Diffusion of Erucamide (13-*cis*-Docosenamide) in Isotactic Polypropylene[†]

I. Quijada-Garrido,[‡] J. M. Barrales-Rienda,*,[‡] and G. Frutos[§]

Departamento de Química-Física de Polímeros, Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva, 3, E-28006 Madrid, Spain, and Departamento de Estadística e Investigación Operativa, Facultad de Farmacia, Universidad Complutense, E-28040 Madrid, Spain

Received September 15, 1995; Revised Manuscript Received June 6, 1996[⊗]

ABSTRACT: Diffusion coefficients of erucamide (13-*cis*-docosenamide, $H_3C(CH_2)_{11}HC{=}CH(CH_2)_7CONH_2$, eru) into isotactic polypropylene (i-PP) were determined under different isothermal conditions, viz., 323, 333, and 353 K in times of 15 days. Some other experiments were performed for several predetermined time intervals (5, 10, and 15 days) at a constant temperature (343 K). The diffusion cell which has been used to establish eru concentration profiles of diffusant within the polymer matrix is similar to that described and used by Roe et al. The concentration profiles of additive in film stacks have been analyzed after soxhlet extraction by capillary gas−liquid chromatography (CGLC). On one hand, these profiles were compared with theoretical curves based on solutions of Fick's diffusion equation for the best fitting, with the appropriate boundary conditions. However, the measured concentration profiles do not show a good agreement with the Fickian law as will be desirable. Values of the diffusion coefficient D in the range from 10^{-9} to 10^{-11} cm^2 s^{-1} have been obtained. On the other hand, probably due to a dual mechanism and/or some other characteristic effects of the diffusion of erucamide through i-PP it is to be expected that the diffusion process itself may be more complex than that predicted by a simple Fickian model. In this paper we present the diffusion or migration of erucamide through i-PP by means of a semiempirical dual mechanism, in which two simultaneous Fickian processes, perhaps with two types of diffusant molecules, with diffusion coefficients D_1 and D_2 are involved. Some plausible explanations are given at this respect. Similarly, we have estimated by means of the method of Matano an overall diffusion coefficient which is related to the erucamide concentration. Furthermore, this overall diffusion coefficient has also been related to the concentration of erucamide and temperature by using an empirical model. The dependence of diffusion coefficients D, D_1, and D_2 on temperature followed Arrhenius-type relationships over the temperature range investigated. The activation energies were calculated as $E_d(D) = 117$, $E_d(D_1) = 100$ and $E_d(D_2) = 130$ kJ mol^{-1}, respectively. The values of diffusion coefficients and activation energies are in the range found for some other additives. The solubility of erucamide in i-PP as a function of temperature has been determined directly by extrapolation of diffusion data to penetration depth equal to zero. From the plot of these solubility parameters as a function of temperature, it is very easy understood that erucamide is insoluble (incompatible) within i-PP for temperatures below 313 K. By using Fujita's equation a good correlation between diffusion coefficient and free volume fraction estimated by means of Williams−Landel−Ferry' equation has been found.

Introduction

Certain surface characteristics of polypropylene films are the key to handling the material in the packing industry. Surface modification of films can be made by changing the chemical character of the surface. The physical and chemical nature of film surfaces can be modified by the use of additives. Additives which enhance slip properties are commonly used. The most common slip agents used for polypropylene films are the unsubstituted amides of long-chain fatty acids.[1,2] The amides commonly used as slip agents also reduce blocking between film surfaces. As a general rule, we can say that the best slip agents are not necessarily the best antiblocking agents. Erucamide (13-*cis*-docosenamide), subsequently referred to as eru, has, to a great extent, replaced the use of oleamide because of its higher melting point and higher heat resistance.[3]

Erucamide is now commonly incorporated into polyethylene and polypropylene at very low concentrations to increase not only their slipping but also as well as their antiblocking properties.There are little data available in the literature on the diffusion of slipping and antiblocking agents such as erucamide, oleamide, palmitamide, stereamide, myristicamide, etc., in polymers in general and polyolefins in particular. The work is restricted to that done by Cohen and Tabor,[4] Briscoe et al.,[5] and Klein and Briscoe[6−9] with the diffusion of stereamide and some other slipping agents in polyethylene as mentioned above. Some of these authors[6−9] have used a measuring technique based on infrared microdensitometry.

The rate of the additive loss depends on the compatibility of the additive with the polymer and is controlled by its volatility, extractability, solubility, and diffusion coefficient.

There exist a series of methods described in the literature for the measurements of the diffusion coefficient and solubility of small molecules in polymers.[10−14]

On one hand, we have only found in the literature a small reduced number of references on the diffusion of several additives[15−20] in i-PP. In general, we can say that most of them are antioxidants and because of its smaller size and chemical structure are not comparable with those of erucamide in i-PP, specially from the point of view of their respective diffusion coefficients. Very recently, Hayashi et al.[21] have carried out a research on the diffusion of the methyl esters of the higher fatty acids in i-PP. Some of these results are open to discussion. Thus, for instance, Hayashi et al.[21] have

---

[†] Dedicated to Prof. Dr. J. de D. López-González on occasion of his 67th birthday.

[‡] Departamento de Química-Física de Polímeros.

[§] Departamento de Estadística e Investigación Operativa.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

S0024-9297(95)01392-1 CCC: $12.00

used a mass uptake technique to study the diffusion. They have considered that the above additives diffuse according to the Fickian law. However, they have found that for short periods of time of diffusion, the fitting of the equation $Q_t/Q_\infty = kt^n$ to their experimental values yields a value of n between 0.69 and 0.74, which is indicative of a certain deviation from the Fickian behavior. On the other, the diffusion coefficients of a fatty acid amide such as erucamide are very scarce. As far we are aware, from a carefully reading of the published work done by Földes,[22,23] it seems to be that he has carried out some type of work on the diffusion of erucamide in low-density polyethylene (LDPE). It is very difficult to extract any conclusion about the diffusion coefficients on this particular additive.

Very little fundamental understanding is known concerning middle-size molecules molecular transport into semicrystalline polymeric materials. Diffusion might be expected to depend on factors such as the own pair matrix-diffusant, the degree of crystallinity, interlamellar morphology, penetrant size and shape, and especially diffusant-matrix interactions, namely, dynamic and thermodynamic interactions of the system. Van Alsten et al.[24−26] have studied very recently the penetration of polystyrene oligomers in semicrystalline hydrogenated isotactic polystyrene and some other systems. They arrive at very interesting conclusions.

Theoretical Considerations

When a step function in the concentration of a diffusant is set up within a host matrix, it will broaden with time under diffusion, the driving force being the *"concentration gradient"*, that is to say, the rate is governed by local migrant concentration gradients. The shape of the resulting concentration profile is established, as a solution of Fick's equations with the appropiate boundary conditions.

For one-dimensional diffusion, the rate of mass transport across unit area of polymer in the direction x is given by Fick's first law:

$$F = -D\, \partial c/\partial x \tag{1}$$

where F is the rate of transfer per unit area of section, c is the concentration of diffusing material in any point x at time t, and D is the diffusion coefficient; D may be constant or an increasing function of the concentration of the diffusant c.

And the rate of change of concentration at any point is given by Fick's second law:

$$\partial c/\partial t = D\, \partial^2 c/\partial x^2 \tag{2}$$

These two equations have been solved for specific boundary conditions.[27,28]

Fick's second law can be solved for the special case of a layer of substance of constant (with time) concentration (source) diffusing into a semi-infinite medium which initially contains no solute; second one of these cases of solutions for a layer of substance constant concentration diffusing into a semi-infinite medium which initially contains no solute (stack of polymer film slices). The boundary conditions are given by the following expressions:

$$\begin{array}{lll} t = 0 & x > 0 & c = 0 \\ t > 0 & x = 0 & c = C_0 \end{array}$$

To obtain these conditions, a source containing excess additive in polypropylene was placed next to a stack of additive-free polymer films. It is assumed that during the experiment the interface concentration remains constant and equals the solubility equilibrium, i.e., the solubility of the additive in the polymer. This concentration is going to remain constant through the whole experiment of diffusion. Using the method of the Laplace transform,[27] the solution yields an expression for the concentration in the medium:

$$c(x,t) = C_0\, \mathrm{erfc}(x/2\sqrt{Dt}) \tag{3}$$

where C_0 is equal to the equilibrium solubility of the additive in the polymer, erfc is the complementary error function, D is the diffusion coefficient, and t is the time of the experiment.

On other hand, we can also calculate the effective diffusion coefficient D_{eff} as a function of concentration, c. It has been calculated from experimental profiles of erucamide concentration vs depth of penetration, by the method of Matano[29] by using the following equation:

$$D_{\text{eff}} = (-1/2t)[\textstyle\int_0^c x\, \mathrm{d}c/(\mathrm{d}c/\mathrm{d}x)] \tag{4}$$

where t is the experimental time. Values of $\int_0^c x\, \mathrm{d}c$ and $\mathrm{d}c/\mathrm{d}x$ have been calculated by integrating and derivating the best-fitting function to experimental points by a computing program.

Experimental Section

Materials. *Polypropylene.* 40 μm thickness Hostalen PPN 1060 free-additives isotactic polypropylene film was supplied by Disper, S. A. Sant Andreu de la Barca (Barcelona/Spain). It has a nominal melt index MFI = 9 g/10 min. at 230 °C and 5 N, nominal density at 23 °C of 0.905 g·cm^{-3}, and 54.2% of crystallinity.

Erucamide (13-cis-Docosenamide, $H_3C(CH_2)_{11}HC{=}CH$-$(CH_2)_7CONH_2$). A commercial sample of ARMOSLIP (EXP) Beads with a 96.5% purity (estimated by CGLC) which has been used as standard material for capillary gas-liquid chromatography testings and calibrations was kindly supplied by AKZO Chemicals, S. A. División Química, El Prat de Llobregat (Barcelona/Spain) was used as received.

6% Erucamide−Propylene Masterbatch. CEPSLIP6, a 6% erucamide-polypropylene masterbatch to prepare the erucamide source was supplied by the Departamento de Investigación de Polímeros del Centro de Investigación de la Compañía Española de Petroleos, S. A. Torrejón de Ardoz (Madrid/Spain).

