Solvent-Induced Crystallization of Quenched Isotactic Polypropylene in Different Liquids

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ABSTRACT: Solvent-induced crystallization of quenched isotactic polypropylene (iPP) films in different solvents was investigated. Diffusion and sorption of the different liquids were measured at 25 °C. The weight uptake and the swelling kinetics in the different solvents imply Fickian behavior, and it was possible to derive the mean $\bar{D}$ in the different systems. The derived diffusion coefficients are roughly inversely related to the smallest cross-sectional area of the penetrant molecule, but the variation is not so large as in the case of systems with limited chain segmental mobility. The desorption phenomenon observed during the weight uptake kinetics indicates that the smectic form of iPP is permeable to the penetrants. As a consequence of the mobilizing presence of penetrant molecules, the smectic phase is induced to crystallize and expels the penetrant from the crystallized fraction, and therefore the desorption is observed. The curve of weight uptake of the different liquids, reported as a function of the solubility parameter of the liquids, shows two zones of interaction, and the same behavior is observed for the degree of crystallinity developed, expressed by the density of the samples, and for the reciprocal of the half-height width of the (110) isotactic polypropylene reflection in the X-ray diffraction patterns.

Introduction

Systematic studies on the transport properties in systems in which the solvent induces structural rearrangements in the polymer have not been very numerous in the past.[1-12]

The diffusion process in the liquid- and vapor-induced crystallization is quite unique in that it involves a redistribution of free volume to accommodate penetrant molecules as well as large-scale concomitant structural rearrangements in the polymer, and these two aspects influence each other.

Most of the past studies dealt with systems initially in the amorphous or glassy state, which undergo solvent-induced crystallization (SINC).

Isotactic polypropylene (iPP) cannot be obtained in the completely amorphous state, since rapid quenching at very low temperatures produces a phase of intermediate order between amorphous and crystalline, variously described in the literature as a smectic, paracrystalline, or glassy phase.[13-15] None of these terms describes the real structure of this phase, whose nature is still in debate. The disorder has been identified as intramolecular imperfections, such as helix reversal and poor intermolecular alignment. Recently Wunderlich[16,17] proposed the term "condis crystal" (conformationally disordered crystal) as possibly more appropriate for this semidisordered state. This author assumes that this supercooled "condis crystal" is prevented by quenching from converting into the fully ordered state. The quenched form can undergo thermal crystallization and the process has been extensively studied;[18,19] on the contrary the process of solvent-induced crystallization has not yet been described. We have found this process to occur in quenched iPP[20] exposed to liquid or high-activity vapor of CH_2Cl_2, and we present here a study of diffusion and crystallization in different liquids.

In the already studied processes the ability of a solvent to interact and induce crystallinity in the amorphous polymers was correlated with its solubility parameter δ $(cal/cm^3)^{1/2}$, defined as the square root of the cohesive energy density.

It has often been found that the degree of interaction leading to SINC is maximum for solvents having a solubility parameter close to the value of the polymer.[21] Although for crystalline polymers the cohesive energy density is not well-defined,[22] the solubility parameter concept is useful in predicting the swelling behavior, and in our case it can also help clarify the interactions that lead to crystallization. Further work will elucidate the kinetics of crystallization and the type of crystals formed in the different solvents depending on the nature and on the extent of interaction with the polymer.

Table I
Solubility Parameter δ, Molar Volume V, and Fractional Polarities P of the Solvents[a]

solvent	δ, $(cal/cm^3)^{1/2}$	V, cm^3/mol	P
n-hexane	7.3	132	0
octane	7.6	164	0
cyclohexane	8.2	109	0
carbon tetrachloride	8.6	97	0
toluene	8.9	107	0.001
benzene	9.2	89	0
chloroform	9.3	81	0.002
chlorobenzene	9.5	107	0.058
dichloromethane	9.7	65	0.120

[a] The fractional polarity (P) is the fraction of total interactions that are due to dipole–dipole attractions.[16]

Experimental Section

Isotactic polypropylene of M_w = 307 000 and M_n = 15 600 is a product of RAPRA (Great Britain).

