I) for PDMS in benzene might be a hint toward a relatively large $\xi_\tau$ which starts to cross the observation range of $Q$ at higher temperatures and thereby lowers the effective exponent.

However, on the basis of the experimental data available up to now, the problem of the crossover from $\Theta$ to good solvent conditions and the related increase of the line width cannot be solved. Further experiments with higher accuracy spin echo technique[14,15] are planned to investigate this problem.

As already stated, measurements of the quasi-elastic spectra $S_{\mathrm{coh}}{}^{\mathrm{poly}}(Q, \omega)$ now allow a line-shape analysis which can distinguish between a Lorentzian-like scattering law and the scattering law $g_c(\tilde{\omega})$, given by Dubois-Violette and de Gennes, as it was possible[16] by measuring $S_{\mathrm{coh}}{}^{\mathrm{poly}}(Q, t)$ in Fourier space. This is not surprising because the line shapes of both scattering laws differ mainly at higher energy transfers,[12] where systematic errors are larger than in the central parts of the spectra. On the other hand, deviations from the initial slope of $S(Q, t)$ are easily observed with the spin echo technique, which has a high accuracy in this range.

**Acknowledgment.** We thank Professor Dr. E. W. Fischer and Professor Dr. T. Springer for their continuous interest in this work and for many stimulating discussions. We are also indebted to the Institut Laue-Langevin, Grenoble, for providing the experimental factilities. The assistance of Dr. A. Heidemann and J. Bauchat in performing these experiments is gratefully acknowledged.

## References and Notes

(1) P. G. de Gennes, *Physics*, **3**, 37 (1967).
(2) E. Dubois-Violette and P. G. de Gennes, *Physics*, **3**, 181 (1967).
(3) Z. Akcasu and H. Gurol, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1 (1976).
(4) Z. A. Akcasu and J. S. Higgins, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1745 (1977).
(5) P. G. de Gennes, *Macromolecules*, **9**, 587 (1976).
(6) P. G. de Gennes, *Macromolecules*, **9**, 594 (1976).
(7) M. Benmouna and Z. A. Akcasu, *Macromolecules*, **11**, 1187 (1978).
(8) Z. A. Akcasu and M. Benmouna, *Macromolecules*, **11**, 1193 (1978).
(9) W. Hess and R. Klein, *Makromol. Chem.*, **180**, 285 (1979).
(10) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(11) G. Allen, R. Ghosh, J. S. Higgins, J. P. Cotton, F. Farnoux, G. Jannink, and G. Weil, *Chem. Phys. Lett.*, **38**, 577 (1976).
(12) J. S. Higgins, G. Allen, R. E. Ghosh, W. S. Howells, and F. Farnoux, *Chem. Phys. Lett.*, **49**, 197 (1977).
(13) A. Heidemann, ILL Internal Report No. 744230T, Grenoble, 1974.
(14) F. Mezei, *Z. Phys.*, **255**, 146 (1972).
(15) J. B. Hayter, *Z. Phys. B*, **31**, 117 (1978).
(16) D. Richter, J. B. Hayter, F. Mezei, and B. Ewen, *Phys. Rev. Lett.*, **41**, 1484 (1978).
(17) H. J. Hölle and B. Lehnen, *Eur. Polym. J.*, **11**, 663 (1975).
(18) G. Meyerhoff in "Kunststoff-Handbuch", R. Vieweg and D. Braun, Eds., Hanser Verlag, München, 1975.
(19) J. P. Cotton and H. Benoit, *J. Phys. (Paris)*, **36**, 905 (1975).
(20) P. Debye, *J. Phys. Chem.*, **51**, 18 (1947).
(21) J. Brandrup and E. H. Immergut, Eds., "Polymer Handbook", Wiley, New York, London, Sydney, 1975.
(22) B. Farnoux, F. Boné, J. P. Cotton, M. Daoud, G. Jannink, M. Nierlich, and P. G. de Gennes, *J. Phys. (Paris)*, **39**, 77 (1978).
(23) W. Burchard, M. Schmidt, and W. H. Stockmayer, *Macromolecules*, in press.