Stearic Acid. Stearic acid of 99% purity (Fluka, A.G.) employed as an internal standard was used as received.

Chloroform. An analytical grade chloroform (Quimicen, S.A., Madrid/Spain) needed for solvent extraction was used as received.

Characterization. *^{13}C Nuclear Magnetic Resonance.* Isotactic pentad fraction (IPF = 0.92) was evaluated by ^{13}C NMR spectroscopy by using a Bruker AC300 spectrometer operating at 75.47 MHz and 7.046 T. The spectrum was measured in 1,3,5-trichlorobenzene solution at 393 K using $Cl_4C_2D_2$ as internal standard.

Molecular Weight Distribution. Molecular weight averages and polydispersity factor (molecular weight averages are in daltons (g mol^{-1}), $\overline{M}_n$ 9.79 × 10^4; $\overline{M}_w$ 4.35 × 10^5; $\overline{M}_z$ 3.34 × 10^6; $\overline{M}_v$ 3.18 × 10^5 and $\overline{M}_w/\overline{M}_n$ 4.44) were estimated by gel permeation chromatography with a Waters ALC/GPC 150 gel permeation chromatograph at 140 °C in 1,3,5-trichlorobenzene, following standard techniques.

Experimental Techniques. *Diffusion Cell.* The diffusion cell used to establish concentration profiles of diffusant within the polymer matrix is similar to those used and described by

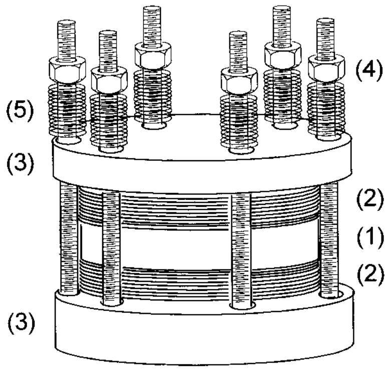

Figure 1. Schematic set up of the measuring diffusion cell. (1) Erucamide source. i-PP sheet 6 mm thick and 6 cm in diameter containing 6% erucamide. (2) i-PP film stack each 40 μm thick and 6 cm in diameter. (3) Brass plates 1 and 1.5 cm thick. (4) Stainless steel bolts, nuts, and axle guards. (5) Compression springs.

Roe et al.[30] and by Al-Malaika et al.[31] The experimental setup used for the studies of diffusion is shown in Figure 1.

It is composed of a central disk of 6.0 cm diameter and a thickness of 6.0 mm. which acts as a source of additive. It contains an excess of additive (5−6% w/w).

Two stacks of additive-free film slices are situated above and below the disk source. Each one of the additive-free films (slices) are 6.0 cm diameter and 40 μm thickness.

The source and the two stacks of slices ensembled all together in the form of a sandwich, are introduced in the measuring cell as is shown in Figure 1. With the aim that the contact between films and that of these with the source be correct, during all the time of the measurements, the sandwich was twice daily kept up at a constant pressure which is attained by tightening each one of the six screws of the measuring cell by means of a constant pair spanner (Norbar, England, with a torque wrench capacity of 1−20 N m). The applied torque wrench was 10 N m.

The whole diffusion cell was then placed in an oven which is very precisely temperature controlled for a long period of time at the required temperature. This oven is in such a manner controlled that the temperature is continuously maintained constant and monitored and recorded during the experiment. The heating oven used for the diffusion experiments was an oven from a Carlo Erba Fractovap Model C type AID/f. The heating oven temperature precision was within 0.5 K. The temperature was monitored by means of a precision quartz Hewlett-Packard 2804 A thermometer with a quartz sound probe Model 18111 A (Mountain View, CA) and a graphic recorder Yew Model 3056. To avoid possible sources of error caused by the additive adsorbed or transported by edge effects on the surface contacting the additive source in the first slices, concentration of the first film slice next to the additive source was not used in the calculation.

Measurement of the Erucamide Content. The general analytical approach chosen was to extract the amide followed by its quantitative determination by capillary column gas chromatography. We have used a procedure given by Brengartner[32] with some modifications[33] for the separation of fatty acid amides using capillary columns. The individual films were extracted at refluxing in a Soxhlet extractor with 100 mL of chloroform during 3−4 h; this time is generally sufficient for complete extraction of the additive, the extracted solution was concentrated under vacuum in a rotovapor until just before the solvent completely disappeared, and then the solution was volumetrically standardized. Calibration was carried out by the peak-area ratio method using as the internal standard Stearic acid not present in the sample.

The gas chromatographic equipment used in the present study was a Perkin-Elmer Model 3920 gas chromatograph equipped with a flame-ionization detector (FID).

A fused silica 10 m, HP-1 (dimethylpolysiloxane) column with an internal diameter of 0.53 mm and a film thickness of 2.65 μm was used. The column was operated using nitrogen as carrier gas with a flow rate of 2 mL/min. The column temperature program was 4-min hold at 230 °C followed by a 8 °C/min ramp to 285 °C. The final temperature was held for 4 min. The injector and detector temperatures were 275 and 290 °C, respectively. Repeated on-column injections of samples with an amide concentration in the 50−4000 ppm resulted in a relative standard deviation of 3−4%.

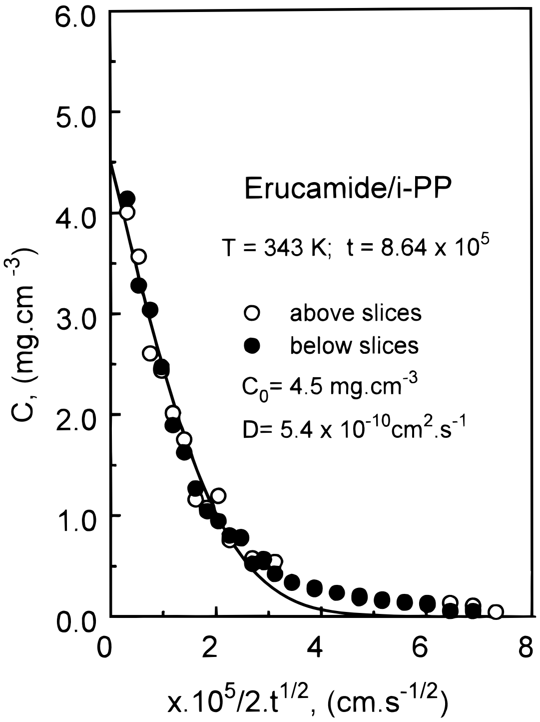

Figure 2. Diffusion−concentration profiles. Comparison of theoretically calculated by the simple Fickian diffusion model (solid line) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 343 K. Experimental points were measured after 10 days in the diffusion device.

Experimental Results

Diffusion profiles were generated from the gas chromatography analyses. There was no consistent variation in the value of *c* as measured over the two stacks, i.e., above and below the source.

For temperature of 343 K the diffusion experiment was carried out at three different times, namely, 5, 10, and 15 days. The experimental results are given in Figures 2 and 3 for the two series of experiments (10 and 15 days, respectively) as a function of the distance to the source *x*. From these experimental results and by means of eq 3, we have estimated the diffusion coefficients *D* at every diffusion time *t*. The results of the diffusion coefficients are gathered in Table 1. The dependence of these diffusion coefficients as a function of the time of diffusion *t* has been done in Figure 4, whereas it can be appreciated that the diffusion coefficient for the present system at this particular temperature depends very smoothly and in a practically inappreciable form on the time of diffusion and within the limits of the errors of the experimental type of the technique employed in its determination. Some other diffusion profiles have been obtained at 323, 333, and 353 K and 15 days. Those obtained at 333 and 353 and 15 days are given in Figures 5 and 6.

For a temperature of 333 K the diffusion experiment was carried out by duplicate in two identical diffusion cells in order to see the reproductivity of the method.

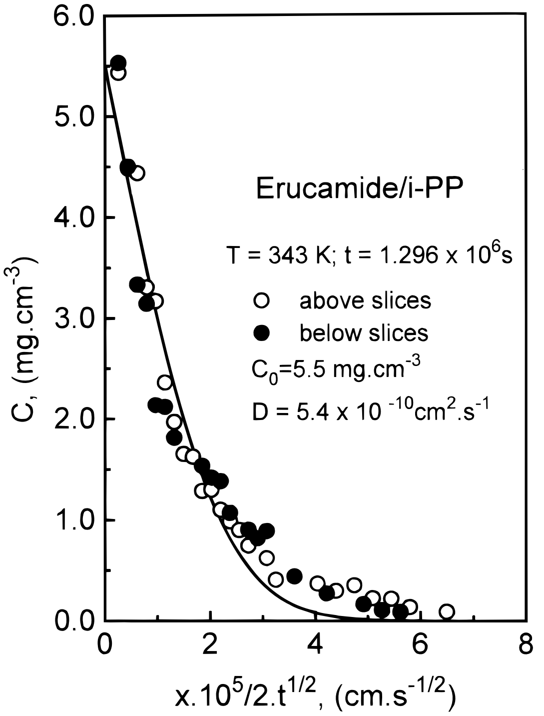

Figure 3. Diffusion–concentration profiles. Comparison of theoretically calculated by the simple Fickian diffusion model (solid line) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 343 K. Experimental points were measured after 15 days in the diffusion device.

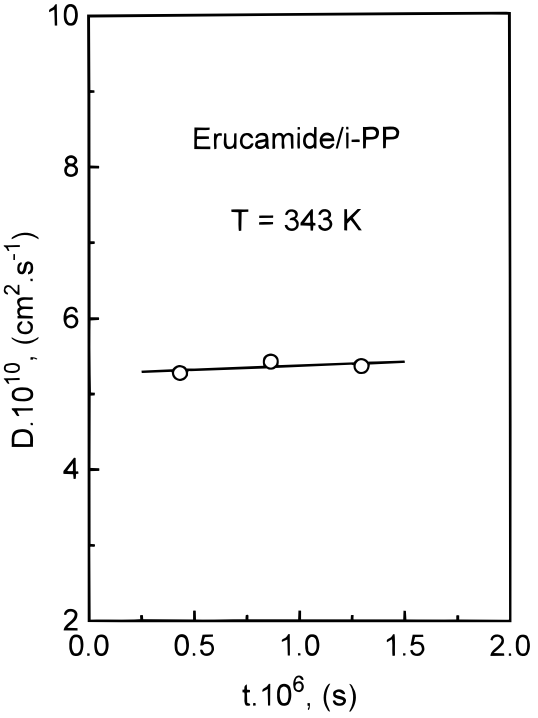

Figure 4. Dependence the diffusion coefficient D (cm^2 s^{-1}) at 343 K on the time of diffusion t for the erucamide/i-PP system.

