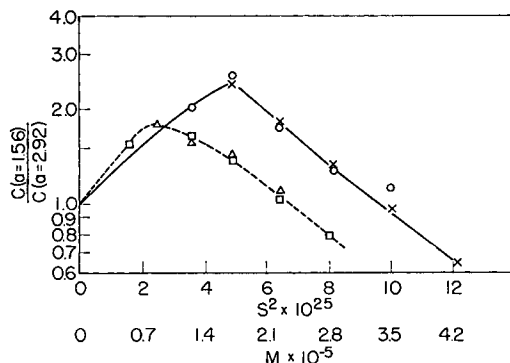


Fig. 6. Ratio of solute concentrations at 1.56 and 2.92 zone lengths from the head end vs. molecular weight, resulting from zone melting 96.6 cm. samples at 4.83 cm./hr. concentration 0.18 g./100 cc.; amorphous broadly distributed polystyrene; sedimentation velocity experiment performed at 35°C. in cyclohexane): (—) 5 zone passes: (O) 6.35 cm. zone length, (X) 4.44 cm. zone length; (---) 6 zone passes: (□) 6.35 cm. zone length, (Δ) 4.44 cm. zone length.

these data were compared with those that would obtain as calculated from Lord's equation:<sup>8</sup>

$$C_n(a) = C_0 \left\{ 1 - \left[ [(1 - K)e^{-Ka}] \left[ n - \sum_{t=1}^{n-1} \sum_{s=1}^t K^{s-1} e^{-sK} \sum_{r=0}^{s-1} \frac{s^{s-r-2} a^r (r+1 - Ka)}{(s-r-1)! r!} \right] \right] \right\}$$

where  $C$  is the solute concentration,  $C_0$  is the initial concentration,  $n$  is the number of zones passed,  $a$  is the distance in the ingot from the head end measured in zone lengths, and  $s$ ,  $r$ , and  $t$  are integers.

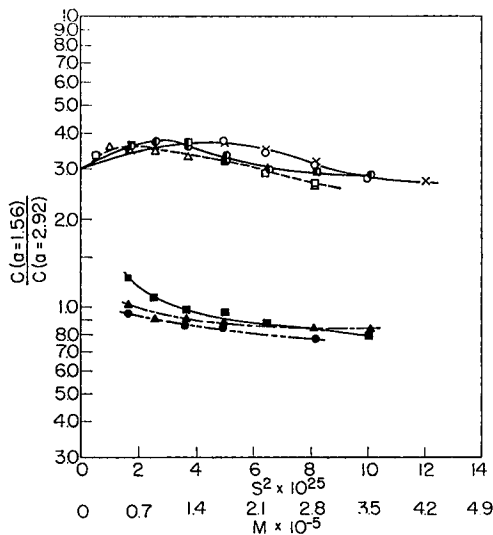


Fig. 7. Amorphous broadly distributed polystyrene sedimentation velocity experiments performed at 35°C. in cyclohexane. Ratio of solute concentrations at 1.56 and 2.92 zone lengths from head end vs. molecular weight, resulting from zone melting 96.6 cm. samples: (⊙) 4.83 cm./hr., 0.75 g./100 cc., 5 zone passes, 6.35 cm. zone length; (×) 4.83 cm./hr., 0.75 g./100 cc., 5 zone passes, 4.44 cm. zone length; (⊠) 4.83 cm./hr., 0.75 g./100 cc., 6 zone passes, 6.35 cm. zone length; (Δ) 4.83 cm./hr., 0.75 g./100 cc., 6 zone passes, 4.44 cm. zone length; (●) 9.66 cm./hr. 1.30 g./100 cc., 5 zone passes, 6.35 cm. zone length; (▲) 9.66 cm./hr., 0.80 g./100 cc., 5 zone passes, 6.35 cm. zone length; (■) 9.66 cm./hr., 0.30 g./100 cc., 5 zone passes 4.44 cm. zone length; (⊙) 4.01 cm./hr., 0.75 g./100 cc., 5 zone passes, 6.35 cm. zone length; (■) 4.01 cm./hr., 0.75 g./100 cc., 5 zone passes, 4.44 cm. zone length.

Ratios of  $C_n (a = 1.56)$  to  $C_n (a = 2.92)$  were computed with the aid of a Bendix G-15 computer for various combinations of the effective segregation coefficient, the number of zones passed, and the location of the ingot, and the results plotted as a function of the corresponding segregation coefficients (Fig. 8). Ambiguity in the choice of the values of the segregation coefficient for cases where the ratio of concentrations was  $> 1$  was resolved by assuming a monotonic relation for segregation coefficients versus molecular weight. In this way, effective segregation coefficients could be assigned to the species, and these results are shown in Figure 9. The linearity of the semilogarithmic plot conforms to the thermodynamic theory.