---

# Polymer/Polymer Diffusion. 2. Effect of Temperature and Molecular Weight on Macromolecular Diffusion in Blends of Poly(vinyl chloride) and Poly($\epsilon$-caprolactone)

**P. T. Gilmore, R. Falabella, and R. L. Laurence***

*Department of Polymer Science and Engineering, University of Massachusetts at Amherst, Amherst, Massachusetts 01003.* *Received July 23, 1979*

ABSTRACT: The effect of molecular weight and temperature on the mutual diffusion coefficient for a miscible binary polymer system has been examined by using a technique combining scanning electron microscopy and energy-dispersive X-ray analysis. The system studied, poly(vinyl chloride)/poly($\epsilon$-caprolactone), has been shown to be compatible on the molecular level. The mutual diffusion coefficients for various molecular weights of the PVC/PCL system were determined to be on the order of $10^{-12}$–$10^{-13}$ cm$^2$/s at 90 °C with the diffusion coefficient roughly proportional to $M^{-1}$, the latter result not predicted by the few existing theories of diffusion of macromolecules in the melt. Measurement of the diffusion coefficient at several temperatures shows an activation energy for diffusion of 11.7 kcal/mol. Comparisons between these results and various other theoretical and experimental investigations of macromolecular diffusion present some interesting contrasts.

Macromolecular diffusion in the solid or melt state is a subject infrequently addressed in the literature. In the first paper in this series,[1] an experimental technique which allows the measurement of the concentration profile of an interdiffused binary polymer system was described. The technique is a combination of scanning electron microscopy and energy-dispersive analysis of X-ray fluorescence, permitting direct observations of the interface between the two polymeric components and measurement of the concentration gradient of one, or both, of the materials. This technique has been applied to the polymer pair poly(vinyl chloride)/poly($\epsilon$-caprolactone). Specifically, the effects of molecular weight and temperature on the mutual diffusion coefficient for the system have been observed, with the diffusion coefficient calculated from the data using a solution to the diffusion equation.

Various theoretical models have been used for describing motion of a polymer molecule in the melt, resulting in as many relationships between the diffusion coefficient and molecular weight. Few studies have been undertaken to actually clarify this dependence. Results presented here will be compared with those of previous investigators and theorists.

## Experimental System

The experimental details are described in ref 1; a brief description is included here. Sheets of PVC, cast on glass from THF solution, are dried and placed in a vacuum oven at the specified

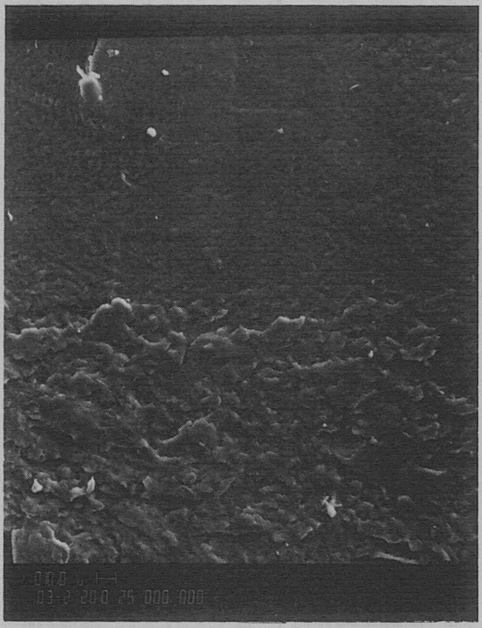

**Figure 1.** SEM micrograph of PVC/PCL interface. 10-$\mu$m bar shown at bottom left.

Table I

| sample | $M_n$ | $M_w$ | $M_w/M_n$ |
|---|---|---|---|
| PVC-2 | 18 500 | 46 500 | 2.5 |
| PVC-3 | 33 200 | 73 700 | 2.2 |
| PVC-4 | 33 600 | 86 400 | 2.6 |
| PVC-5 | 40 300 | 97 800 | 2.4 |
| PVC-6 | 40 600 | 102 000 | 2.5 |
| PCL-1 | 1 200 | 1 800 | 1.5 |
| PCL-2 | 1 400 | 2 600 | 1.8 |
| PCL-3 | 5 400 | 9 400 | 1.7 |
| PCL-4 | 19 200 | 37 200 | 1.9 |