Quenched films were obtained by heating the iPP pellets at 200 °C, pressing them into the film shape with a thickness of 0.02 cm, and quickly cooling them in an acetone–dry ice bath to −70 °C.

It is well-known that isotactic polypropylene, quenched very rapidly from the melt, undergoes a marked enhancement of its mechanical properties and a macroscopic increase in density during its subsequent aging at room temperature.[23-25] A linear increase in density with the logarithm of film age was reported. Therefore relatively large changes should occur in the first minutes of aging, while there is a tendency for leveling off after a few days. We therefore used for this study films aged for 10 days at room temperature, in which there is no further observable change of density with time. The value of density after aging at room temperature was 0.883 g/cm^3, and we calculated for this sample a fraction of amorphous component α_a = 0.53.[26]

For weight-uptake studies different strips of the original film, of approximately 20-mg weight, were immersed in various liquids at 25 °C for different times. Upon removal, the samples were blotted on filter paper to remove the solvent excess from the surface and weighed in closed bottles. After determination of weight, the thickness was measured with a micrometer.

The liquids used in this study are listed in Table I. They were reagent-grade and used without further treatment. In the table

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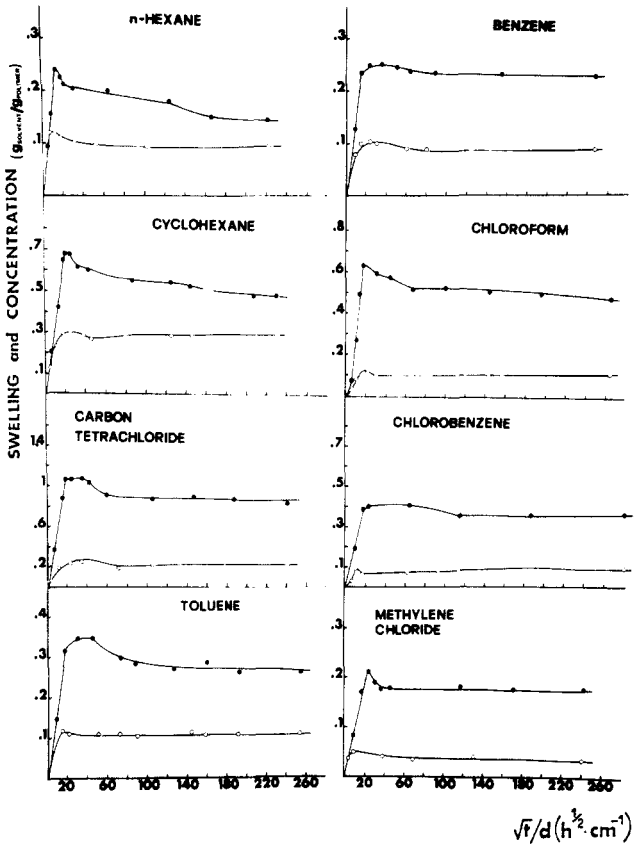

Figure 1. Absorption bulk concentration of the different liquids (g solvent/g polymer) (●) and swelling percent (○) as the relative difference between the final and the initial thickness $(d_t - d)/d$ as a function of $t^{1/2}/d$, where t (h) is the absorption time and d (cm) the initial thickness of the sample.

the solubility parameter δ $(cal/cm^3)^{1/2}$, the molar volume V, and the fractional polarities P of the liquids[16] are also reported.

Density measurements were performed on samples immersed in the solvents 24 h and 10 days, by floating the sample in a mixture of 1,2-dimethoxyethane and 2-ethoxyethanol. Before measurement, the samples were desorbed under vacuum until they recovered the initial weight. In many cases the final weight after desorption was lower than the initial one, indicating a loss of low molecular weight fractions. The amount of this loss was of the order of magnitude of 3–4%.