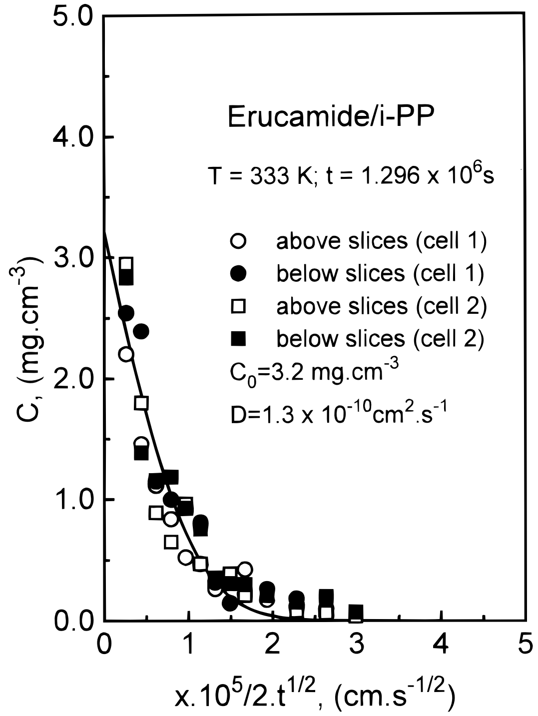

Figure 5. Diffusion–concentration profiles. Comparison of theoretically calculated by the simple Fickian diffusion model (solid line) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 333 K. Experimental points were measured after 15 days in the diffusion device.

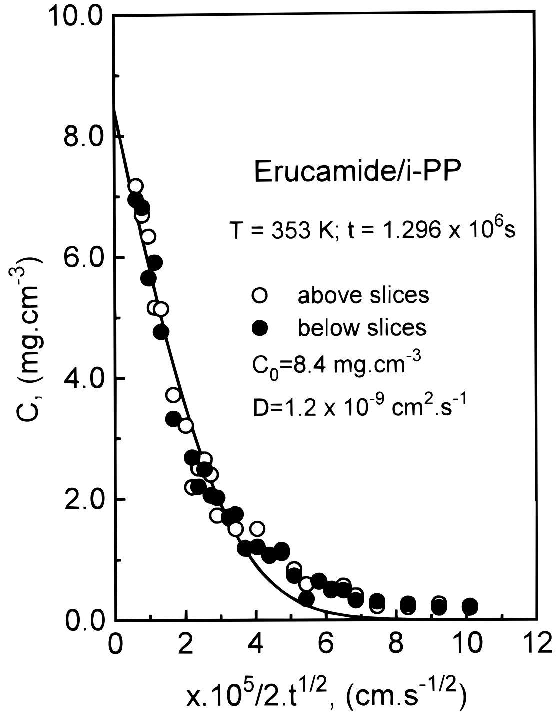

Figure 6. Diffusion–concentration profiles. Comparison of theoretically calculated by the simple Fickian diffusion model (solid line) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 353 K. Experimental points were measured after 15 days in the diffusion device.

The experimental results have also been plotted in Figure 5.

The experimental profiles given in Figures 2, 3, 5, and 6 have been compared with theoretical curves calculated by means of eq 3. These calculated values have been drawn as full lines on the same figures and are based on a solution of Fick's diffusion equation given by the expression 3 for the best-fitting curve. They were selected with the aid of a basic computer program and used to calculate the diffusion coefficients. Table 1 shows also the equilibrium solubility C_0 and the intrinsic diffusion coefficient D of erucamide in i-PP measured over the temperature range 323–353 K. This Table 1

Table 1. Initial Equilibrium Concentration of Diffusant at the Surface or Equilibrium Solubility C_0, Diffusion Coefficient D, Correlation Coefficient R^2, and Standard Error S_E for the Diffusion of Erucamide into Propylene at Several Temperatures for the Simple Fickian Model

T (K)	$10^6 t$ (s)	film side	C_0 (mg cm^{-3})	S_E (C_0)	$10^{10}D$ (cm$^{2\cdot}$ s^{-1})	$10^{11}S_E$ (D)	R^2	S_E(curve)
323	1.296	a	1.78	0.077	0.276	0.19	0.998	0.017
		b	0.94	0.077	0.422	0.64	0.990	0.024
		[a + b]	1.35	0.222	0.325	0.93	0.925	0.082
333	1.296	a(1)[a]	2.70	0.211	1.32	2.10	0.949	0.152
		b(1)[a]	3.42	0.299	1.37	2.43	0.939	0.219
		a(2)[a]	3.85	0.455	0.868	1.95	0.907	0.264
		b(2)[a]	3.07	0.335	1.51	3.44	0.897	0.258
		[a + b](1) + [a + b](2)[b]	3.21	0.170	1.27	1.36	0.900	0.24
343	0.432	a	4.27	0.277	4.35	5.91	0.967	0.206
		b	3.85	0.555	6.76	23.20	0.823	0.491
		[a + b]	4.07	0.319	5.27	9.20	0.886	0.362
	0.864	a	4.45	0.159	5.63	4.69	0.976	0.179
		b	4.58	0.152	5.23	3.89	0.980	0.166
		[a + b]	4.52	0.108	5.43	2.97	0.978	0.170
	1.296	a	5.86	0.215	4.91	4.21	0.971	0.266
		b	5.18	0.337	5.98	10.21	0.920	0.438
		[a + b]	5.53	0.199	5.35	4.75	0.946	0.356
353	1.296	a	8.48	0.345	12.2	10.99	0.963	0.414
		b	8.33	0.329	12.3	10.99	0.966	0.398
		[a + b]	8.41	0.234	12.3	7.64	0.964	0.399

[a] These values correspond to two series of independent experiments carried out at the same time but in two similar but separated diffusion devices, i.e., from two series of measurements. [b] This value corresponds to the mean value from measurements of two series of independent experiments carried out at the same time but in two similar but separated diffusion devices, i.e., from four series of measurements. [c] Solubility values may be transformed in the usual (%) units, i.e., weight percentage by taking into account the matrix density.

also shows the standard error for C_0 ($S_E(C_0)$) and for D ($S_E(D)$), the standard error for the fitted curve (S_E-(curve)) and the correlation coefficient R^2. In general, we can say that the ideal Fickian model fails in part to provide a totally satisfactory representation of the experimental data points in the case of lower erucamide concentrations. As can be also noted, the shape of the final part of the diffusion curve, i.e., for slices far away from the source, suggests that some other process is superimposed to the simple Fickian diffusion mechanism, perhaps by giving rise to some anomalous process such as a two-stage process mechanism, for instance. If we have a look at the data of the correlation coefficients (R^2) or to the standard error deviations of the adjusted curve (S_E) which are given in the sixth and seventh columns of Table 1 on the fitting of Fick's equation to our experimental data, we do believe that they are not good enough and we must think that there must be some type of effect on the coefficient of diffusion which has not been taken into account in the simple Fickian diffusion model. An inspection of Figures 2, 3, 5, and 6 makes clear that for the intermediate distances to the source the amount of diffused erucamide is lower than that predicted by the diffusion model of Fick; similarly in the other zone of diffusion, i.e., at higher values of x, the distance to the source, the diffused amounts are higher than those predicted by the equation of Fick. Both phenomena bring to us to think that this can be due to the simultaneous existence of two different mechanisms of diffusion, one of which may be fundamentally operative at low and the other at high distances to the source. In other words, at high and low concentrations in the series of slices. These two mechanisms may have well-differentiated coefficients of diffusion. The erucamide concentration in the slice has a predominating effect on each one of these two mechanisms of diffusion. This assumption may be well justified by the morphology and texture of polypropylene and the nature of this incompatible long-chain additive and their thermodynamic and hydrodynamic interactions.

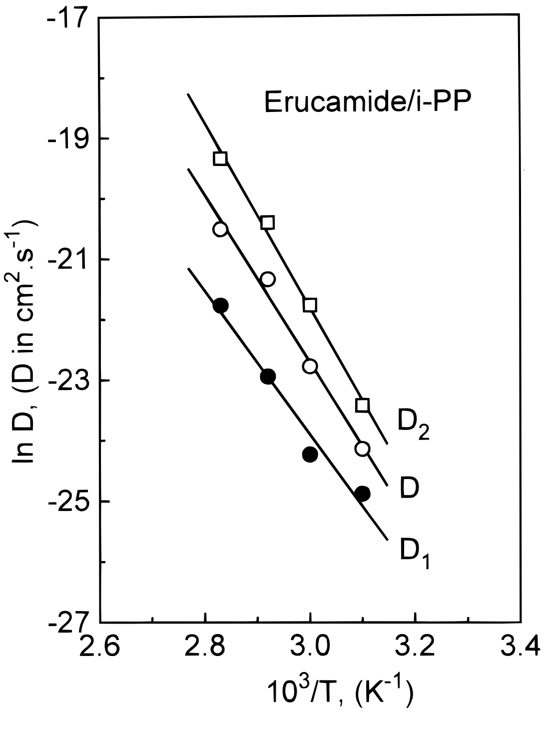

Figure 7. Arrhenius plot as ln D against $1/T$ of diffusion coefficients D (simple Fickian diffusion model), and D_1 and D_2 (semiempirical two Fickian diffusion model) of erucamide/i-PP system at several temperatures. The diffusion coefficients D and D_1 and D_2 have been calculated by means of the simple Fickian model and the dual model, respectively.

