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Effect of Morphology on the Transport of Gases in Block Copolymers

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ABSTRACT: Transport studies of CO₂ in several solvent-cast poly(styrene-co-butadiene) block copolymers of controlled morphology are presented. The morphology is documented by means of transmission electron microscopy and the transport is examined by means of sorption. The transport properties predicted by simple models involving ordered microstructures agree surprisingly well with the experimental results. Transport studies are a sensitive measure of the connectedness of the most conductive phase (polybutadiene). By change of the composition of the copolymer or the casting solvent, the microdomain morphology, i.e., the connectedness of the polybutadiene domains, can be systematically changed. The variation in effective diffusion as a function of domain morphology is well captured by the models.

Introduction

The interaction of transport and morphology in multiphase polymer systems arises under many practical conditions, for example, in devolatilization in polymer blends and in the design of membranes, photographic films, coatings, packaging materials, and protective clothing, to name but a few. Nevertheless, there have been few combined studies of transport and morphology in multiphase polymer blends, with only simple diffusion and morphological models being considered.

Recently, Sax and Ottino¹ have presented models for predicting the effective diffusion coefficient of small-molecule gases in two-phase polymer blends exhibiting small-scale order but large-scale disorder. As shown in Figure 1 (reprinted from this work), for the case of alternating lamellar domains the structure is considered to consist of small (relative to the size of the sample) grains, in which there is a high degree of order, oriented randomly with respect to each other so that macroscopically the structure is isotropic. The models predict that the effective diffusion coefficient is not only a function of the volume fractions of the phases but also highly dependent on the domain morphology. Especially important in determining the transport behavior is the connectivity of the more diffusive (conductive) phase. Therefore, transport measurements can provide guidance in cases where other experimental techniques do not indicate which of the two phases is continuous. The models can predict the effective diffusion coefficient, D_{eff} , as a function of composition of spherical, cylindrical, and lamellar domains. These are exactly the type of domain structures often encountered for ordered block copolymers. Therefore, these materials should serve as model experimental systems with which to test the predictions of Sax and Ottino's models. In addition, when different casting solvents are employed, the domain morphology of block copolymers (i.e., the con-

nectivity of the phases) can be systematically altered, enabling the effect of morphology on transport to be independently investigated.

Review of the Models

With the assumption of Fickian diffusion, the transport behavior within the small-scale ordered grain is assumed to be given by

$$\mathbf{J} = -\mathbf{D} \cdot \nabla C \quad (1)$$

where \mathbf{J} is the flux vector, \mathbf{D} is the diffusion tensor, and C is concentration. As shown by Sax and Ottino,¹ if there is random orientation of the grains the effective diffusion coefficient is given simply by the average of the diffusion coefficients in the principal directions

$$D_{\text{eff}} = (1/3)(D_{11} + D_{22} + D_{33}) \quad (2)$$

For example, in the alternating lamellar grains of Figure 1, the diffusion coefficients along the principal directions are given by

$$D_{11} = D_B[(1 - \Phi_B)/Sx + \Phi_B][S(1 + \Phi_B(1 - S)/S)]^{-1} \quad (3)$$

$$D_{22} = D_{33} = \frac{D_B[(1 - \Phi_B)Sx + \Phi_B]}{[S(1 + \Phi_B(1 - S)/S)]} \quad (4)$$

where Φ_A and Φ_B are the volume fractions of phases A and B, $S = S_A/S_B$, and $x = D_A/D_B$. S_A and S_B are the penetrant solubilities, and D_A and D_B are the penetrant diffusion coefficients in components A and B. Equations 3 and 4 were obtained by combining the classical results for electrical conductivity in layered domains (i.e., series and parallel laws) with the fact that the driving force for diffusion is the gradient of chemical potential rather than the gradient of concentration.² Solutions for the effective dielectric permeability of a dilute suspension of spheres³ and a cubic lattice of cylinders⁴ have also been presented, from which expressions for the effective diffusion coefficient