Wide-angle X-ray scattering (WAXS) spectra were carried out at 20 ± 1 °C by a PW 1050/71 Philips powder diffractometer (Cu Kα, nickel-filtered radiation) in the reflection mode, scanning the scattering 2ϑ angle in continuous.

Results and Discussion

Diffusion and Sorption. The absorption bulk concentration of different liquids in quenched iPP is reported in Figure 1 as a function of $t^{1/2}/d$, where t is the absorption time in hours and d the thickness of the sample in centimeters.

It is evident in all the curves of Figure 1 that a very large desorption occurs during the measurement. The quenched film sorbs up to the maximum concentration (C_{max}); after a while the sample starts to reject a fraction of the penetrant and thus a new equilibrium concentration is obtained. We interpreted this phenomenon as an indication of crystallization of the smectic component. We found in the case of sorption and diffusion of CH_2Cl_2 vapor that at low penetrant activity the smectic phase is impermeable to the vapor, whereas at activities higher than 0.5 it becomes permeable.[20,26] As soon as the penetrant molecules diffuse into the smectic phase they can induce large-scale structural rearrangements and thus a crystallization phenomenon.

Table II
Diffusion $\bar{D}$, Percent Swelling Sw,[a] and Reciprocal of the Half-Height Width A of the (110) Reflection of the iPP[b] for Samples Immersed in the Different Liquids

solvent	$\bar{D} \times 10^7$, cm²/s	% Sw	$1/A$, deg^{-1} of 2ϑ 24 h	$1/A$, deg^{-1} of 2ϑ 10 days
n-hexane	2.70	6.0	0.59	0.60
octane			0.36	0.61
cyclohexane	1.06	15.0	0.65	0.70
carbon tetrachloride	1.10	14.0	0.74	0.74
toluene	1.00	8.1	0.53	0.67
benzene	1.96	7.1	0.61	0.62
chloroform	1.06	8.3	0.71	0.77
chlorobenzene	1.30	8.3	0.38	0.60
dichloromethane	1.30	4.1	0.51	0.63

[a] Percent swelling calculated from the volume of penetrant sorbed at 24 h. [b] The $1/A$ value for quenched iPP is 0.23 deg^{-1} of 2ϑ.

In our study we kept the samples in the different liquids at activity $a = 1$, and therefore we can assume that also in this case the smectic phase is permeable to the penetrant molecules. When the crystallization starts, due to the mobilizing presence of solvent molecules, we observe the rejection of a fraction of solvent, as already reported for other systems.[11,27,28] The crystals are in fact completely impermeable.

The desorption behavior is very different from solvent to solvent. In some cases as in *n*-hexane, cyclohexane, methylene chloride and chloroform, the desorption is at first sharp, followed by a slower rejection of sorbed liquid; in the other cases there is a constant value of C_{max} for a longer time and then the desorption starts.

The extent and the form of the desorption phenomenon in the different liquids will depend on many factors: among these there are the critical concentration at which the crystallization starts, the relative kinetics of crystallization with respect to the diffusion time, and the thickness of the film;[29] all these aspects have to be investigated in order to have a full explanation of the phenomenon.

All the curves for the different solvents in the first stage show a Fickian behavior, and from the linear part of the reduced curve it is possible to calculate the diffusion coefficient $\bar{D}$ (cm^2/s)[30] from

$$\frac{C_t}{C_{eq}} = \frac{4}{d}\left[\frac{Dt}{\pi}\right]^{1/2} \tag{1}$$

where C_t is the concentration at time t and C_{eq} the equilibrium concentration. However, C_{eq} must be evaluated with the utmost care. In Figure 1 the value of C_t corresponding to 24 h of immersion in the different liquids is reported as the final point; it is not yet the equilibrium value because we found a further desorption after 10 days of immersion in the liquids. Moreover the values after a long time refer to a system with a different structure, in which the smectic phase, initially permeable, has partially crystallized and rejected the solvent. We therefore think that the best choice for C_{eq} is to use C_{max} before desorption. With the use of these values for the reduced absorption curve, we obtained the diffusion coefficient $\bar{D}$ (cm^2/s) listed in Table II.