However, the results obtained so far may be interesting for comparative purposes as we will see later on in this paper.

Figure 7 shows the variation of ln D with $1/T$ on an Arrhenius plot. The points signify values of D obtained from each experiment corresponding to the two stacks of slices over which diffusion took place after 15 days. The values plotted represent the value of D calculated within the two stacks measurements.

In all these experiments, as it is very easily observed in Figures 2, 3, 5, and 6 the values of the concentration in the tail interval at the end of the curve, lay above of the calculated ones by means of the theoretical model represented by the first law of Fick, as can be very easily seen. We must intend to attain a best agreement between our experimental results and some other theoretical approach in order to interpret correctly the diffusion process in the erucamide/i-PP system.

In the past, there have been many studies addressed to understand the different non-Fickian behaviors found below the glass transition in amorphous polymers.[34−52] A series of models have been proposed in some of these studies. These models take into account the double nature of anomalous sorption mechanism involving penetrant diffusion and polymer relaxation.[40] The deviation from Fickian behavior has been associated with the finite rate at which the polymer structure rearranges to accommodate penetrant molecules, in these polymers the diffusion behavior is referred as case II. Case II is a non-Fickian or *viscoelastic* gradient diffusion phenomenon in polymer/fluid systems.[53] It is an extreme deviation from Fickian diffusion when *nonlinaerities* dominate.[54] In general, a rubbery polymer above its glass transition it is expected that obeys Fick's law.

The term *anomalous diffusion* has been coined to term sorption behaviors which depart from the ideal Fickian behavior and case II behaviors. In the anomalous diffusion a continuous concentration profile moves into the polymer with decreasing rate and intensity. The most characteristic anomalous behaviors may be classified[55] in the following categories: (i) pseudo-Fickian behavior; (ii) sigmoidal behavior; (iii) two-stage behavior; (iv) overshoot; (v) super case II.

In the case of semicrystalline polymers, the diffusion is restricted to the amorphous fraction, but the state of the latter will be of course affected by the presence of crystallinity. Studies on the anomalous diffusion or non-Fickian diffusion in semicrystalline polymers above T_g are very scarce.

Even though the case II has been classically restricted to the diffusion of molecules in glassy polymers, in the case of semicrystalline polymers above of the glass transition T_g, crystallites impose some limitations to the amorphous phase motions. This fact would justify the use of the same models employed for glassy polymers. To this effect we have applied the generalized diffusion equation of Wang et al.,[56,57] which described the combination of Fickian and case II mechanisms:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x} - vc\right) \tag{5}$$

where D is the Fickian diffusion coefficient and v is the velocity of case II, which has been interpreted as a stress coefficient. These authors provide a solution for eq 5 that relates the concentration profile into the polymer. We have analyzed our experimental results by means of this equation. However, despite that our data can be fitted to this equation and the agreement, represented by the correlation coefficient R^2, is higher than that found for the simple Fickian model, the values for the parameter v were negative. This does not make any sense, since v represents the velocity of the advancing penetrant front. However, we must keep in mind that we are dealing with a system that is incompatible from the thermodynamic point of view.

None of the models previously described are applicable to our system. For this reasons, we have analyzed our experimental results by means of which we call a *semiempirical sorption model*. The overall diffusion process in our system may be considered as a linear superposition of phenomenologically independent contributions from two simultaneous Fickian diffusion processes or for long-chain molecules diffusing under two different species or for two different types of routes. Such diffusion behavior may be explained here by assuming that erucamide diffusing within i-PP may be present in two different sites, voids, cavities, holes, etc., whatever you like, namely, cells in which the penetrant molecules can diffuse, with different geometries (size, shape, and tortuosity and so on in the matrix) and accessibilities and therefore in two distinct thermodynamic states. Or on the contrary, we have two types of long-chain additive species, either because their own physical structure or because they move in cells with two different types of motion. Their precise definition does not affect the description of the system. Let assume that our long-chain diffusant has a relative distribution of molecular species such that its initial concentration in the matrix is

$$c_0 = \sum_i c_{i,0} \tag{6}$$

where $c_{i,0}$ is the concentration of species of type i of diffusant in the polymeric matrix. Therefore, and assuming we have two different type of long chain diffusant molecules, we can write

$$c(x,t) = \sum_i c_i(x,t) = c_1(x,t) + c_2(x,t) \tag{7}$$

where $c(x,t)$ is the total concentration of penetrant in the polymer in the plane x and at time t, $c_1(x,t)$ is the concentration of penetrant molecules as species of type 1, and $c_2(x,t)$ is the concentration of penetrant molecules as species of type 2. And if we assume that each one of them diffuses by a simple Fickian diffusion model, from eq 3, i.e., $c(x,t) = C_0 \operatorname{erfc}[x/2(Dt)^{1/2})]$ and assuming that we have two types of molecular species only, we can write finally

$$c(x,t) = C_{01} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_1 t}}\right) + C_{02} \operatorname{erfc}\left(\frac{x}{2\sqrt{D_2 t}}\right) \tag{8}$$

where C_1 and C_2 represent the equilibrium solubilities of the additive in polymer cells of the types 1 and 2, respectively, and D_1 and D_2 the diffusion coefficients of the additive in polymer cells of the types 1 and 2, respectively. When $x = 0$, therefore, $c(0,t) = C_{01} + C_{02}$. We have considered this concentration as the equilibrium solubility $C_0 = C_{01} + C_{02}$ for our *semiempirical sorption model*.

Figures 8−12 show the best fitting of some of our experimental results to this model. Thus, for instance, Figure 10 shows the best fitting for the experimental results obtained at 343 K and three times of diffusion. The dashed line represents the concentration of penetrant molecules of type 1. They diffuse with a diffusion coefficient D_1, and the dotted line represents the concentration of penetrant molecules of type 2. They diffuse with a diffusion coefficient D_2. The full line is the global concentration of erucamide diffusing by both mechanisms. As it can be observed in these figures there exists a very good agreement between the values

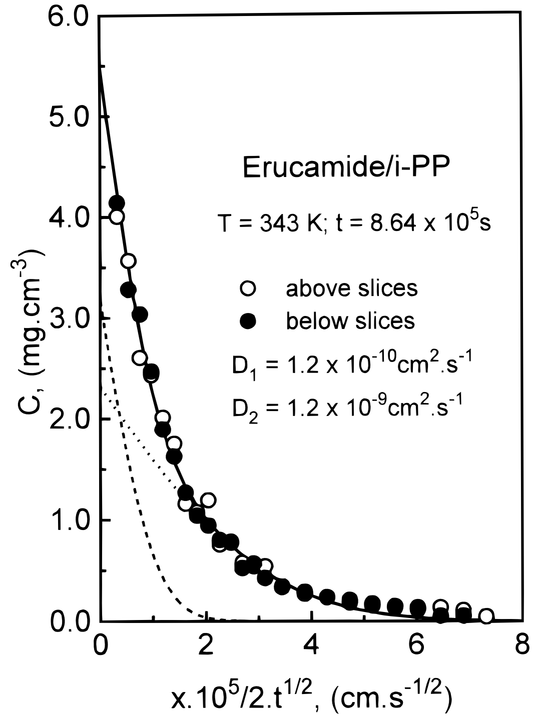

Figure 8. Diffusion−concentration profiles. Comparison of theoretically calculated by a semiempirical two Fickian diffusion model (dotted and dashed lines) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 343 K. Experimental points were measured after 10 days in the diffusion device. The full line represents the overall diffusion−concentration profile for the two separate mechanisms.

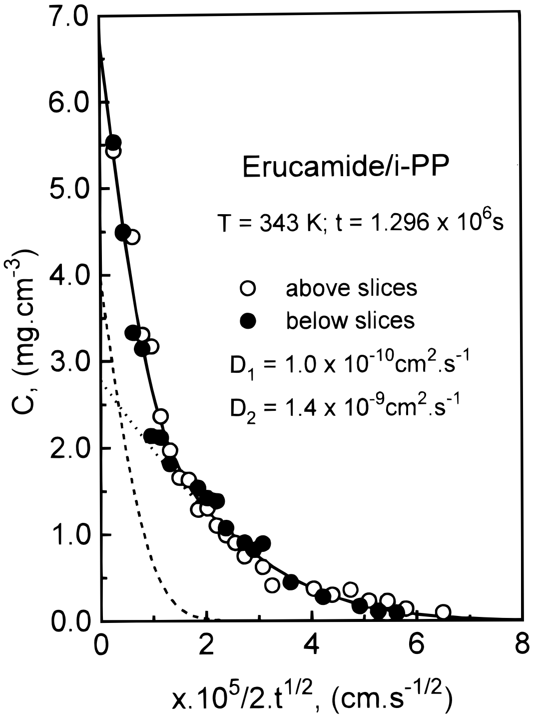

Figure 9. Diffusion−concentration profiles. Comparison of theoretically calculated by a semiempirical two-Fickian diffusion model (dotted and dashed lines) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 343 K. Experimental points were measured after 15 days in the diffusion device. The full line represents the overall diffusion−concentration profile for the two separate mechanisms.

obtained experimentally and those calculated with the semiempirical theoretical model which we have proposed. Values calculated for the respective parameters by means of this theoretical model are gathered in Table 2. As it can be observed the correlation coefficients R^2 found with this model are higher than those given in Table 1 for the simple Fickian diffusion model represented by eq 3 and for the generalized diffusion eq 5 of Frisch et al.[56,57]

Arrhenius plots for these two diffusion coefficients are also shown in Figure 7.

Discussion of Results

Since the system eru/i-PP has shown to be incompatible,[58,59] we do not expect to have any plasticizing or diluting action due to erucamide, at the temperature of our experiments, to bring about any solvent-induced crystallization at all the investigated temperatures for the i-PP within the slices in contact with erucamide. Furthermore, melting points of i-PP in erucamide/i-PP blends do not depend on blend composition.[58] In addition during the diffusion experiment times no morphological changes in the matrix have been observed. Therefore, we cannot attribute the non-Fickian diffusion behavior to bulk or/and to structural changes within the matrix. At the same time, i-PP melting point is high enough and it is far away to minimize complications due to changes in crystallinity or morphology by annealing during the experiments.