It is clear from the above results that the redistribution of solute species in the faster experiments is controlled by a time-dependent phenomenon. Diffusion of solute species from the bulk liquid to the interface cannot provide the determining effect since this process alone cannot shift an effective segregation coefficient to the opposite side of 1.0 from the equilibrium value. A plausible explanation for the results of the faster experiments can be obtained if it is assumed that the rate-controlling process involved the polymer-rich phase breaking down to provide solute species which are

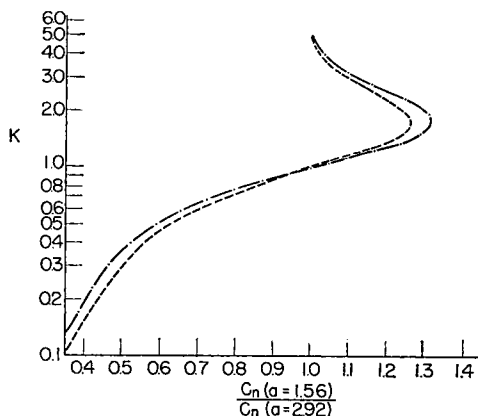


Fig. 8. Effective segregation coefficient  $K$  vs. the ratio of resulting solute concentrations in the zone melted ingot at 1.56 and 2.92 zone lengths from the head end: (---) 5 zones passes; (—) 6 zones passes.

more soluble in the solid than in the liquid (resorption). If the time necessary for the three-phase reaction to occur is longer than the time allowed by the advance of the freezing interface, the polymer-rich phase will be carried along in the liquid. This results in concentration ratios  $<1.0$ , even when the equilibrium values are  $>1$ . Any process which enhances the formation or retention of the second phase in the liquid zone contributes to an increase in the polymer carried in the liquid toward the tail end of the sample. Thus, increased total concentration of polymer or increased proportion of high molecular weight components result in more species being carried in the liquid.

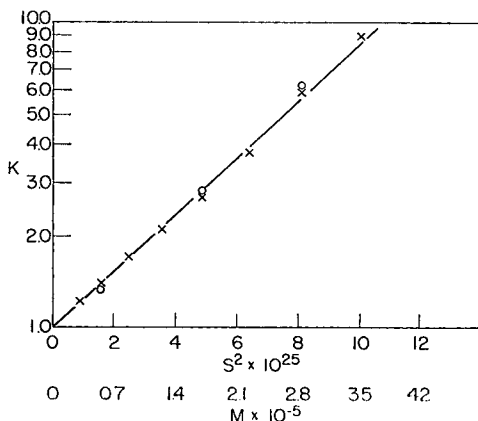


Fig. 9. Amorphous broadly distributed polystyrene in cyclohexane. Effective segregation coefficient vs. molecular weight, determined by zone melting 96.6 cm. samples at 4.01 cm./hr. Initial concentration 0.75 g./100 cc.; sedimentation velocity experiment performed at 35°C. in cyclohexane; 5 zone passes: (O) 6.35 cm. zone length; (X) 4.44 cm. zone length.

The decrease in the magnitude of the slope of the curves of concentration ratios versus molecular weights upon increased total initial concentration or zone travel rate (at rates greater than 4.83 cm./hr.) may be attributed to a decrease in mobility of the individual species that comprise the polymer-rich phase under these conditions.

Reduction of the amount of polymer-rich phase through the resorption reaction is a diffusion-controlled process, and thus dependent upon the mobility of the species in the polymer-rich phase. Some justification for this explanation of the observed redistributions is provided by the comparison between the diffusion velocity with the rate of zone travel for a typical zone melting experiment. (See Appendix.) The results of the calculation show that the diffusion velocity is comparable to the rates of advance of the freezing interface. However, it should be recognized that the rate of the resorption reaction does not explain why the behavior, measured in terms of concentration ratios, is intermediate between that expected from thermodynamic considerations and the limiting non-equilibrium case. Although several suggestions can be advanced to rationalize this behavior, the present results are not able to justify any particular explanation.

We wish to thank the Dow Chemical Company for the gift of the narrow distributed polystyrene samples.