It is worth noting that these $\bar{D}$ values are mean values in the concentration interval explored and are not thermodynamic parameters. To obtain the real diffusion coefficient D_0 we must know the dependence of diffusion on concentration so as to extrapolate at zero concentration of penetrant.

We derived the D_0 parameter only in the case of CH_2Cl_2, for which we studied the vapor sorption and diffusion as

a function of concentration.[26] The dependence of diffusion on concentration was found to be in accordance with the relation

$$\bar{D} = D_0 \exp(\gamma c) \quad (2)$$

where D_0 is the zero concentration diffusion coefficient and γ the concentration coefficient. We obtained for D_0 and γ the values of 2.2×10^{-9} cm^2/s and 28.5, respectively.

In the case of the different solvents studied here, the mean diffusion coefficients obtained are only indicative of the polymer–solvent interaction. They are roughly inversely related to the apparent smallest cross-sectional area of the penetrants, but the variation is not so large as in the case of systems with limited chain segmental mobility. In fact the values range from 2.7×10^{-7} for *n*-hexane, which has the smallest cross-sectional area, to 1.0×10^{-7} for cyclohexane and toluene.

In Figure 1 the swelling percent in terms of the difference between initial and final thickness is also reported. As for the swelling, the same trend of the weight uptake as function of $t^{1/2}/d$ is observable. The initial rapid increase, in most cases proportional to the square root of time, is followed by a decrease and then by a constant value of swelling. In Table II the values of swelling, calculated from the volume of penetrant sorbed at 24 h, are reported. If we compare this table with Figure 1 we notice that there is a quasi-additivity of volumes between polymer and penetrant only for the solvents with a higher solubility parameter. In the case of chlorobenzene and dichloromethane the measured and calculated values coincide.

To conclude we can say that, as in the already studied systems,[4,8,31,32] the weight-uptake kinetics in the different solvents imply apparent Fickian diffusion behavior and the swelling kinetics follow the same trend. Only in some cases, as in $CHCl_3$, a short induction period precedes the linear weight uptake.

From Figure 1 it can also be observed that the solubility, shown by the equilibrium weight uptake, varies considerably among the different iPP–liquid systems. The relative solubility may be considered as a measure of the interaction between polymer and liquid, and this interaction depends on many factors such as molecular size of the penetrant, polarizability, and closeness of the solubility parameters. We have chosen for this study liquids in the class of "poorly hydrogen bonded" solvents, with zero or low polarizability and having a molar volume in a narrow range, except octane (the diffusion of which is not reported), with the greatest molar volume, and dichloromethane, with the smallest. Therefore we can compare the weight uptake according to the solubility parameter of the solvents.

In Figure 2 we report the volume of liquid sorbed, expressed as percent of the original volume of polymer (a), and the weight of liquid sorbed by the polymer, expressed as percent of the original weight of polymer (b), as a function of the solubility parameter δ (cal/cm^3)$^{1/2}$ of the solvents. The three curves refer to the maximum concentration sorbed, as shown in Figure 1, and to the value of liquid sorbed after 24 h and after 10 days. We notice the greatest desorption in the first 24 h, but a further decrease in the subsequent days is still observable. Since the desorption is indicative of crystallization, it means that this phenomenon continues for a long time.