Figure 7 shows the variation of these two diffusion coefficients D_1 and D_2, obtained by means of eq 8, with temperature following the Arrhenius' plot as ln D against $1/T$. As it is very easily appreciated both coefficients behave similarly and they follow the Arrhenius' equation (with correlation coefficients of $R^2{}_1 = 0.970$ and $R^2{}_2 = 0.992$, respectively). The activation energies for each process are $E_d(D_1) = 100$ and $E_d(D_2) = 130$ kJ mol^{-1}, respectively. This means that there exists a difference about of 30 kJ mol^{-1} between the two processes or mechanisms of diffusion represented by these two diffusion coefficients. However, it is somewhat greater for the prominent process, i.e., that which takes place at low concentrations.

In our semiempirical two-Fickian diffusion model we have considered, the two diffusion coefficients which correspond to each one of the hypothetical mechanisms, represent averages values of the diffusivity. Values of the diffusion coefficients estimated assuming that the diffusion obeys either a simple Fickian diffusion model or semiempirical two Fickian diffusion model agree very well with the values obtained by Gondo and Utsunomiya,[60] who have studied by the same procedure the diffusion of an antioxidant such as BHT (2,6-di-*tert*-butyl-*p*-cresol) into i-PP. The activation energies also agree quite well with the value they reported. And with the results given by Hayashi and Matsuzawa[20] obtained on the same system BHT/i-PP by the rolling procedure.

It is now generally accepted that transport of diffusants through semicrystalline polymers such as polypropylene takes place primarily in the amorphous regions separating the lamellae, while the crystals are practically impermeable.[61−65] The crystals can be mainly considered as an impermeable obstacle hampering the diffusive current through the material. Even the sorption is so much reduced that, without any major error, one can treat the sample as if the crystalline phase were not acting as a sorbent.[65] It has long been recognized that the spherulite structure is heterogeneous in nature and very complex and that any manageable morphologi-

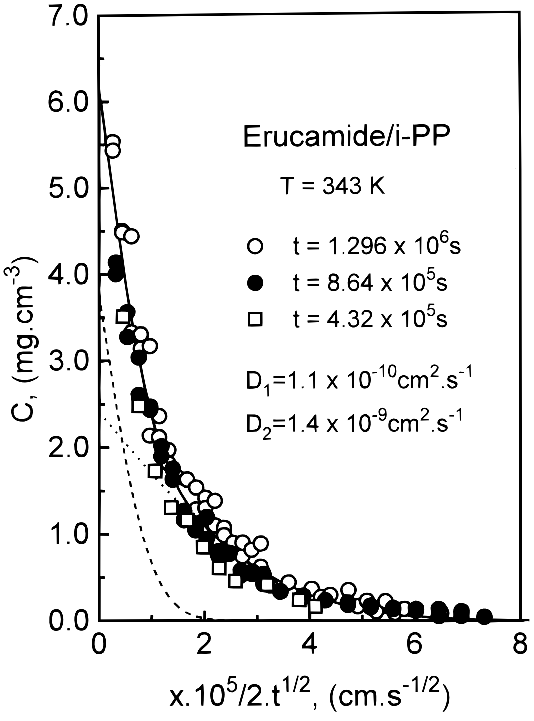

Figure 10. Diffusion−concentration profiles. Comparison of theoretically calculated by a semiempirical two Fickian diffusion model (dotted and dashed lines) and experimentally obtained data (open and full circles and open squares) concentration profiles for erucamide/i-PP system at 343 K. Experimental points represent mean values for the above and the below slices. They were measured after 5 days (open squares), 10 days (full circles), and 15 days (open circles) in the diffusion device. The full line represents the overall diffusion−concentration profile for the two separate mechanisms.

cal model necessarily must incorporate a large number of simplifications. Coming back again on our experimental data and eq 8, we can present two arguments. Peterlin[66] pointed out, some years ago, that for semicrystalline polymers the diffusive transport proceeds only through the thin amorphous layers between the lamellae and the amorphous boundaries between the randomly oriented stacks of lamellae and between the spherulites. This morphological model is good enough to explain the two types of diffusion found in the present paper. Therefore, we may have two types of diffusion paths which may be different from the point of view of their tortuosity factors giving place to two similar but differentiated diffusion coefficients. The activation energies for diffusion, however, must be different, but quite similar, which may be indicative that the mobility of the penetrant is affected in a very smooth fashion. On other hand, Peterlin[66] also suggested that the majority of transport anomalies in polypropylene[67−69] are either artifacts or a consequence of gross structural defects (holes) which are not considered in the two-component model of semicrystalline polymers. i-PP is known to be a complicated system, even by polymeric standards. This was put forward by the change of birefringence of its spherulites[70] and the different crystal forms.[71] Complex twinning of the usual monoclinic form has been found and interpreted in lamellar objects grown from solution.[72] In the same manner certain ambiguities in the inferred twin law were resolved by Lovinger[73] using epitaxial crystallization of thin films on mica. Finally, Bassett and Olley[74] have studied an intricate fine structure (cross-hatching) in spherulites of monoclinic polypropylene which are different from that traditionally believed to occur. Its explanation requires a theory of branching and splaying of individual dominant lamellae, not of the instability of a planar crystal interface as considered by Keith and Padden.[75] They suggested that the probable cause of splaying is pressure from compressed cilia between adjacent lamellae. Another quite plausible explanation to account for our results is that which has been proposed by Wada et al.[76] They observed two breaks in the temperature dependence of both specific volume and logarithmic retardation time in i-PP, indicating two glass transitions. These two transitions gave two loss peaks in isochronal dynamic mechanical at 3 MHz. The lower transition T_{g1} was assigned to the amorphous phase, which is rich in atactic chains (A_1 phase); the upper transition T_{g2} to the amorphous phase rich in isotactic chains (A_2 phase). They have also considered[76] the following two situations of the amorphous phase in the spherulite of i-PP: (i) the space between lamellae aligned in the radial direction of the spherulite and (ii) the space between folded surfaces of the lamellae. All these facts and peculiarities and probably some others may be taken into account to interpret our experimental results at least from a qualitative point of view.

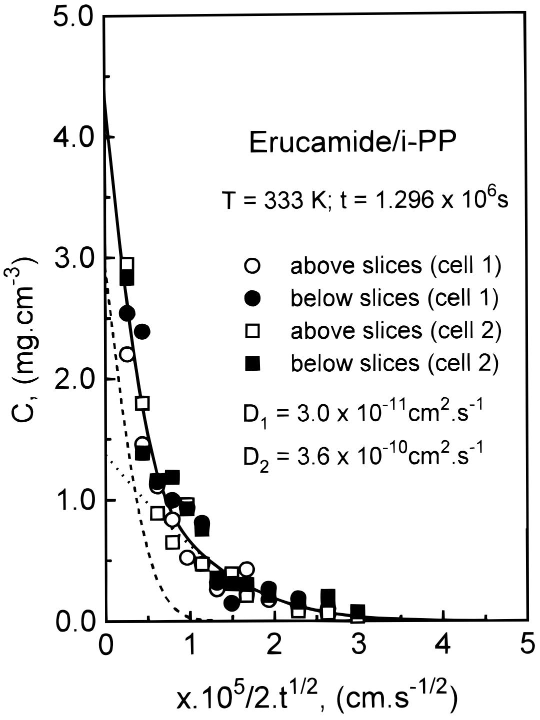

Figure 11. Diffusion−concentration profiles. Comparison of theoretically calculated by a semiempirical two-Fickian diffusion model (dotted and dashed lines) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 333 K. Experimental points were measured after 15 days in the diffusion device. The full line represents the overall diffusion−concentration profile for the two separate mechanisms.

All we have made mention above can be rationalized in the light of new interpretations given by Van Alsten et al.[24−26] We can assume that there exist structural restrictions to the diffusion on one hand and entropic barriers on the molecular transport on the other.[77−80] As has been done by Van Alsten et al.,[24−26] we also adopt the correlation function approach of Santa Cruz et al.,[81] which invokes a morphological model for semicrystalline polymers. The two-phase model is composed of bundles

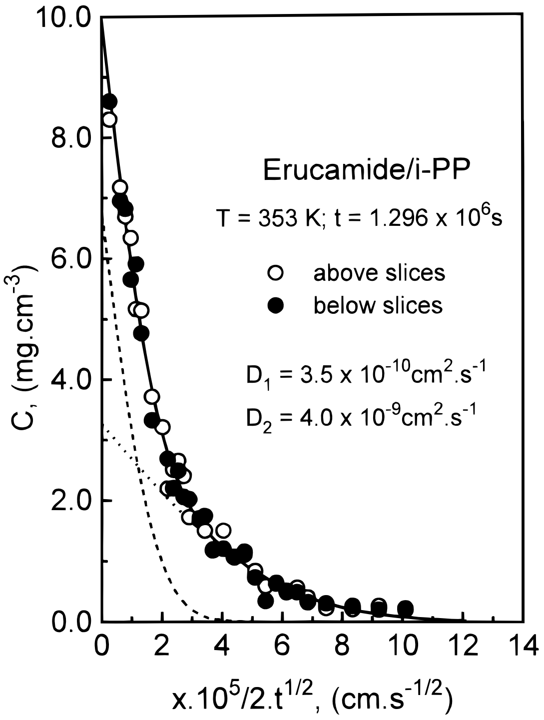

Figure 12. Diffusion−concentration profiles. Comparison of theoretically calculated by a semiempirical two-Fickian diffusion model (dotted and dashed lines) and experimentally obtained data (open and full circles) concentration profiles for erucamide/i-PP system at 353 K. Experimental points were measured after 15 days in the diffusion device. The full line represents the overall diffusion−concentration profile for the two separate mechanisms.

of lamellae of long period L and spacing l_a separated by a large amorphous region of width d_a. The lamellar thickness is l_c. The bundles are further segregated by an intervening amorphous phase, which may be referred to as amorphous pockets. Van Alsten et al.[26] think that these pockets are the primary arteries for diffusant transport. Spherulites will contain a large volume of material unaccessible to penetrant molecules in the centre, and large volumes of accessible volume at the periphery. Transport will be limited to these regions in which the lamellar structure has defined chanels of a dimension adequate to accommodate a penetrant molecule. On the entropic barriers point of view, Muthukumar and Baumgartner[77−80] have carried out simulations of chains undergoing Brownian motion while ensconced between both regularly spaced and randomly distributed, impenetrable obstacles. In random media there are three time regimes of the center-of-mass mean-squared displacement. At short times there are Fickian kinetics due to unhindered displacement over distances smaller than the average separation between obstacles. At intermediate times the chain explores bottlenecks and narrow channels between obstacles over time scales comparable to the correlation time of the chain's radius of gyration. Anomalous, sub-Fickian diffusion kinetics result as chain configurational motion is retarded.