diffusion temperature. PCL is placed on top of the PVC sheet. The temperature is maintained above the melting temperature of PCL ($T_m$ = 63 °C) and PCL flows sufficiently to provide excellent surface contact between the two polymers. After diffusing for a period of time, between $5 \times 10^5$ and $10^7$ s (7 days to 3 months), the interdiffused sheets are fractured normal to the interfacial plane, exposing the interface for examination in the scanning electron microscope (SEM). An example of the interface of the interdiffused materials is shown at low magnification in Figure 1. The change in morphology is obvious and due to the crystallinity of the PCL. (Crystallinity was not expected to affect the measured concentration profile. PVC is excluded from the PCL crystallites but remains in the interstitial areas of the semicrystalline material.[2] The phase size is, therefore, on the order of 100 Å, several orders of magnitude below the distances across which the concentration profile is measured.)

The materials used are shown in Table I. The density of blends of PVC/PCL has been shown to be very nearly a linear average of the densities of the two components,[3] implying constant partial mass density in the blend. The measurement of a single glass transition temperature of blends of PVC/PCL has indicated that the materials are miscible.[4] In addition, small-angle X-ray scattering of blends of PVC-6/PCL-4 of various concentrations demonstrates that these materials are compatible at the molecular level.[3] The molecular weights shown in Table I were determined by gel permeation chromatography. The diffusion coefficient was calculated for all molecular weights of PVC and PCL, using one PCL or PVC, respectively, as the base material.

The method of concentration measurement is detailed in ref 1. Essentially, the technique makes use of the phenomenon of electron-beam-induced X-ray fluorescence of the chlorine atoms of PVC. With the interface exposed as in Figure 1, the number of X-ray events occurring within a fixed time period are counted at several positions at varying distances from the interface. Extreme care is taken to ensure that the direction from one point of concentration measurement to the next is normal to the interfacial plane.[5] The electron beam is used in line form rather than full scan to give adequate X-ray count rates yet minimize sample damage. At each position, the position of the electron beam, and therefore the position of X-ray generation, is recorded photographically and the number of X-ray events also recorded. A micrograph with electron beam positions superimposed is shown in Figure 2. Since the number of X-ray events is directly proportional to the number of atoms from which they originate,[6] a concentration profile is developed for chlorine, and PVC, in the interdiffused sample. A typical concentration profile is shown in Figure 3. Several of these profiles are recorded at each diffusion time and several diffusion times are used for each polymer pair.

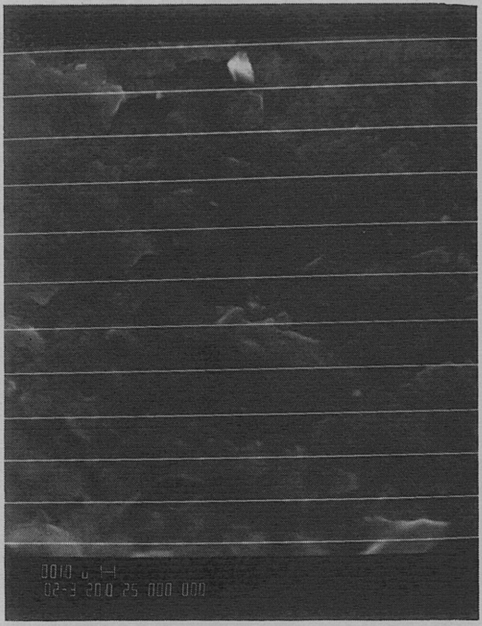

**Figure 2.** SEM micrograph of PVC/PCL interface. Lines correspond to positions of chlorine X-ray emission measurement. 1-$\mu$m bar shown at bottom left.