For the three curves of volume liquid sorbed a net maximum corresponding to cyclohexane (δ = 8.2) and a small but still appreciable maximum corresponding to chloroform (δ = 9.3) are evident. We found in the literature two different values reported for the solubility parameter of polypropylene, and indeed they do correspond

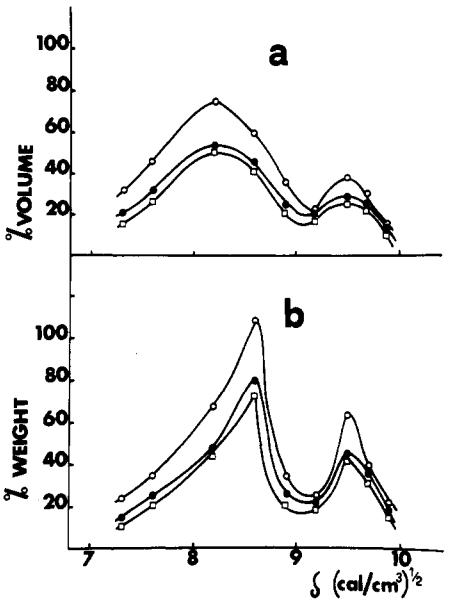

Figure 2. Volume of sorbed liquid as the percent of the original volume of polymer (a) and weight of the sorbed liquid as the percent of the original weight of polymer (b), corresponding to the maximum concentration sorbed (○) and to the value after 24 h (●) and 10 days (□), as a function of the solubility parameter δ (cal/cm^3)$^{1/2}$ of the liquids.

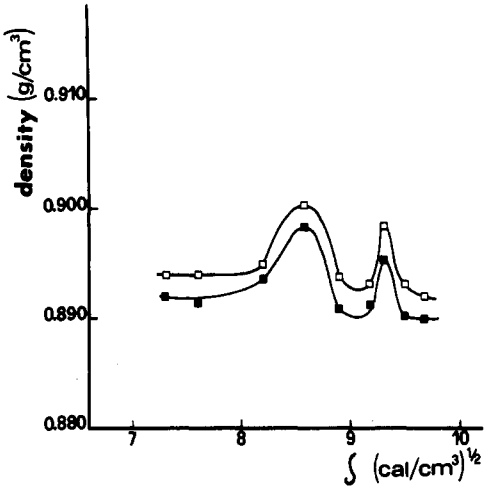

Figure 3. Density (g/cm^3) for the samples immersed 24 h (■) and 10 days (□) in the different liquids as a function of the solubility parameter δ (cal/cm^3)$^{1/2}$ of the liquids.

to the two observed maxima, that is, 8.1[32] and 9.2–9.4.[33,34] As for the curves of percent weight sorbed the first maximum is shifted to a higher value of δ (8.6) corresponding to CCl_4.

Density and Crystallinity. In Figure 3 the values of the density for samples immersed 24 hours and 10 days in the liquids are reported as a function of the solubility parameter. Before density measurements the samples were dried under vacuum until they recovered the initial weight or a lower one. Since the density of the starting sample is 0.883 g/cm^3, a substantial increase in density, indicative of the crystallization phenomenon, is evident in all the samples. Moreover the difference observed in many cases between the 24-h and 10-day values indicates that the process of crystallization went on for many days, as the sorption data had already led us to conclude.

The measurement of density is a very accurate one but the reliability of the values obtained is limited by two factors,[21] i.e., the possibility of void formation during SINC, which would decrease the density, and the possible pres-

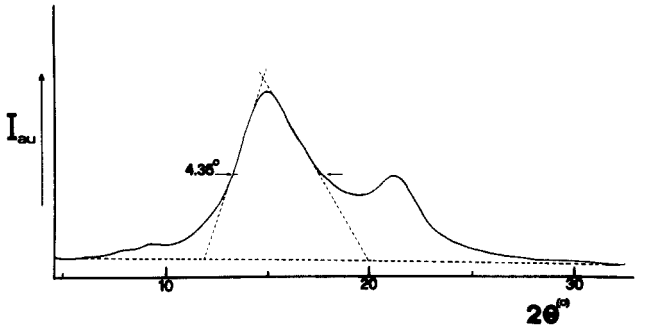

Figure 4. WAXS spectrum of quenched isotactic polypropylene: the $1/A$ value is 0.23 deg^{-1} of 2ϑ.