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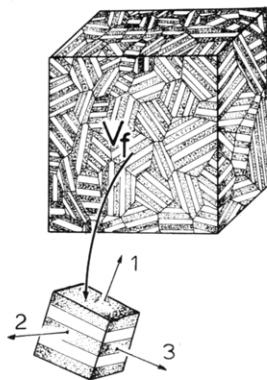


Figure 1. Structured composite having random orientation of ordered lamellar grains. The grain volume, V_f , is much smaller than the volume of the sample. (Reprinted with permission from ref 1. Copyright 1983 Society of Plastics Engineers.)

cients for these structures can also be obtained. The corrections to these solutions, taking into account the actual cubic lattice packing of spherical domains and the hexagonal packing of cylindrical domains, are expected to be small. Therefore, in terms of predicting diffusion behavior, these microstructure models are a good approximation to the equilibrium microstructures observed in block copolymers. Incorporation of these microstructure equations into eq 2 provides simple models for predicting effective diffusion equations for materials having small-scale order and large-scale disorder. The equations given by Sax and Ottino for spheres (eq 5), cylinders (eq 6), and lamellae (eq 7) are

$$D_{\text{eff}} = D_c \left(1 + 3\Phi_d \left(\frac{\bar{s}\bar{x} + 2}{\bar{s}\bar{x} - 1} - \Phi_d \right)^{-1} \right) / [\bar{s}(1 + \Phi_c(1 - \bar{s})/\bar{s})] \quad (5)$$

$$D_{\text{eff}} = [\bar{s}(1 + \Phi_c(1 - \bar{s})/\bar{s})]^{-1} D_c \left[(1/3)[(1 - \Phi_d) + \Phi_d \bar{x}\bar{s}] + (2/3) \left[1 + 2\Phi_d \left(\frac{\bar{s}\bar{x} + 1}{\bar{s}\bar{x} - 1} - \Phi_d + 0.3 \frac{\bar{s}\bar{x} - 1}{\bar{s}\bar{x} + 1} \Phi_d^4 + 0.013 \frac{\bar{s}\bar{x} - 1}{\bar{s}\bar{x} + 1} \Phi_d^8 \right)^{-1} \right] \right] \quad (6)$$

$$D_{\text{eff}} = D_c [(1/3)[(1 - \Phi_c)/S_x + \Phi_c]^{-1} + (2/3)[(1 - \Phi_c)S_x + \Phi_c]/S(1 + \Phi_c(1 - S)/S) \quad (7)$$

where c is the continuous phase, d is the dispersed phase, \bar{s} is the solubility ratio (S_d/S_c), and \bar{x} is the diffusivity ratio (D_d/D_c).

Experimental Section

The molecular characteristics of the poly(styrene-*co*-butadiene) block copolymers used for this study are listed in Table I. Except for samples SB 22/10 (D) and SBS Kraton (J), these are the same samples used in studying micelle formation and structure in poly(styrene-*co*-butadiene) block copolymer/polystyrene homopolymer blends.⁵ [The samples are identified by the composition and a letter designation (see Table I).] The molecular weights and compositions of the copolymers were determined by a combination of GPC and UV absorption analysis. All of these copolymers, with the exception of the SBS Kraton, which was obtained from Shell Co., were prepared by Dr. L. J. Fetters of Exxon Research and Engineering Co. using the butyllithium-initiated anionic synthesis technique.⁶

The polystyrene and polybutadiene homopolymers used to obtain the pure-component diffusion properties were Lustrex polystyrene, obtained from Monsanto, which had a weight-average molecular weight of 250 000, and Diene 35 NFA/AC, an alkyl-lithium-polymerized polybutadiene made by Firestone Synthetic