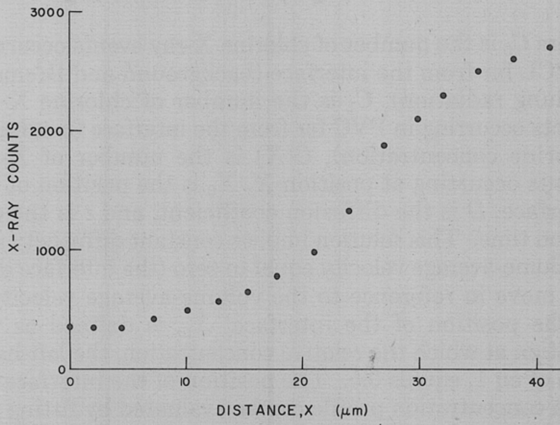

**Figure 3.** Example of experimentally measured concentration profile. Chlorine X-ray counts vs. distance.

There will be some smearing of each concentration measurement since an electron has a finite mean free path within the polymeric material; the X-rays are not generated at a unique point.[1] Therefore, an attempt was made to measure what was known to be an infinitely sharp concentration profile. A sample of PVC/PCL was placed in the vacuum oven only long enough to allow contact between the two materials (about 0.5 h). The resulting concentration profile measured by this technique was precisely as expected—infinitely sharp. Smearing was negligible since the concentration drop from PVC to PCL occurred in less than 1 $\mu$m.

## Data Analysis

The materials used in this study demonstrate a constant partial mass density. Using this and the fact that the

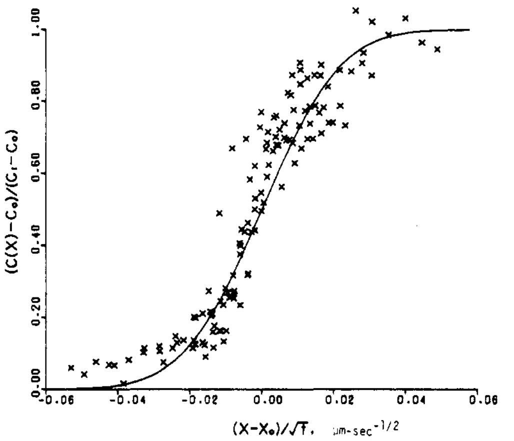

**Figure 4.** Example of master curve. Reduced concentration vs. $(X - X_0)/t^{1/2}$ (eq 1).

sheets of material are much thicker than the depth of interpenetration, the solution to the diffusion equation[7] is

$$\frac{C(X) - C_0}{C_1 - C_0} = \tfrac{1}{2}\left[1 + \mathrm{erf}\left(\frac{X - X_0}{(4Dt)^{1/2}}\right)\right] \qquad (1)$$

where $C_0$ is the number of chlorine X-ray events occurring in PCL far from the interface (background and Bremsstrahlung radiation), $C_1$ is the number of chlorine X-ray events occurring in PVC far from the interface (maximum chlorine concentration), $C(X)$ is the number of X-ray counts occurring at position $X$, $X_0$ is the position of the interface, $D$ is the diffusion coefficient, and $t$ is the diffusion time. This solution implies constant diffusivity and a volume-average velocity equal to zero (the interface does not move in reference to the volume-average velocity).[5]

The position of the interface, $X_0$, is defined as the position at which the relative concentration, the left-hand side of eq 1, equals 0.5. The position of the interface for each concentration profile can be evaluated by fitting the data to eq 1 by using a nonlinear least-squares analysis. Minimization of the error between the actual data and the calculated curve yields a value for $X_0$ for each profile. Then, all profiles can be taken in congress since all should fit on one master curve for the particular polymer pair. Again, the data are fit to eq 1 and a value is calculated for the diffusion coefficient. An example of a master curve is shown in Figure 4. The line is simply that determined by the value of $D$ returned from the regression analysis (best fit line). The standard error in $D$ as calculated from the points is ±10%. A more realistic error determined from a propagation of error analysis[5] is ±25%.