Some of the present authors[82] have studied very recently the erucamide/polyamide 12 system using the same experimental technique and setup, i.e., cell of diffusion, chromatographic analysis, and systematic procedure of numerical analysis. In this case the diffusion of erucamide in polyamide 12 obeys very precisely a Fickian law of diffusion. This fact means that the results found in the present case of diffusion of erucamidere in i-PP do not emanate either as an experimental artifact of the measurement setup (experimental methodology) or from any casuistic numerical analysis. Both do confirm once again the goodness of our experimental results and setup as well as our analysis. From the transport point of view, this finding permits to us to point out that in the transport in semicrystalline polymers two factors must be considered: one, a morphological which is conditioned by the morphological and structural peculiarities of every matrix and a second one in which the thermodynamic interactions between the diffusant and matrix may be of capital importance. The diffusion coefficients found for the present system may be controlled in a certain extension by both factors.

Diffusion results found by Vittoria et al.[83] indicate that the behavior of the amorphous phase in quenched i-PP samples, after 24 h immersed in solvents such as dichloromethane, cyclohexane, carbon tetrachloride, or chloroform, are very similar to the starting sample, although the non-Fickian behavior of the sample immersed in cyclohexane after 5 days indicates that the thermodynamic state of the amorphous component is changed, despite the constant sorption.

To know the morphological behavior and possible interactions between erucamide and i-PP we have studied,[58,59] a series of erucamide/i-PP blends prepared by dry mixing using differential scanning calorimetry (DSC), polarized optical microscopy, scanning electron microscopy (SEM), dynamic mechanical thermal analysis (DMTA), and dielectric thermal analysis (DETA). In both studies, erucamide/i-PP show a characteristic behavior typical of incompatible systems. These DCS studies[58] have demonstrated that the crystallization of erucamide/i-PP blends results in separate crystals of the two components rather than cocrystallization. The temperature of melting at the maximum of the melting endotherm of i-PP does not depend on the erucamide composition in blends. The apparent melting enthalpy is also almost unaffected by the composition. Most of the erucamide in the polymeric matrix is segregated forming a second phase as globules, and only a minor part is located in the amorphous regions of the i-PP spherulites. Similarly, the detected dynamic mechanical and dielectric relaxations[59] do not vary appreciably on composition, thus suggesting that the amorphous phase in spherulites has a constant composition.

The problem of diffusion in semicrystalline can become more complex,[84,85] as occurs in the case of the diffusion of certain crystallizable polymers which have been prepared in the glassy state without any significant levels of crystallinity but because the introduction of a diffusant with interactive properties (diluent) may remove the hindrances to crystallization by plasticizing the material locally and therefore crystallizing the glass during the permeation of the diffusant (diluent) into the polymer. Nevertheless, this does not seem to be the present case.

It is evident that if we consider the overall interval of concentration, the diffusion coefficient can not be considered constant. There is not a unique coefficient of diffusion all over the stack of slices which can explain our experimental results.

We have also calculated the overall diffusion coefficients D_{eff} calculated by the method of Matano[17] by means of eq 4 at temperatures of 323, 333, 343, and 353 K, for experiments carried out for 15 days. The effective

Table 2. Initial Equilibrium Concentrations of Diffusant at the Surface C_{01} and C_{02} (Equilibrium Solubility), Diffusion Coefficients D_{01} and D_{02}, Correlation Coefficient R^2, for the Dual Mechanism of Diffusion of Erucamide into Isotactic Polypropylene at Several Temperatures

T (K)	10^6t (s)	film side	C_{01} (mg cm^{-3})	$10^{10}D_1$ (cm^2 s^{-1})	C_{02} (mg cm^{-3})	$10^{10}D_2$ (cm^2 s^{-1})	C_0 (mg cm^{-3})	R^2
323	1.296	[a + b]	1.1	0.16	0.5	0.66	1.6	0.928
333	1.296	[a + b](1) + [a + b](2)	2.9	0.30	1.4	3.56	4.3	0.936
343	0.432; 0.864; 1.296	[a + b]	3.8	1.08	2.4	13.6	6.2	0.962
	0.432	[a + b]	3.5	0.95	1.9	15.2	5.4	0.951
	0.864	[a + b]	3.2	1.24	2.3	12.3	5.5	0.991
	1.296	[a + b]	3.9	1.02	2.8	14.4	6.7	0.984
353	1.296	[a + b]	6.7	3.78	3.3	39.6	10.0	0.989

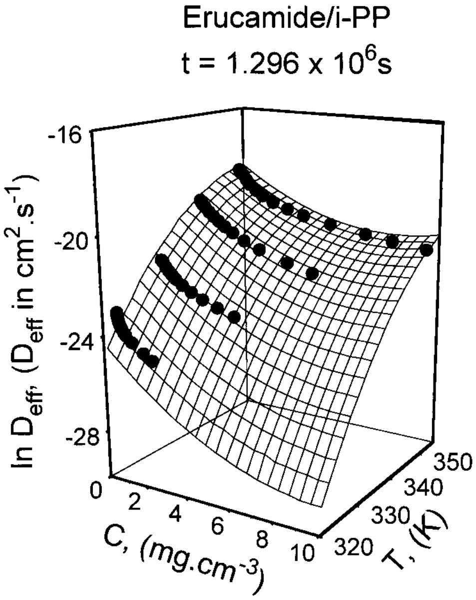

Figure 13. Tridimensional plot of the effective diffusion coefficient D_{eff} as ln D_{eff} against temperature T and concentration C for erucamide/i-PP system for a time period of 15 days (1.296×10^6 s).

coefficient of diffusion decreases as the concentration increases. This result seems to be obvious since if we take into account the results derived from our semiempirical model which we have proposed, we can see that at low concentrations we have basically only species belonging to type 2. The diffusion coefficient for this species 2 is larger than that for the species of type 1.

In Figure 13 we have made a threedimensional plot of the effective diffusion coefficient D_{eff} as ln D_{eff} against temperature T and against concentration c. The values of these coefficients of diffusion D_{eff} have been calculated by means of the method of Matano[17] as we have seen above. This dependence can be represented by a quadratic surface which corresponds to the theoretical model represented by the following equation:

$$\ln D_{\mathrm{eff}} = A_1 + A_2c + A_3T + A_4c^2 + A_5T^2 + A_6cT \quad (9)$$

in which T and c are the temperature and the concentration, respectively. The coefficients have the following series of values: $A_1 = -607.039$; $A_2 = -2.957\,29$; $A_3 = 3.299\,55$; $A_4 = 0.040\,469\,0$; $A_5 = -0.004\,624\,82$ and $A_6 = 0.006\,586\,82$.

The free-volume concept of Fujita et al.[34,86] has been used as an empirical tool to relate the diffusion coefficient with free volume. Lower glass transition temperatures are associated with polymers having a large proportion of free volume in the rubbery state. According to the Williams–Landel–Ferry theory[87] the free-volume fraction $f_v(T)$ in a polymer at a temperature T above T_g can be conveniently expressed in the form

$$f_v(T) = f_v(T_g) + (\alpha_l - \alpha_g)(T - T_g) \quad (10)$$

where $f_v(T_g)$ is the free volume fraction at the glass transition. It has the universal value of *0.025* for all polymers and $(\alpha_l - \alpha_g) = \Delta\alpha$ is the difference between the thermal expansion coefficients above and below T_g. This expression enables values of $f_v(T)$ to be calculated at any experimental temperature such as those of our experimental diffusion coefficients of Tables 1 and 2. The diffusion coefficient of a diffusant into a polymer matrix seems to depend on fractional volume and it can be given to a good approximation by Fujita et al.[86] equation in terms of our diffusion coefficients through the free volume fraction by

$$D(T) = D_0 \exp(-B/f_v(T)) \quad (11)$$

which relates the diffusion coefficient $D(T)$ to the fractional free volume $f_v(T)$. D_0 and B are two parameters depending on the polymer (D_0) and on the polymer and diffusant (B). They are assumed to be independent of temperature. D_0 may also denote the value of $D(T)$ at zero diffusant concentration. At higher concentration the diffusant makes a contribution to the free volume of the system and then the above equation may no longer obey.

To estimate the fraction of free volume $f_v(T)$ according to eq 10, the values for $\alpha_g = 6.5 \times 10^{-5}$ K and $\alpha_l = 14.5 \times 10^{-5}$ K have been adopted.[88] The value for $T_g = 268$ K for the present unadditivated i-PP has been taken from ref 58. In Figure 14 we have plotted Fujita's equation as a function of ln D for the three series of diffusion coefficients calculated by means of the simple Fickian model D, and those calculated from our semiempirical two-Fickian diffusion model D_1 and D_2, respectively, as a function of $1/f_v(T)$. In these three cases the plot yields straight lines. This fact signifies that at least in the temperature range investigated the diffusion coefficients of our system obey Fujita's and Williams–Landel–Ferry's equations.

From our experimental results we have also estimated the *equilibrium solubility* of the additive in the polymer C_0 at each temperature by extrapolation the diffusion data to penetration depth equal to zero according to eq 8 for our semiempirical dual-diffusion model. But before going into details, to see how is affected this equilibrium solubility C_0 by the time of diffusion, we have made a plot of this magnitude C_0 as a function of the time of diffusion for three different times of diffusion as can be seen in Figure 15. As it is very easily appreciated C_0 depends on t very smoothly. It does not affect the conclusion derived from our experimental results.