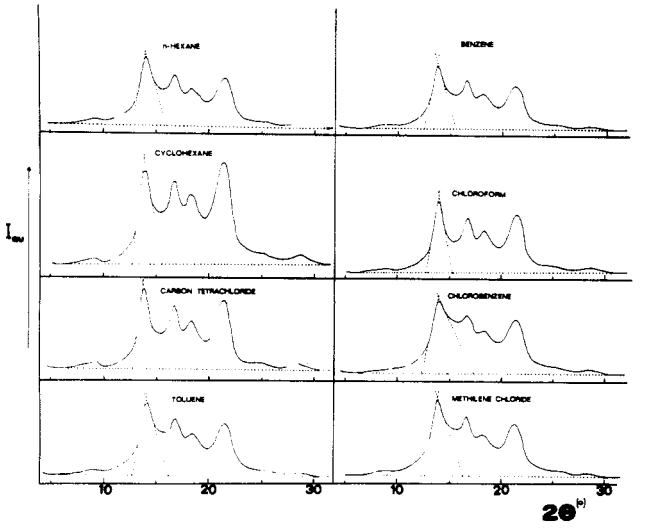

Figure 5. WAXS spectra of iPP samples immersed 24 h in the different liquids.

ence of liquid entrapped within or between crystallites.

Upon removal of samples from liquids and desorption, we obtained the initial weight or a lower one, but we cannot rule out the possibility that a part of the solvent has replaced a low molecular weight species extracted by the liquid.

In spite of some uncertainity, the density values we obtained agree well with the sorption behavior and we think they are fairly reliable.

Although level of sorption and tendency to crystallization are not directly related, we observe from Figure 3 that with greater sorption and swelling, the density and hence the level of crystallinity attained increase.

As a matter of fact sorption is a measure of the interaction between the polymer and the liquid, and the development of crystallinity may depend on such interaction. In fact the degree of enhanced mobility and the depression of T_g are dependent on the uptake of solvent. In our case the density data relate better to the weight-uptake curve than to the volume curve, in that the first maximum corresponds to CCl_4, as in the curve (b) of Figure 2.

WAXS Structural Analysis. The WAXS spectrum of quenched isotactic polypropylene (Figure 4) shows the shape usually reported in the literature for the smectic form of iPP.[13]

WAXS spectra of iPP samples, immersed for 24 h in the above-mentioned solvents and desorbed until the initial weight was restored, are presented in Figure 5: The crystallization phenomenon induced by the solvents is evident in all the cases.

The reciprocal of the width at half-height (A) for the (110) polypropylene strongest reflection ($2\vartheta \simeq 14°$) was chosen as an index of the order level attained by the iPP

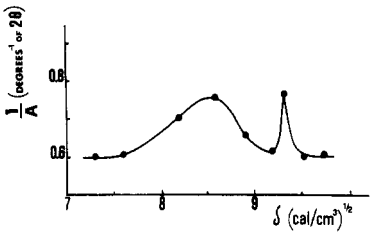

Figure 6. Reciprocal of the half-height width (A) for the (110) reflection of the isotactic polypropylene as a function of the solubility parameter of the liquids.

crystallized in the different solvents. In fact, for a powder composed of relatively perfect crystalline particles, the mean crystallite size (L) can be determined by the well-known Scherrer equation,[36] in which L is inversely related to the width at half-height of the reflection. However, at this stage we prefer to use the $1/A$ parameter instead of L, because, for imperfect crystals, the intensity profile is also affected by lattice distortions.[36] This parameter is evaluated[18] as schematically represented in Figure 4: the $1/A$ value for quenched iPP is 0.23 deg^{-1} of 2ϑ.

The comparison between the values of $1/A$ at 24 h and 10 days (Table II) shows that a noticeable variation of this parameter is observable only for octane and chlorobenzene. This means that in these solvents the crystallization process is slower.