This method of data handling is greatly different from that described in ref 1 and offers much more accuracy since all data are used.

## Results and Discussion

**Effect of Molecular Weight.** The effect of molecular weight on the diffusion coefficient for macromolecules in the melt state has been only infrequently described in theoretical terms, due to the difficulty of describing the cooperative motion of many entangled chains. Bueche[8] made an attempt to directly relate the diffusion coefficient to the bulk zero-shear viscosity. This, of course, would lead to the expectation that the diffusion coefficient would be proportional to $M^{-3.4}$ since Bueche claimed that the product $D\eta$ was a constant and $\eta$ is known to vary with $M^{+3.4}$ when $M$ is greater than some critical molecular weight.[9] More recently, de Gennes[10] proposed the concept of reptation to describe the motion of a single polymer chain whose motion is constrained by the fixed positions of surrounding macromolecules. The free molecule must move within a pipe defined by these fixed points, the result being a dependence of the diffusion coefficient upon $M^{-2}$.

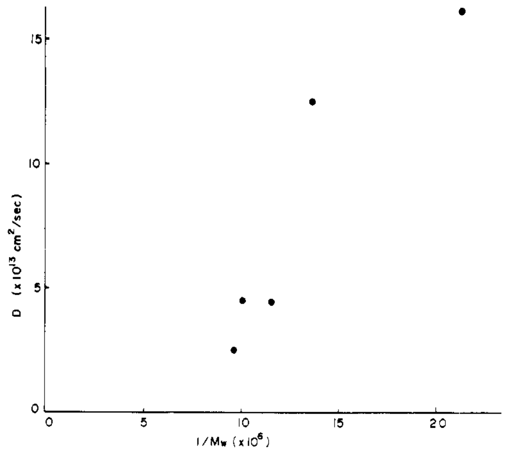

**Figure 5.** $D$ vs. $1/M_w$ for PVC. $\bar{M}_w$(PCL) = 3.7 × 10$^4$.

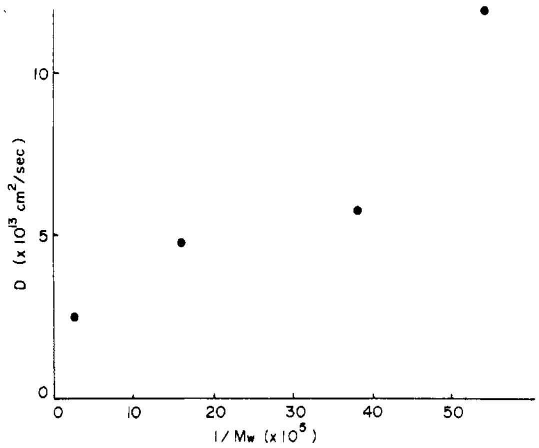

**Figure 6.** $D$ vs. $1/M_w$ for PCL. $\bar{M}_w$(PVC) = 1.02 × 10$^5$.

The results of this study agree with none of these theoretical descriptions. Rather, the indication is that the mutual diffusion coefficient of the PVC/PCL system, as shown in Figures 5 and 6, demonstrates a linear dependence on $M^{-1}$, a result predicted for a free Rouse chain.[11] A plot of log $D$ vs. log $M$, a more usual method of presenting such data, does not clarify the $D$ vs. $M$ relationship because of the scatter in the points. Figures 5 and 6 do show one interesting aspect of the data, i.e., that if straight lines are constructed they will not pass through the origin, as one would expect. This is attributed to polydispersity and the actual profile of the molecular weight distribution.

