

# Transport of Small Molecules in Polyolefins. I. Diffusion of Irganox 1010 in Polyethylene

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## SYNOPSIS

Transport properties of antioxidants in polymers have a very important role in their effectiveness. Lifetime of a product is strongly influenced by the physical loss of the stabilizer. The diffusion coefficient ( $D$ ) and solubility ( $S$ ) of Irganox 1010 in low-density polyethylene (LDPE) were studied at 45 and 80°C, changing the physical state of the antioxidant in the additive source. Irganox 1010 is a polymorphous material; its actual morphology depends on the thermal history. It was proved that the morphology of the additive has a determining effect on the measured  $D$  and  $S$  values. Contradictions in the literature data can be explained by the differences in the experimental conditions, i.e., in the physical state of the penetrant in the additive source and the crystallinity and orientation of the polymer.

## INTRODUCTION

Most commercially available polymers are stabilized against thermo- and photooxidative degradation with small molecules. It was shown by several authors (e.g., Refs. 1–7) that the effectiveness of long-time stabilization depends not only on the chemical nature of the additive, but also that physical loss has an even more important role. 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.

Different methods are described in the literature for the measurement of the diffusion coefficient and solubility of small molecules in polymers.<sup>4–8</sup> A technique was developed for simultaneous measurement of these two parameters in a stack of polymer films kept in contact with an additive source.<sup>3,6</sup> Although, studying the diffusion of ethane gas in polyethylene, Lowell and McCrum<sup>9</sup> found some effect of the surface layer on the measured diffusion coefficient, Roe et al.<sup>3</sup> could not detect any when additive diffusion was studied in PE films of different thickness.

Irganox 1010 is one of the most widely used polyolefin antioxidants. Its compatibility with polyethylene was investigated by several authors.<sup>3,6,10,11</sup> The published solubility data measured under 130°C vary in a wide range. It was attributed by Moisan<sup>7</sup> to the different measuring techniques, while Billingham<sup>8</sup> suggested that the differences are due to the different crystalline forms of the used additive. Kuck<sup>11</sup> observed discontinuity in the equilibrium solubilities between 40 and 60°C and explained it with the phase transition of the additive.

In this work, the physical state of Irganox 1010 was investigated as an effect of pretreatment. The solubility and diffusion coefficient were measured in low-density polyethylene (LDPE) using different types of additive source. The measured values were related to the phase structure of the additive.

## EXPERIMENTAL

### Characterization of the Additive

Irganox 1010, chemical name of pentaerythrityl-tetrakis [3 - (3,5 - di - *tert* - butyl - 4 - hydroxyphenyl) - propionate] (PTHP), MW = 1178, was kindly supplied by Ciba-Geigy AG as commercial material.

Volatility of the additive was determined in air. After storing the material in an atmospheric oven

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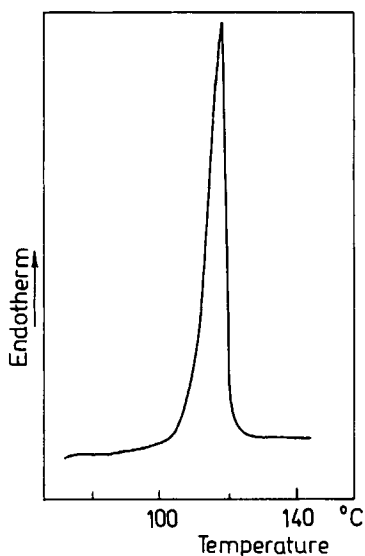
at 80°C for 350 h, no weight loss could be measured. Thermogravimetric analysis (measured with the TG 50 Thermobalance of a Mettler TA 3000 Thermal Analyzer System using a 2°C/min rate of heating) revealed that the material is not volatile up to 178°C.

Melting and crystallization properties were studied by DSC (DSC-30 unit of the Mettler TA 3000 System) with a heating and cooling rate of 10°C/min. Eight milligrams of material was measured each time. For identification of the different crystal modifications of PTHP, IR spectroscopy was also applied using the KBr technique. Results were compared with those of Zweifel.<sup>12</sup>

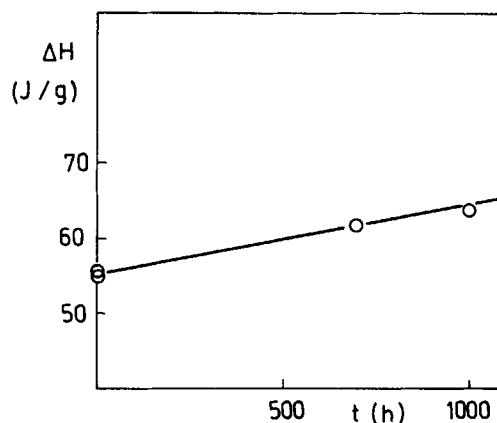
PTHP crystallizes in different forms. The melting endotherm of the material as received is shown in Figure 1. One peak was obtained between 94 and 134°C with a maximum at 117.5°C and  $\Delta H = 55$  J/g. Comparing the data with Ref. 12, we concluded that the untreated additive consisted of delta crystals. The IR spectra also confirmed this result.

Structural changes of PTHP as an effect of heat treatment were studied by DSC. Figure 2 shows the change of melting enthalpy of crystalline PTHP as a function of annealing time at 80°C. With increasing time, the heat of fusion increased and the shape of the melting curve became asymmetric with a peak temperature at 119°C and a shoulder around 117.5°C. This suggests that the material recrystallized into another crystalline form.