### APPENDIX

#### Comparison of Polymer Diffusional Velocities with the Rate of Zone Travel in Zone Melting a Cyclohexane-Rich Polystyrene-Cyclohexane System

Diffusion flux is defined as

$$J = - D(\partial c/\partial x) \tag{1}$$

and diffusion velocity as

$$V_D = J/(\text{concn.}) \tag{2}$$

where

$$-\frac{\partial c}{\partial x} \simeq (C_0 - C_L)/\delta - C_s \left( \frac{1}{K_{\text{equil}}} - \frac{1}{K_{\text{eff}}} \right) / \delta \tag{3}$$

where  $C_s/C_L = K_{\text{eff}}$  and  $C_s/C_0 = K_{\text{equil}}$  and  $C_0$ ,  $C_s$ ,  $C_L$ , and  $\delta$  for  $K < 1$  and  $K > 1$  are shown diagrammatically in Figure 10.

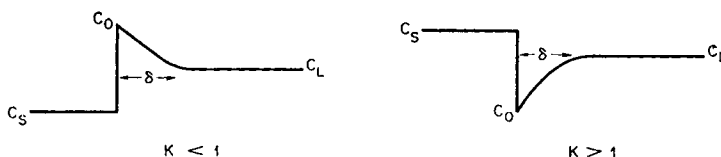


Fig. 10. Relationships for  $K > 1$  and  $K < 1$ .

Thus,

$$V_D \simeq \frac{D(\text{concn.}) \left( \frac{1}{K_{\text{equil}}} - \frac{1}{K_{\text{eff}}} \right)}{\delta(\text{concn.})} \quad (4)$$

$$\simeq \frac{D}{\delta} \left( \frac{1}{K_{\text{equil}}} - \frac{1}{K_{\text{eff}}} \right) \quad (5)$$

Thus, a value of  $D/\delta$  is required. This can be obtained as follows:<sup>9</sup>

$$\ln\left(\frac{1}{K_{\text{eff}}} - 1\right) = \ln\left(\frac{1}{K_{\text{equil}}} - 1\right) - \frac{f\delta}{D} \quad \text{for } K < 1 \quad (6)$$

$$\ln\left(1 - \frac{1}{K_{\text{eff}}}\right) - \ln\left(1 - \frac{1}{K_{\text{equil}}}\right) - \frac{f\delta}{D} \quad \text{for } K > 1 \quad (7)$$

where  $f$  is the rate of advance of the freezing interface.

For the case at hand, data are selected for the species whose molecular weight is  $1.4 \times 10^5$  ( $S^2 = 0.40 \times 10^{-24}$ ). By extrapolation of static test data, Figure 1, to 0.75 g./100 cc., a value of  $K_{\text{equil}} = 2.60$  is obtained. From Figure 9 an effective segregation coefficient of 2.37 is obtained when  $f = 4.01$  cm./hr. =  $1.15 \times 10^{-3}$  cm./sec. From these data,  $\delta/D$  is found to be 53.9 sec./cm. Thus, by eq. (5) above,  $V_D$  is calculated to be  $0.687 \times 10^{-3}$  cm./sec. Thus, the diffusional velocity is comparable to the rate of zone travel ( $1.15 \times 10^{-3}$  cm./sec.).

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### Résumé

Nous avons rassemblé dans une communication les résultats expérimentaux de l'application des techniques de fusion par zone à des solutions diluées de polystyrène dans le cyclohexane, dans des conditions opératoires différentes, de même que les observations de solidification statique de ces solutions. Nous avons étudié les variables suivantes: la concentration en polymère, le nombre de régions traversées, la longueur de ces régions et la vitesse à laquelle on les traverse. Les résultats démontrent que lors