The scatter in the data as presented is believed to be a result of the polydispersity of the materials employed. As can be seen in Table I, the molecular weight distributions of all samples are slightly broader than a most probable distribution. Given that molecular weight affects the diffusion coefficient, it is expected that shorter molecules will diffuse faster than longer ones. Obviously, any attempt at experimental determination of the precise relationship between the diffusion coefficient and the molecular weight must require the use of monodisperse materials. As well, since the the investigation described here and in ref 1 makes use of two polymers, the ideal situation would have both components of identical molecular weight. Nonetheless, the indication from this data is that $D \sim M^{-1}$.

Kumagai et al., using a variation of Bueche's technique,[23] obtained similar results. Polystyrene was tagged with tritium; diffusion of a thin layer of this material into a block of untagged polystyrene was measured by the decrease in radiation as a function of time.[20] Tagged materials were monodisperse, and the diffusion coefficient was seen to depend upon $M^{-1.0}$, a result consistent with our study.

The only other studies which examine the effect of molecular weight on the diffusion of macromolecules are those reported by Klein[12-14] and Kishimoto and co-workers.[15-19] Klein and Briscoe[14] used infrared microdensitometry to obtain the result that $D \sim M^{-2.0}$ for the diffusion of deuterated polydisperse polyethylene in polyethylene at 176 °C. The Kishimoto work also used microspectrophotometry and produced results qualitatively in agreement with the observation of Klein and Briscoe. The Kishimoto studies involved chemically tagged polystyrene and nylon-12. One major criticism of the Kishimoto work is that the field of measurement was of the order of the samples thickness, 50 $\mu$m. This would lead to considerable diffraction broadening. Such a problem was negligible in the experimental configuration of Klein and Briscoe, since their slit width, though comparable to the sample thickness, 90 $\mu$m, was a small fraction of the total field ($\sim$1 cm). The Klein–Briscoe technique, by their admission, is limited to systems with diffusion coefficients larger than $10^{-10}$ cm$^2$/s. This was attainable with relatively high temperatures and oligomeric deuterated polyethylene (i.e., the largest $M_w$ was $2.3 \times 10^4$). It was surprising to find diffusion coefficients for modestly large molecules reported to be as large as $10^{-6}$ cm$^2$/s, comparable to $CCl_4$ in ethylene–propylene rubber at 80 °C. It should be noted that the Klein–Briscoe determination used only the central part of the concentration profile, whereas in this work, observations are made at several intervals in the course of the experiment, offering through the Matano–Boltzmann analysis a master curve from which the diffusivity can be determined. Other attempts to measure macromolecular diffusion in the melt have yielded values for $D$ several orders of magnitude lower than Klein and Briscoe's value and are in reasonable agreement with this investigation.[20-24]

**Effect of Temperature.** By employing an Arrhenius-type expression for the diffusion coefficient

$$D = D_0 \exp(-Q/RT)$$

a value for the apparent activation energy for diffusion, $Q$, can be calculated from diffusion data at several temperatures. Figure 7 demonstrates this ($T_d$ : 70, 90, 110 °C), giving a value for $Q$ of 11.7 kcal/mol for the PVC-6/PCL-4 system. This is near the value reported for poly($n$-butyl acrylate) of 13.2 kcal/mol.[18] It is also close to values reported for the activation energy for viscous motion[9] but markedly lower than that reported by Klein and Briscoe.

## Conclusion

The experimental determination of the mutual diffusion coefficient for the compatible system poly(vinyl chloride)/poly($\epsilon$-caprolactone) indicates that the diffusion coefficient is inversely proportional to the first power of the molecular weight. The combination of scanning electron microscopy and energy-dispersive X-ray analysis possesses sufficient resolution, not available in optical systems, to measure the concentration profile of the interdiffused materials with diffusion times of about 1 month. Diffusion coefficients were determined to be in the range $10^{-12}$–$10^{-13}$ cm$^2$/s. By variation of the temperature at which diffusion took place, an activation energy for diffusion of 11.7 kcal/mol was determined.