Although the procedure mentioned above to get C_0 seems to be less satisfactory, when there are data available on the same system additive matrix/temper-

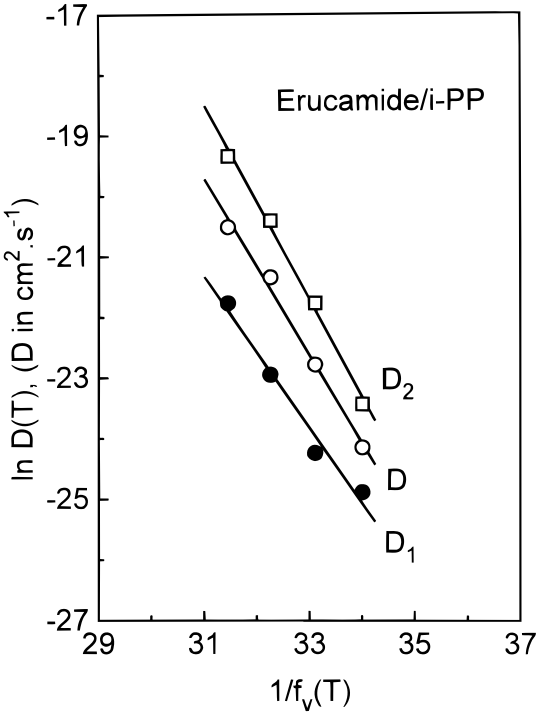

Figure 14. Plot of the Fujita equation as a function of the ln *D(T)* against $1/f_v(T)$ for the erucamide/i-PP system. Here $f_v(T)$ represents the free-volume fraction at each temperature.

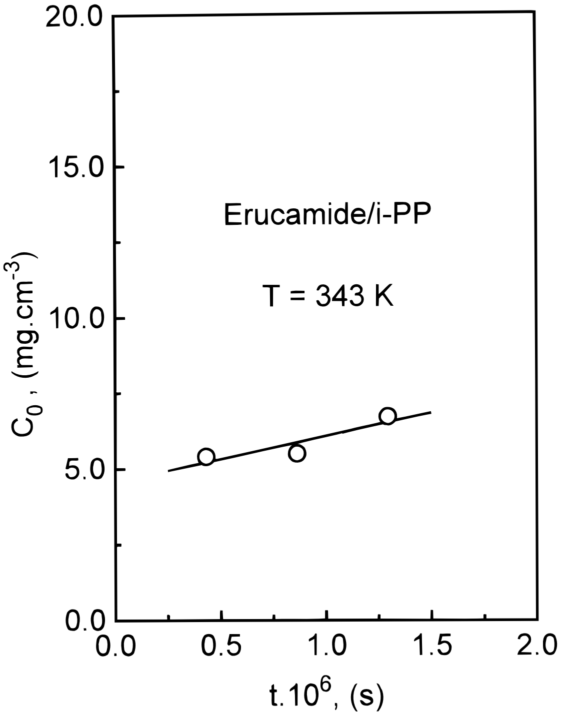

Figure 15. Dependence of the equilibrium solubility C_0 (mg cm^{-3}) on the time of diffusion *t* for erucamide/i-PP system.

ature obtained by this method and that of the equilibrium, the agreement is mostly good.[12,89,90] The values of this parameter obtained for the *semiempirical dual-diffusion model* are given in the eighth column of Table 2. They have been plotted in Figure 16 as a function of temperature. This behavior is typical of an incompatible additive, namely, soluble at high temperatures, i.e., in the melt and insoluble on cooling, i.e., at room temperature.[91] Practically the same can be said for the equilibrium solubility C_{01} and C_{02} calculated for each of two simultaneous Fickian diffusion processes separately.

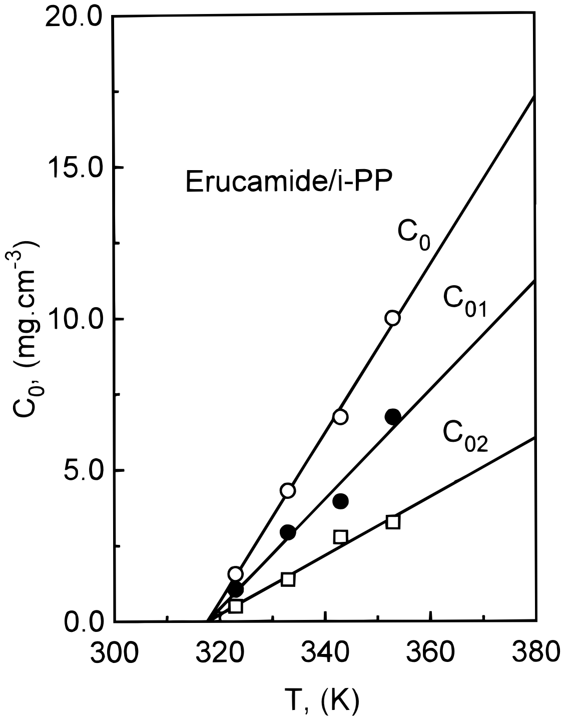

Figure 16. Solubility of the erucamide/i-PP system expressed as the dependence of the equilibrium solubility C_0 (open circles), C_{01} (full circles), and C_{02} (open squares) (mg cm^{-3}; semiempirical two Fickian diffusion model) on the temperature of diffusion *T* for the system erucamide/i-PP.

Conclusions

In the present work on the diffusion of erucamide in isotactic propylene, as a first approximation, we have analyzed our experimental data by means of a simple Fickian diffusion model. The system may be considered as nearly Fickian. However, we have proceeded by means of some other more suitable model.

Diffusion of erucamide (eru) in isotactic polypropylene (i-PP) film is described very precisely in terms of a semiempirical two-Fickian diffusion model over a wide range of penetrant concentration in the polymer and temperature. The overall process is represented by two simultaneous Fickian processes. The penetrant diffuses in the polymer through the thin amorphous layers between the lamellae and the amorphous boundaries between the randomly oriented stacks of lamellae and between the spherulites. Morphology of the films play an important role in the diffusion processes which take place in eru/i-PP system.

The dependence of diffusion coefficients for the simple Fickian diffusion model *D* and for the semiempirical two-Fickian diffusion model D_1 and D_2 on temperature *T* follow Arrhenius-type relationships over the temperature range investigated. Estimated activation energies lay in the range found for some other common additives which diffuse in i-PP.

Diffusion data have also been employed to estimate the solubility of erucamide in i-PP as a function of temperature. It has been directly done by extrapolation of diffusion data to penetration depth equal to zero. Erucamide is insoluble (incompatible) within i-PP for temperatures below 313 K. This is a prerequisite for an additive to be considered as a slip and/or antiblocking agent.

A good correlation by means of Fujita’s equation has been found between the diffusion coefficient and its respective free volume fraction estimated by means of Williams−Landel−Ferry’s equation.

It will be interesting and advisable, though very complex and probably very difficult, to extend the methods of dynamics and transition-state theory of small molecules in bulk polymers[92] to the diffusion of middle size molecules in semicrystalline polymers.

Acknowledgment. We give our special thanks to Mr. V. M. Cabrera Martín for his technical assistance in the maintenance of the experimental equipment. We are also indebted and express own thanks to the following persons: To Dr. A. Bisbal from DISPER, S. A., San Andreu de la Barca (Barcelona, Spain) for kindly providing the Hostalen PPN 1060 sample of free-additives propylene film which was prepared specially to carry out the present series of experiments. This project would not have been possible without the cooperation of Dr. P. Miró, Director of the Centro de Investigación y Desarrollo of Compañía Española de Petroleos, S. A. (CEPSA), Torrejón de Ardoz (Madrid, Spain) for access to the Center facilities, and to Dr. J. Gómez Martinench for the gift of the capillary chromatographic column and some recommendations for the quantitative determination of erucamide by CGLC and to Dr. J. M. Mazón-Arechederra from the same company who prepared the 6% erucamide−propylene masterbatch of CEPSLIP6, respectively. I.Q.-G. thanks to the Consejería de Educación of the Comunidad Autónoma de Madrid for a maintenance grant Beca for Formación del Personal Investigador y Técnico of the Plán Regional de Investigación. This work was partially supported by the DCICYT through Grant PB 92-0773-03-1.