Table I
Characteristics of Poly(styrene-*co*-butadiene) Block Copolymers

sample	desig	M_n		Φ_{PS}	morphology
		PS	PB		
SB 60/10	A	56 600	10 900	0.818	PB spheres
SB 40/10	B	42 000	10 300	0.779	PB cylinders
SB 23/10	C	22 200	9 000	0.682	PB cylinders
SB 22/10	D	21 700	10 100	0.651	OBDD (see text)
SB 10/10	E	12 000	10 000	0.512	disordered
SB 20/20	F	20 500	20 500	0.465	lamellar
SB 40/40	G	42 300	45 000	0.447	lamellar
SB 80/80	H	81 000	74 500	0.486	lamellar
SB 80/80 MEK	I	81 000	74 500	0.486	PB spheres
SBS Kraton	J	30 000	70 000	0.27	PS cylinders
SB 10/65	K	10 700	63 100	0.127	PS spheres

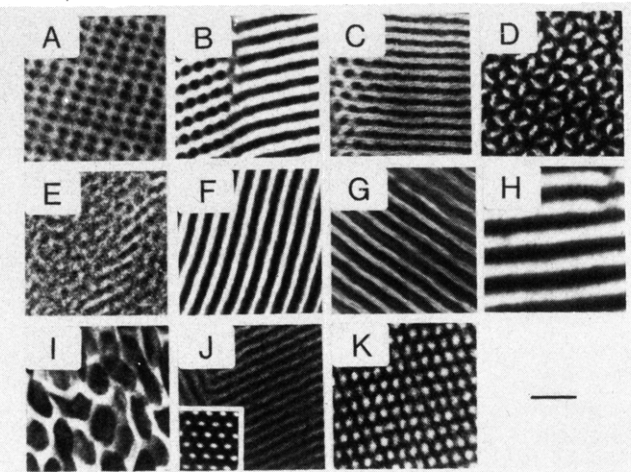


Figure 2. Electron micrographs of the block copolymer samples. The letters refer to the designation given in Tables I and II. The magnification bar corresponds to 1000 Å except for D and E, for which it corresponds to 667 Å.

Rubber and Latex Co., which had a weight-average molecular weight of 182 000.

Films, approximately 0.5 mm thick, for morphological characterization and diffusion measurements were cast from a 3% (w/v) solution in toluene. The solvent was slowly evaporated over a period of 1 week. The films were then annealed at 125 °C for 3 days under vacuum. This sample preparation technique was utilized in order to obtain, as near as possible, equilibrium microstructures. Electron microscopy and SAXS were performed in the manner described previously.⁷

The measurement of effective diffusion coefficients and solubilities utilized CO₂ in a constant-pressure sorption apparatus that consisted of a gas delivery system and a Cahn Model 2000 electrobalance. The details of this apparatus have been given elsewhere.⁸ The mass of the sample as a function of diffusion time was monitored within 2 μg continuously and output to a chart recorder and an Apple 2e minicomputer. Sorption and desorption measurements were made at approximately 25 °C and from sub-atmospheric (0.2 atm) to nearly atmospheric pressures. Sample dimensions were typically 1 cm × 1 cm × 0.05 cm so that they could be approximated as semiinfinite slabs. The calculation of effective diffusion coefficients from sorption and desorption curves for this geometry has been described by Felder and Huvard.⁹ Four different methods of calculating effective diffusion coefficients from the mass vs. time curves have been employed here: initial slope, half-time, moment, and limiting slope methods. Solubility coefficients were determined from the equilibrium weight gain or loss.