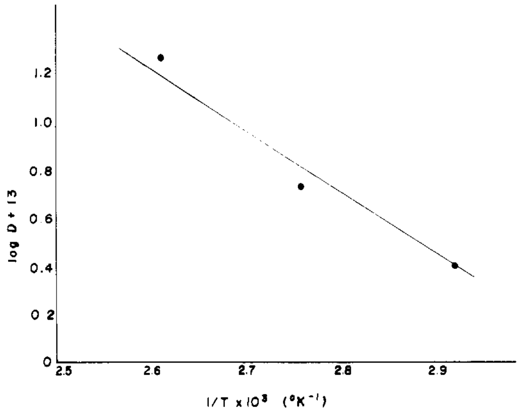

**Figure 7.** log $D$ vs. $1/T$ for PVC-6/PCL-4. Slope of the linear least-squares line gives an apparent activation energy for diffusion of 11.7 kcal/mol. $M_w$(PVC) = 102 000; $M_w$(PCL) = 37 000.

**Acknowledgment.** We thank R. Jenkins for the GPC analysis of all materials used in this investigation, Professors F. E. Karasz and W. J. MacKnight for many useful discussions, and the National Science Foundation for support through the Materials Research Laboratory and NSF DMR 7820606.

## References and Notes

(1) F. P. Price, P. T. Gilmore, E. L. Thomas, and R. L. Laurence, *J. Polym. Sci., Polym. Symp.*, **No. 63**, 33 (1978).
(2) R. S. Stein, F. Khambatta, F. Warner, and T. Russell, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1391 (1976).
(3) T. Russell, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1978.
(4) J. V. Koleske and R. D. Lundberg, *J. Polym. Sci., Part A-2*, **7**, 795 (1969).
(5) P. T. Gilmore, Ph.D. Thesis, University of Massachusetts, Amherst, MA, 1978.
(6) D. C. Joy and D. M. Maher, *IITRI/SEM*, 1, 325 (1977).
(7) A. Fick, *Ann. Phys. Chem.*, **170**, 59 (1855).
(8) F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).
(9) W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1 (1973).
(10) P. G. de Gennes, *J. Chem. Phys.*, **55**, 572 (1971).
(11) P. G. de Gennes, *Macromolecules*, **9**, 954 (1976).
(12) J. Klein, *Nature (London)*, **271**, 143 (1978).
(13) J. Klein and B. J. Briscoe, *Polymer*, **17**, 481 (1976).
(14) J. Klein and B. J. Briscoe, *Proc. R. Soc. London, Ser. A*, **365**, 53 (1979).
(15) H. Veno, S. Otsuka, and A. Kishimoto, *Kobunshi Ronbunshu*, **35**, 339–44 (1978).
(16) H. Veno, S. Otsuka, and A. Kishimoto, *Kobunshi Ronbunshu*, **35**, 461–6 (1978).
(17) H. Veno, S. Otsuka, K. Taira, and A. Kishimoto, *Kobunshi Ronbunshu*, **35**, 455–9 (1978).
(18) H. Veno, S. Otsuka, K. Taira, and A. Kishimoto, *Kobunshi Ronbunshu*, **35**, 729–33 (1978).
(19) H. Veno, S. Otsuka, K. Taira, and A. Kishimoto, *Kobunshi Ronbunshu*, **35**, 759–64 (1978).
(20) Y. Kumagai, H. Watanabe, K. Miyasaka, and T. Hata, *J. Chem. Eng. Jpn.*, **12**, 1 (1979).
(21) S. S. Voyutskii, A. N. Kamensii, and N. M. Fodimann, *Kolloid Z. Z. Polym.*, **215**, 36 (1966).
(22) H. Sillescu, *Makromol. Chem.*, **178**, 2759 (1977).
(23) F. Bueche, W. N. Cashin, and P. Debye, *J. Chem. Phys.*, **20**, 1956 (1952).
(24) F. Bueche, *J. Chem. Phys.*, **48**, 1410 (1968).