References and Notes

(1) Breuer, T. E.; Ben Martin, N.; Tomlinson, H.; Leonard, E. C. *Proc. SPE 41st ANTEC ‘83,* **1983**, 896.
(2) Breuer, T. E.; Martin, B.; Tomlinson, H.; Gloyer, S. E.; Crawford, H. *Proc. SPE 42nd ANTEC ‘84,* **1984**, 141.
(3) Molnar, M. M. *J. Am. Oil Chem. Soc.* **1974,** *51,* 84.
(4) Cohen, S.; Tabor, D. *Proc. R. Soc. London, Ser. A* **1966,** *291,* 186.
(5) Briscoe, B. J.; Mustafaev, V.; Tabor, D. *Wear* **1972,** *19,* 399.
(6) Klein, J.; Briscoe, B. J. *Nature* **1975,** *257,* 386.
(7) Klein, J.; Briscoe, B. J. *Polymer* **1976,** *17,* 481.
(8) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979,** *365,* 53.
(9) Klein, J.; Briscoe, B. J. *J. Polym. Sci., Polym. Phys. Ed.* **1977,** *15,* 2065.
(10) Luston, J. In *Developments in Polymer Stabilization;* Scott, G., Ed.; Applied Science: London, 1980; Vol. 2, Chapter 5, p 185.
(11) Billingham, N. C.; Calvert, P. D. In *Developments in Polymer Stabilization;* Scott, G., Ed.; Applied Science: London, 1980; Vol. 3, Chapter 5, p 139.
(12) Moisan, J. Y. *Eur. Polym. J.* **1980,** *16,* 979.
(13) Moisan, J. Y. In *Polymer Permeability;* Comyn, J., Ed.; Elsevier: London, 1985; Chapter 4, p 119.
(14) Billingham, N. C. In *Oxidation Inhibition in Organic Materials*; Pospisil, J., Klemchuk, P. P., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. 2, Chapter 6, p 249.
(15) Westlake, J. F.; Johnson, M. *J. Appl. Polym. Sci.* **1975,** *19,* 319.
(16) Johnson, M.; Westlake, J. F. *J. Appl. Polym. Sci.* **1975,** *19,* 1745.
(17) Jackson, R. S.; Oldland, S. R. D.; Pajaczkowski, A. *J. Appl. Polym. Sci.* **1968,** *12,* 1267.
(18) Schwarz, T.; Steiner, G.; Koppelmann, J. *J. Appl. Polym. Sci.* **1989,** *37,* 3335.
(19) Cotton, N. J.; Bartle, K. D.; Clifford, A. A.; Dowle, C. J. *J. Appl. Polym. Sci.* **1993,** *48,* 1607.
(20) Hayashi, H.; Matsuzawa, S. *J. Appl. Polym. Sci.* **1992,** *46,* 499.
(21) Hayashi, H.; Saka, M.; Matsuzawa, S. *J. Appl. Polym. Sci.* **1994,** *51,* 2165.
(22) Földes, E. *Polym. Deg. Stab.* **1995,** *49,* 57.
(23) Földes. E. *Abstract Book. Communication MSDS 11*; pp 1.201−1.204. Fifth European Polymer Federation Symposium on Polymeric Materials, Basel, Switzerland, Oct 1994.
(24) Van Alsten, J. G.; Lustig, S. R. *Macromolecules* **1992,** *25,* 5069.
(25) Lustig, S. R.; Van Alsten, J. G.; Hsiao, B. *Macromolecules* **1993,** *26,* 3885.
(26) Van Alsten, J. G.; Lustig, S. R.; Hsiao, B. *Macromolecules* **1995,** *28,* 3672.
(27) Cranck, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon Press: Oxford, 1979; Chapter 2.
(28) *La Diffusion dans les Solides*; Adda, Y., Philibert, J., Eds.; Presses Universitaires de France: 1966.
(29) Matano, C. *Jpn. J. Phys.* **1933,** *8,* 109.
(30) Roe, R. J.; Bair, H. E.; Gieniewski, C. *J. Appl. Polym. Sci.* **1974,** *18,* 843.
(31) Al-Malaika, S.; Goonetileka, M. D. R. J.; Scott, G. *Polym. Deg. Estab.* **1991,** *32,* 231.
(32) Brengartner, D. A. *J. Am. Oil. Chem. Soc.* **1986,** *63,* 1340.
(33) Gómez Martinench, J., personal communication.
(34) Fujita, H. *Fortschr. Hochpolym. Forsch.* **1961,** *3,* 1.
(35) Rogers, C. E. In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M., Weissberger, A., Eds.; Interscience: New York, 1965; Chapter 6.
(36) Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: London, 1968.
(37) Hopfenberg, H. B.; Stannett, V. *The Physics of Glassy Polymers*; Haward, R. N., Ed.; John Wiley: New York, 1973; Chapter 9.
(38) Alfrey, T. *Chem. Eng. News* **1965,** *43,* 64.
(39) Berens, A. R.; Hopfenberg, H. B. *Polymer* **1978,** *19,* 489.
(40) Frisch, H. L. *Polym. Eng. Sci.* **1980,** *20,* 2.
(41) Baglay, E.; Long, F. A. *J. Am. Chem. Soc.* **1955,** *77,* 2172.
(42) Newns, A. C. *Trans. Faraday Soc.* **1956,** *52,* 1533.
(43) Long F. A.; Richman, D. J. *J. Am. Chem. Soc.* **1960,** *82,* 513.
(44) Koshimoto, A.; Fujita, H.; Odani, H.; Kurata, M.; Tamura, M. *J. Phys. Chem.* **1960,** *64,* 594.
(45) Kwei, T. K.; Zupko, H. M. *J. Polym. Sci., Part A-2* **1969,** *7,* 867.
(46) Frisch, H. L.; Wang, T. T.; Kwei, T. K. *J. Polym. Sci., Part A-2* **1969,** *7,* 879.
(47) Hopfenberg, H. B.; Frisch, H. L. *J. Polym. Sci., Polym. Phys. Ed.* **1969,** *7,* 405.
(48) Hopfenberg, H. B.; Holley, R. H.; Stannett, V. *Polym. Eng. Sci.* **1969,** *9,* 242.
(49) Hopfenberg, H. B.; Nicolais, L.; Drioli, E. *Polymer* **1976,** *17,* 195.
(50) Enscore, D. J.; Hopfenberg, H. B.; Stannett, V. *Polym. Eng. Sci.* **1980,** *20,* 102.
(51) Korsmeyer, K. K.; Lustig, S. L.; Peppas, N. A. *J. Polym. Sci., Polym. Phys. Ed.* **1986,** *24,* 395.
(52) Lustig, S. R.; Peppas, N. A. *J. Appl. Polym. Sci.* **1987,** *33,* 533.
(53) Durning, C. J.; Hassan, M. M.; Tong, H. M.; Lee, K. W. *Macromolecules* **1995,** *28,* 4234.
(54) Fu, T. J.; Durning, C. J. *AIChE J.* **1993,** *39,* 1030.
(55) Del Nobile, M. A.; Mensitier, G.; Netti, P. A.; Nicolais, L. *Chem. Eng. Sci.* **1994,** *49,* 633.
(56) Wang, T. T.; Kwei, T. K.; Frisch, H. L. *J. Polym. Sci., Part A-2* **1969,** *7,* 2019.
(57) Frisch, H. L.; Wang, T. T.; Kwei, T. K. *J. Polym. Sci., Part A-2* **1969,** *7,* 867.
(58) Quijada-Garrido, I.; Barrales-Rienda, J. M.; Pereña, J. M.; Frutos, G., to be submitted for publication.
(59) Quijada-Garrido, I.; Pereña, J. M.; Barrales-Rienda, J. M.; Frutos, G., to be submitted for publication.
(60) Gondo, Y.; Utsunomiya, T. *Kogyo Kagaku Zasshi* **1967,** *70,* 534.
(61) Rogers, C. E.; Stannett, V.; Szwarc, M. *J. Phys. Chem.* **1959,** *63,* 1406.
(62) Michaels, A. S.; Parker, R. B. *J. Polym. Sci.* **1959,** *41,* 53.
(63) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961,** *50,* 393.
(64) Michaels, A. S.; Bixler, H. J. *J. Polym. Sci.* **1961,** *50,* 413.
(65) Peterlin, A. *J. Macromol. Sci.-Phys.* **1975,** *B11,* 57.
(66) Peterlin, A. *Pure Appl. Chem.* **1974,** *39,* 239.
(67) Kosovova, Z. P.; Restlinger, S. A. *Vysokomol. Soedin.* **1967,** *A9,* 415; *Polym. Sci. USSR* **1967,** *9,* 468.
(68) Savin, A. G.; Shaposhnikova, T. K.; Karpov, V. L.; Sogolova, T. I.; Kargin, V. A. *Vysokomol. Soedin.* **1968,** *A10,* 1584; *Polym. Sci. USSR* **1968,** *10,* 1834.
(69) Savin, A. G.; Karpov, V. I.; Shaposhnikova, T. K.; Sogolova, T. I. *Vysokomol. Soedin.* **1967,** *A9,* 496.

(70) Padden, F. J.; Keith, H. D. *J. Appl. Phys.* **1959,** *30,* 1479.
(71) Turner-Jones, A.; Aizlewood, J. M.; Becket, D. R. *Makromol. Chem.* **1964,** *75,* 134.
(72) Khoury, F. A. *J. Res. Natl. Bur. Stand.* **1966,** *70A,* 29.
(73) Lovinger, A. *J. Polym. Sci.; Polym. Phys. Ed.* **1983,** *21,* 97.
(74) Bassett, D. C.; Olley, R. H. *Polymer* **1984,** *25,* 935.
(75) Keith, H. D.; Padden, F. J. *J. Appl. Phys.* **1963,** *34,* 2409.
(76) Wada, Y.; Hotta, Y.; Suzuki, R. *J. Polym. Sci., Part C* **1968,** *23,* 583.
(77) Baumgartner, A.; Muthukumar, M. *J. Chem. Phys.* **1987,** *87,* 3082.
(78) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989,** *22,* 1937.
(79) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989,** *22,* 1941.
(80) Baumgartner, A. In *Springer Series in Chemical Physics;* Tanaka, F., Doi, M., Ohta, T., Eds.; Springer-Verlag: Berlin, 1989; Vol. 51.
(81) Santa Cruz, C.; Stribeck, N.; Zachmann, H. G.; Baltá-Calleja, F. J. *Macromolecules* **1991,** *24,* 5980.
(82) Quijada-Garrido, I.; Barrales-Rienda, J. M.; Fernández de Velasco Ruiz, M., to be published.
(83) Vittoria, V.; Olley, R. H.; Bassett, D. C. *Colloid Polym. Sci.* **1989,** *267,* 661.
(84) Durning, C. J.; Russel, W. B. *Polymer* **1985,** *26,* 119.
(85) Durning, C. J.; Russel, W. B. *Polymer* **1985,** *26,* 131.
(86) Fujita, H.; Kishimoto, A.; Matsumoto, K. *Trans. Faraday Soc.* **1960,** *56,* 424.
(87) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955,** *77,* 3701.
(88) Quirk, R. P.; Alsamarraie, A. A. *Physical Constants of Polypropylene*, 3rd ed.; in *Handbook of Polymers*; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.
(89) Billingham, N. C.; Calvert, P. D.; Okopi, I. W.; Uzuner, A. *Polym. Deg. Stab.* **1991,** *31,* 23.
(90) Moisan, J. Y. *Eur. Polym. J.* **1983,** *19,* 1127.
(91) Billingham, N. C. *Makromol. Chem., Makromol. Symp.* **1989,** *27,* 187.
(92) Gusev, A. A.; Müller-Plathe, F.; van Gunsteren, W. F.; Suter, U. W. *Adv. Polym. Sci.* **1994,** *116,* 207.

MA951392A