Results and Discussion

Electron micrographs of the block copolymer samples listed in Table I are shown in Figure 2 (the letters on the micrographs refer to the sample designation given in Table I). The domain morphology of each sample, determined from an inspection of these micrographs, is also listed in

Table II
Transport Data for Pure Components and Block Copolymers

sample	desig	$D_{\text{eff}} (\pm 15\%), \text{cm}^2/\text{s}$				$S_{\text{eff}} (\pm 5\%),$ $\text{cm}^3_{\text{STP}}/(\text{g atm})$
		initial slope	half-time	moment	limiting slope	
polystyrene		4.8E-8	4.7E-8	4.7E-8	5.3E-8	1.90
polybutadiene		3.6E-6	3.1E-6	3.1E-6	2.9E-6	0.78
SB 60/10	A	7.4E-8	7.7E-8	8.2E-8	8.7E-8	1.62
SB 40/10	B	1.4E-7	1.6E-7	1.7E-7	1.9E-7	1.48
SB 23/10	C	2.6E-7	2.8E-7	2.9E-7	3.1E-7	1.10
SB 22/10	D	4.5E-7	4.7E-7	4.8E-7	5.3E-7	0.92
SB 10/10	E	2.5E-7	3.1E-7	3.5E-7	4.1E-7	1.02
SB 20/20	F	5.8E-7	6.4E-7	6.4E-7	7.1E-7	1.17
SB 40/40	G	5.5E-7	6.1E-7	6.4E-7	7.3E-7	1.26
SB 80/80	H	6.0E-7	6.3E-7	6.6E-7	7.3E-7	1.30
SB 80/80 MEK	I	2.2E-7	2.4E-7	2.6E-7	2.8E-7	1.13
SBS Kraton	J	1.3E-6	1.4E-6	1.5E-6	1.7E-6	1.01
SB 10/65	K	1.9E-6	2.1E-6	2.2E-6	2.5E-6	0.91

Table I. Except for samples SB 80/80 MEK (I) and SB 10/10 (E), the morphologies are those expected considering the relative volume fractions of the two components. Sample SB 22/10 (D) exhibits the recently discovered⁷ ordered bicontinuous double diamond (OBDD) structure in which the polybutadiene and polystyrene phases are both continuous. The structure consists of two translationally displaced, mutually interwoven, but unconnected three-dimensional networks of polybutadiene (minority phase) rods embedded in a polystyrene matrix. Each of the separate polybutadiene networks has the symmetry of a diamond cubic lattice. Although one might expect SB 10/10 (E) to have a lamellar domain structure, it exhibits a rather disordered phase-separated structure (see Figure 2) reminiscent of that seen by Chen-Tsai et al.¹⁰ in amorphous random segmented polyurethanes having total molecular weights of about 20 000. Further annealing had no effect on the structure. Hadziioannou and Skoulios¹¹ have observed similar disordered structures in poly(styrene-co-isoprene) di- and triblock copolymers having approximately 50% polystyrene, for which the total molecular weight was less than about 20 000 and 40 000, respectively. This was explained in terms of a melting transition between an ordered lamellar structure and a disordered phase-separated structure. While sample SB 80/80 (H) cast from toluene has the expected alternating lamellar morphology for this composition, the same sample cast from methyl ethyl ketone [SB 80/80 MEK (I)], a preferential solvent for the polystyrene block, has the morphology of discrete (roughly spherical) polybutadiene domains in a continuous matrix of polystyrene (see Figure 2). The effective diffusion coefficient of this copolymer cast from the different solvents should therefore show a marked difference, even though the composition is constant.

The transport properties of the pure components, which are needed in the model calculations, have been determined previously by Sax and Ottino¹² using the same apparatus used here. It was found that the transport of CO_2 in polystyrene and polybutadiene at pressures less than 1 atm and at approximately 25 °C was Fickian, and the curves of dimensionless mass vs. time for the sorption and desorption runs were found to be superimposable. The pure-component solubility and effective diffusion coefficients determined by the four aforementioned methods are listed in Table II. Good agreement between the methods is found; in particular, the values of D_{eff} determined from the half-time and moment method are virtually identical.