d'une vitesse lente de passage de région (à peu près 4.01 cm/heure), il apparaît une redistribution des espèces en solution conformément aux prédictions thermodynamiques. Dans ce cas, les deux liquides, l'un riche en cyclohexane, l'autre riche en polymère, qui coexistent à des températures justes supérieures à la région de solidification, réagissent pour former une solution solide riche en cyclohexane lors de la solidification. La solution solide contient une concentration en espèces polymériques supérieure à celle du liquide riche en cyclohexane; de plus, le rapport de la concentration en solide à la concentration en liquide augmente de manière exponentielle en fonction du poids moléculaire du soluté. Le résultat concret est l'accumulation des espèces du soluté dans la première partie du lingot en fusion (c.à.d. celle qui fond et se solidifie la première); dans cette ordre de choses les espèces de poids moléculaires les plus élevés subissent la plus forte redistribution. À des vitesses de passage de zone plus rapides (à peu près 4.83 cm/heure), on a observé une inversion de la direction d'accumulation en fonction du poids moléculaire; les espèces de poids moléculaires les plus élevés, sont transportés de plus en plus vers la dernière partie (c.à.d. celle qui gèle la dernière de l'échantillon). Une augmentation de la concentration en polymère favorise cet effet. Ces faits ont reçu leur interprétation en supposant que la résorption de certaines espèces de poids moléculaire élevé à partir de la phase riche en polymère n'est pas suffisamment rapide en comparaison de la vitesse de gélification, et qu'une partie de la phase riche en polymère est transportée par le mouvement de la région liquide. Avec des vitesses de passage nettement plus élevées (à peu près 9.66 cm/heure) on a trouvé une diminution de la redistribution des espèces solides. Une augmentation de la concentration totale en polymère diminue la sélectivité du fractionnement. Cet effet est interprété comme étant le résultat de la diminution du temps pendant lequel la réaction de résorption s'effectue dans ces expériences par rapport à la vitesse du mouvement de l'interphase. On a discuté des considérations qualitatives des caractéristiques thermodynamiques du système polymère-solvant le plus favorable à un fractionnement de zone effectif. On rapporte l'effet du fractionnement de zone sur la distribution du poids moléculaire de quelques uns de ces échantillons.

### Zusammenfassung

Versuchsergebnisse bei der Anwendung des Zonenschmelzverfahrens auf verdünnte Polystyrollösungen in Cyclohexan unter verschiedenen Arbeitsbedingungen werden zusammen mit Beobachtungen bei statischen Erstarrungstests an den Lösungen mitgeteilt. Der Einfluss der Polymerkonzentration, der Anzahl der Zonenpassagen, der Zonenlänge und der Zonenwanderungsgeschwindigkeit wurde untersucht. Die Ergebnisse zeigten, dass bei niedriger Zonenwanderungsgeschwindigkeit (ca 4,01 cm/Stunde) die Verteilung des Gelösten in Übereinstimmung mit den thermodynamischen Erwartungen erfolgte. In diesem Fall reagieren eine cyclohexan-reiche flüssige Phase und eine polymer-reiche flüssige Phase, die bei Temperaturen gerade oberhalb des Erstarrungsbereiches koexistieren, bei der Erstarrung unter Bildung einer cyclohexan-reichen festen Lösung. Die feste Lösung enthielt alle Polymermoleküle in höherer Konzentration als die cyclohexan-reiche Flüssigkeit, wobei das Verhältnis der Konzentration in der festen zu der in der flüssigen Phase mit dem Molekulargewicht des Gelösten exponentiell zunahm. Das Gesamtergebnis war eine Anhäufung aller gelösten Stoffe am Kopf- (d.h. zuerst geschmolzenen und zuerst gefrorenen)-ende des zonengeschmolzenen Blockes, wobei die höhermolekularen Anteile in dieser Hinsicht die stärkste Verteilung zeigten. Bei etwas höherer Geschwindigkeit der Zonenwanderung (ca. 4,83 cm/Stunde) trat eine Umkehrung der Anhäufungstendenz in Abhängigkeit vom Molekulargewicht ein; die höhermolekularen Anteile wurden gegen das Schwanz- (d.h. zuletzt gefrorene)ende der Probe geführt. Erhöhung der Gesamtkonzentration des Polymeren verstärkte diesen Effekt. Diese Erscheinungen wurden dahingehend gedeutet, dass die Resorption des höhermolekularen Anteils aus der polymer-reichen Phase nicht schnell genug im Vergleich zur Gefrierungsgeschwindigkeit war und ein Teil der polymer-reichen Phase in der

sich bewegenden flüssigen Zone mitgeführt wurde. Bei wesentlich höherer Wanderungsgeschwindigkeit der Zone (ca. 9,66 cm/Stunde) wurde eine Herabsetzung der Verteilung des Gelösten gefunden. Erhöhung der Gesamtkonzentration des Polymeren setzte die Selektivität der Fraktionierung herab. Dieser Effekt wurde als Folge des geringeren Ausmasses der Resorptionsreaktion bei diesen Versuchen im Verhältnis zur Bewegungsgeschwindigkeit der Interphase gedeutet. Qualitative Überlegungen über die thermodynamische Charakteristik der zur wirksamen Zonenfraktionierung am besten geeigneten Polymer-Lösungsmittelsysteme werden angestellt. Der Einfluss der Zonenfraktionierung auf die Molekulargewichtsverteilung einiger Proben wird angegeben.

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