If the $1/A$ values for the samples immersed 10 days in the liquids are plotted (Figure 6) as a function of the solubility parameter δ of the solvents, we observe again a bimodal distribution of the values: the curve presents in fact two clearly resolved maxima corresponding (as in the curves of the density and the sorption) to CCl_4 (δ = 8.6) and $CHCl_3$ (δ = 9.3) solubility parameter. The shape of the curve does not change even if we introduce the experimental error of about 10%.

Furthermore if compared with thermally crystallized samples,[12] the $1/A$ values obtained would correspond to samples with a lower density. This result suggests that the concentration of crystallites induced by SINC is high and that they are relatively small in size, as described for other systems.[15]

Conclusions

All the investigated liquids induce crystallization of the smectic form of iPP into the monoclinic form.

The study of solvent-uptake kinetics shows that the smectic form is permeable to the different liquids and the crystallization phenomenon takes place during sorption. Since the crystals are impermeable they expel the penetrant and we observe an evident desorption during the measurement.

The weight-uptake and the swelling kinetics are linearly related to the square root of time, implying Fickian diffusion behavior.

The maximum concentration of sorbed liquid depends on the solubility parameter of the solvents, and two zones of interaction are distinguishable.

At the temperature of the experiment also the final degree of crystallinity and structural order of iPP depend on the nature of the solvent, and we observe the maximum effect in the same zones of the curve in which solubility is higher.

This bimodal effect, already found for poly(ethylene terephthalate),[37] was attributed to the preferential interaction of the solvent either with the aromatic residue of PET or with the aliphatic portion. We do not have at the moment a conclusive explanation for this effect. Often solvents with different polarities define different interac-

tion zones; in our case we can speculate that, since also the smectic form in the liquid is permeable to the penetrant, the two different zones of the various curves refer to the interaction with either the amorphous or the smectic form of iPP.

In order to draw more thorough conclusions further investigations are needed on the crystallization kinetics in these solvents and on the growing crystalline structure.

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Registry No. iPP, 25085-53-4.

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Molecular Weight Distribution Dependence of the Viscoelastic Properties of Linear Polymers: The Coupling of Reptation and Tube-Renewal Effects

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ABSTRACT: Considering that the terminal relaxation of every chain in a linear melt is dominated by reptational and constraint release motions, we propose an expression for the relaxation modulus $G(t)$ of entangled polymers as a function of the molecular weight distribution (MWD). The expressions of zero-shear viscosity η_0 and steady-state compliance J_e^0 derived from $G(t)$ describe correctly the experimental behavior: η_0 scales with average molecular weight as $\eta_0 \propto M_w^{3.4-3.8}$ for a constant polydispersity P; J_e^0 increases strongly with P and varies widely with the shape of MWD. We also predict a decrease of viscosity with polydispersity; this is a possible explanation of some experimental variations of viscosity, which do not follow the classical power law with M_w. The behavior expected for strictly monodisperse samples shows that it is necessary to consider a relaxation times distribution in the terminal region.

Introduction

It is well-known that the viscoelastic properties of polymers depend mainly on their molecular weight distributions (MWD). Experimental data on the molecular weight dependence of zero-shear viscosity η_0 generally support the power law $\eta_0 \propto M_w^{3.4}$ for binary blends of narrow distribution samples,[1-3] but results differ for broad distribution samples. Data for high-density polyethylene[4] agree with the above expression, whereas commercial polystyrenes[5,6] follow higher power laws: $M_w^{5.25}$ or $M_w^{5.7}$.

The steady-state compliance J_e^0 is very sensitive to molecular weight distribution, especially to the tail of the distribution at high molecular weights. The increase of J_e^0 with the broadness of the distribution can reach 2 or 3 orders of magnitude for binary blends whose components are very different in molecular weight.[1,7,8]

Several blending laws have been proposed to account for the behavior of binary blends.[9-11] Masuda et al.[12] reviewed them, discussed their applicability, and suggested some improvements. These theories are based on a linear

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