Sorption and desorption experiments were also performed for the block copolymer samples; the values of D_{eff} determined by all four methods, as well as S_{eff} , are listed in Table II. The values found by the sorption and de-

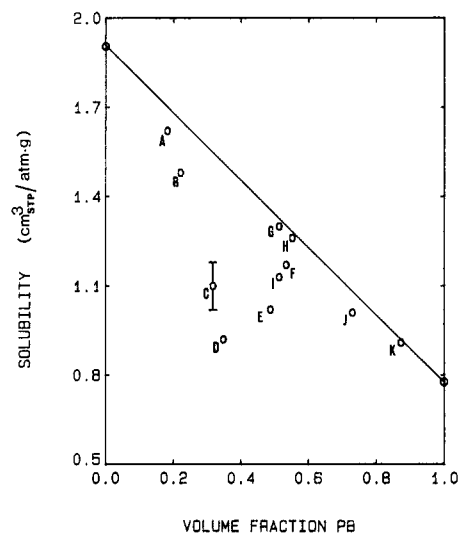


Figure 3. Effective solubility coefficients as a function of composition. The bar in measurement C indicates representative errors.

sorption experiments were the same within the error of the measurements; therefore, the values listed in Table II are averages of the sorption and desorption values. Although the methods give values for D_{eff} that are within approximately 30% of each other for a given sample, the values of D_{eff} determined by the initial slope method are always found to be greater than those determined by the limiting slope method (the half-time and moment methods give intermediate values). Sax and Ottino¹² found the opposite trend in mechanically interdispersed blends of polystyrene and polybutadiene. This was attributed to the presence of dead-end clusters of the more conductive phase at the surface of the sample leading to a relatively rapid weight increase during the initial portion of the experiment. Near the end of the experiment, the domains of the more conductive phase are near equilibrium while the domains of the less conductive phase are still sorbing a significant amount of penetrant. Thus, the weight increase with time near the end of the experiment is relatively slow. This effect should be more pronounced as the less conductive domains become large. The reason that the initial slope method consistently yielded smaller effective diffusion coefficients for the present samples is not clear.

The values of the effective solubilities for these samples are plotted as a function of composition in Figure 3. The letters refer to the designations in Table II. The straight line represents the predicted solubility based on the additivity rule

$$S_{\text{eff}} = \Phi_A S_A + \Phi_B S_B \quad (8)$$

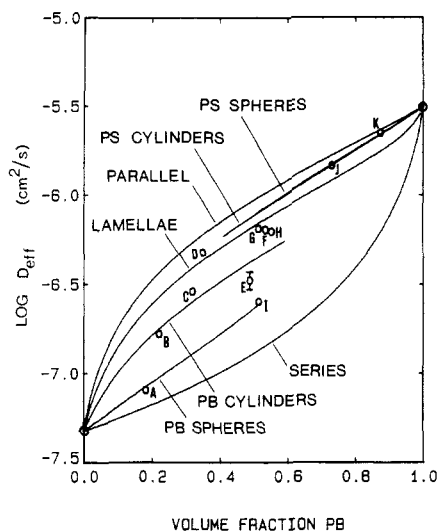


Figure 4. Effective diffusion coefficients as a function of composition and morphology. The bar in measurement E indicates representative errors.

While the values of S_{eff} are all found to be somewhat less than that predicted by eq 8, except for three samples [SB 10/10 (E), SB 22/10 (D), and SB 23/10 (C)], the values of S_{eff} agree, within the error of the measurements, with the predictions of the additivity rule. While samples C, D, and E possess the greatest amount of interfacial material (due to their lower molecular weights), it is not known if this is the cause of the negative deviation.

Figure 4 shows the measured effective diffusion coefficients, taken as the average given by the four different methods, as a function of composition for the samples listed in Table I. Also shown in Figure 4 are the predicted effective diffusion coefficients as a function of composition for different domain morphologies as predicted by the models of Sax and Ottino. Good agreement between the experimental and predicted effective diffusion coefficients as a function of copolymer morphology is seen in the case of samples having spherical, cylindrical, or lamellar domains.

The four samples containing approximately 50% polystyrene were examined with the intention of studying the effect of the interfacial region on diffusion, while maintaining a lamellar structure [however, as shown by the micrograph in Figure 2, SB 10/10 (E) did not have a lamellar structure]. In order to determine the change in diffusion coefficients arising solely from changes in the amount of interfacial material, it is necessary for the samples studied to possess the same amount of orientation of lamellar grains. While some workers¹³ have been able to produce samples in which the lamellae are parallel to the film surface, the present samples possessed little, if any, preferential orientation, as SAXS patterns obtained with the beam normal and parallel to the film surface showed little difference.

It has been shown experimentally that, above a molecular weight of about 10 000, the interface thickness t changes little with molecular weight,¹³⁻¹⁷ being about 20 Å. On the other hand, the lamellar spacing should increase with about the $2/3$ power of molecular weight. Therefore, the volume fraction of interfacial material, given by $2t/d_1$, where d_1 is the lamellar spacing, should decrease with the molecular weight of the copolymer. The lamellar spacings obtained from the positions of the SAXS lattice peaks were 375, 600, and 810 Å giving interfacial volume fractions 0.11, 0.7, and 0.05 for samples SB 20/20 (F), SB 40/40 (G), and SB 80/80 (H), respectively.

Within the error of the transport measurements, no effect of interfacial volume fraction on the effective diffusion coefficient was observed, although a rather limited range of interfacial volume fractions was examined. A better experimental system to test for the effect of interface might be that of graded block copolymers in which the change from one type of monomer unit in the chain to another is not abrupt but has a region of controlled width over which the composition changes gradually. Annighofer and Gronski¹⁸ have produced such copolymers consisting of styrene and isoprene in which the interfacial volume fraction was as high as 0.66.

The lack of preferential alignment of the lamellar domains manifests itself in the measured values of D_{eff} , as well as in the SAXS experiments. If the lamellar domains were aligned parallel to the film surface, then one would expect to observe D_{eff} values as predicted by the series law. The agreement between the experimental D_{eff} values and those predicted by assuming a random orientation of grains is further evidence of the lack of significant orientation of the lamellar domains in these samples over the length scale of the film thickness.

It should be noted that sample SB 10/10 (E), which had a rather disordered phase-separated structure, had a measured D_{eff} much lower than the other samples containing 50% polystyrene and cast from toluene. Evidently, the connectivity of the polybutadiene phase in this disordered structure is appreciably less than that of the lamellar structure. This is also apparent in the electron micrographs. Sample SB 80/80 MEK (I), which has a morphology of PB spheres in a PS matrix, has an even lower D_{eff} .

Electron microscopy showed that by changing the casting solvent from toluene to methyl ethyl ketone the morphology of sample SB 80/80 could be changed from alternating lamellae to isolated spheroidal polybutadiene domains embedded in a continuous polystyrene matrix. This change in morphology, i.e., in the connectedness of the more conductive polybutadiene phase, shows up remarkably well in the diffusion measurements. The average value of the effective diffusion coefficient dropped from $6.5\text{E-}7$ for the toluene cast film to $2.5\text{E-}7$ for the film cast from MEK. In addition, the value of D_{eff} for the MEK cast film agreed well with that predicted for spherical polybutadiene domains.

Also noteworthy is the difference in the diffusion coefficients of samples SB 22/10 (D) and SB 23/10 (C). Although their compositions are nearly the same, the measured values of D_{eff} differ by over 65%, which can be explained very nicely in terms of sample morphology. As seen by the micrographs in Figure 2, sample SB 23/10 (C) exhibits the morphology of polybutadiene cylinders, and the measured value of D_{eff} for this sample agrees rather well with that predicted for this structure. Sample SB 22/10 (D), on the other hand, has the ordered bicontinuous double diamond structure in which the more conductive polybutadiene exists as a three-dimensional continuous phase compared to the one-dimensional continuous polybutadiene cylinders of sample SB 23/10 (C). Therefore, the increase in D_{eff} for SB 22/10 (D) is to be expected. Indeed, the effective diffusion coefficient of SB 22/10 (D) is slightly greater than that predicted for a lamellar morphology of the same composition.

Conclusions

Two main conclusions can be drawn from this study: (1) The morphology of two-phase block copolymers, in addition to their composition, plays a large role in determining their transport properties. Especially important

is the connectivity of the more conductive phase. Increasing the connectedness of this phase will increase the effective diffusion coefficient; conversely, decreasing its connectedness will decrease the effective diffusion coefficient. No obvious effect of interfacial volume fraction on the effective diffusion coefficient was found, although the solubilities of the samples with the larger interfacial volume fractions were observed to be less than that predicted by the additivity rule. (2) The highly simplified models presented by Sax and Ottino for predicting the diffusion properties of materials having small-scale order and large-scale disorder work very well for the case of ordered two-phase block copolymers. It should be noted that the models neglect the effect of orientation of the ordered grains, the effect of interfacial material, and the phase continuity across grain boundaries which is often observed for block copolymers. In addition, the models assume that the transport behavior in the polybutadiene and polystyrene microdomains is the same as that in the pure components, which may not be the case. Although the models could be improved to account for these effects, they seem to do quite well as they are.

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Registry No. CO₂, 124-38-9; (styrene)(butadiene) (block copolymer), 106107-54-4; polystyrene, 9003-53-6.

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Viscosity and Self-Diffusion Coefficient of Linear Polyethylene

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ABSTRACT: The viscosity and self-diffusion coefficient were measured for polyethylene samples in the molecular weight range $200 < M < 120,000$. The viscosity η was determined by capillary flow or in a parallel-plate rheometer; the diffusion coefficient was obtained from the attenuation of NMR spin echoes in a pulsed-field gradient. The molecular weight dependence of the viscosity at 175 °C can be described by two power-law regions, $\eta \propto M^{1.8}$ below $M = 5000$ and $\eta \propto M^{3.6}$ above 5000. The diffusion coefficient on the other hand can be characterized by a single power law $D \propto M^{-2}$ over the entire range studied. Comparisons with molecular theory were made by examining the product ηD . At low molecular weights ηD agrees well with predictions of the Rouse model. At high molecular weights ηD increases with molecular weight, approaching the prediction of the reptation model from below. The temperature dependence of the viscosity follows the Vogel-Fulcher equation, $\eta \sim e^{B/(T-T_0)}$, with parameters that are consistent with the free volume theory of the liquid state. When the data at low molecular weights are compared at a constant free volume state, the viscosity and diffusion coefficient are proportional to M and M^{-1} as required by the Rouse model.

Introduction

Data on the viscosity, η , and the self-diffusion coefficient, D , of polymer melts have often been used to test molecular theories of transport properties.^{2,3} Qualitative comparisons that are concerned only with establishing the molecular weight dependence of these functions are easily made. Quantitative comparisons are frequently hampered because both η and D depend on the monomeric friction factor, ζ , a parameter that is difficult to determine. The current theories of liquids are not sufficiently developed to calculate it directly and experimental methods to estimate ζ are often inaccurate. This is especially so for low molecular weight polymers and for crystallizable polymers like polyethylene that are tested far from their glass transition temperature.²

There have been very few studies in which both η and D were measured on the same polymer samples.^{4,5} A

systematic program to do so could be very worthwhile because the product ηD is predicted to be independent of ζ , thereby providing rather direct and simple tests of theory. In this study we report new data on the viscosity and self-diffusion coefficient for a number of polyethylene samples. The experiments include a sufficiently wide range of molecular weights to test models of transport for both unentangled and entangled liquids.

Our findings are also valuable in a more practical sense since they provide a simple method to estimate the diffusion coefficient from a knowledge of chain length and viscosity alone.

Molecular Characterization

It is well-known that the melt rheological behavior of polymers is very sensitive to molecular weight, molecular weight distribution, and long-chain branching.⁶ To avoid complications from the latter