The additive was melted at 150°C, then cooled by different rates and annealed at different temperatures. PTHP did not crystallize during cooling from



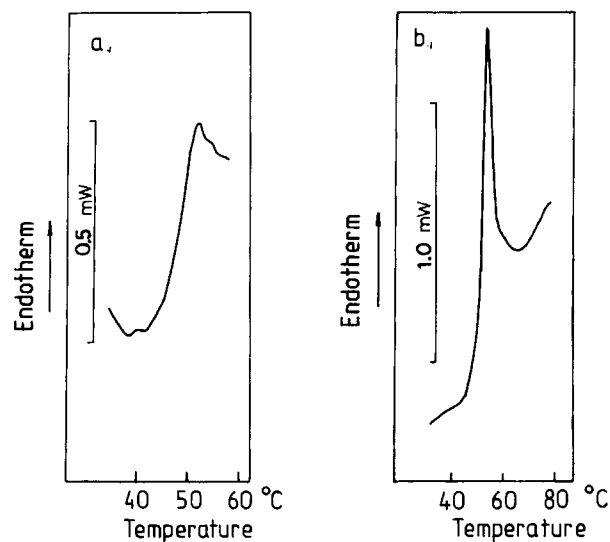
**Figure 1** Melting endotherm of Irganox 1010 as received. Rate of heating: 10°C/min.



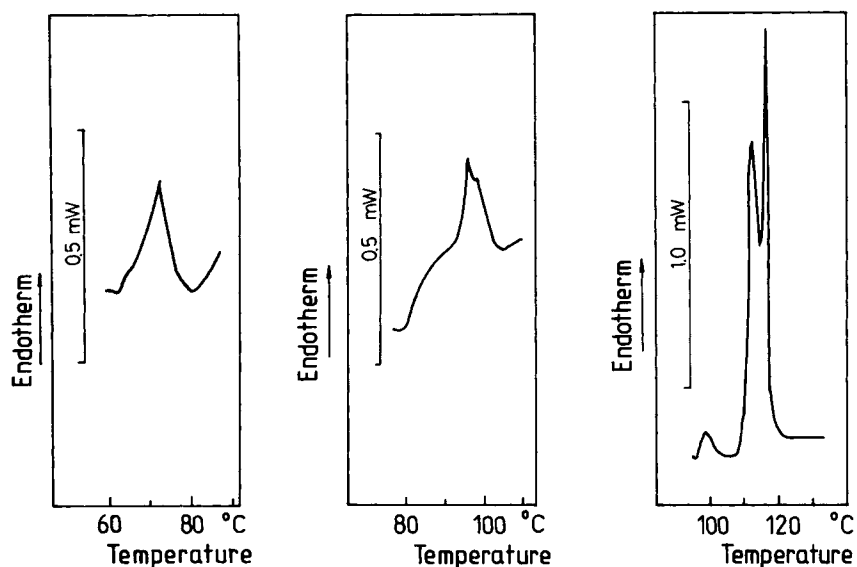
**Figure 2** Changes of the heat of fusion of crystalline Irganox 1010 with annealing time at 80°C.

melt even if the rate was as slow as 1°C/min. After cooling, glassy material was obtained with a glass transition range between 44 and 52°C. In Figure 3(a), the glass transition of the quenched material is shown. In Figure 3(b), that of the slowly cooled material can be seen. The first curve shows typical heat capacity changes of a quenched glass; the second one is characteristic for a more stable glass, either slowly cooled or annealed, measured by fast heating.<sup>13,14</sup>

When the quenched antioxidant was annealed at room temperature or at 45°C, crystallization could not be observed even after 1000 h. Only some increase of the overheating peak at the glass transition was experienced.



**Figure 3** Glass transition of Irganox 1010 cooled from melt. Cooling rate: (a) quenched; (b) 1°C/min. Rate of heating: 10°C/min.

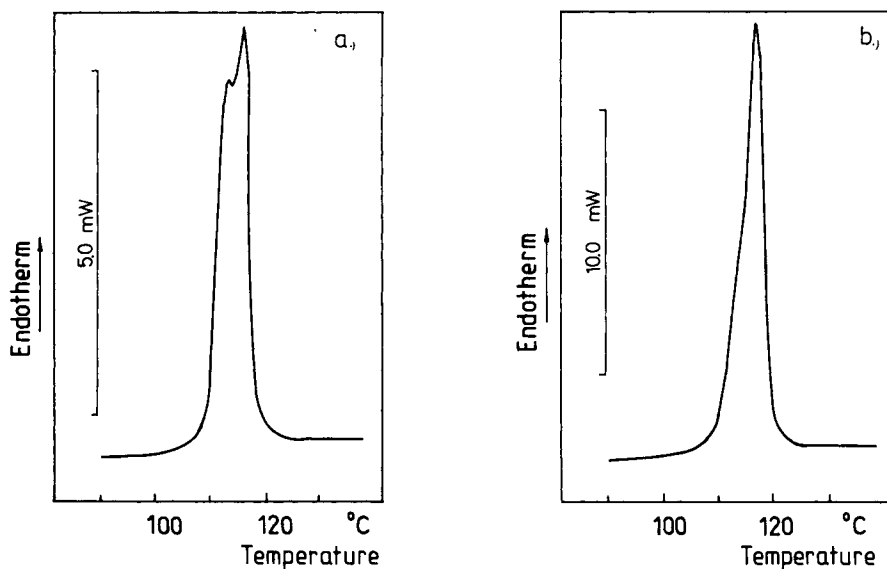


**Figure 4** Melting endotherms of Irganox 1010 melted, quenched, and annealed at 55°C for 1000 h. Rate of heating: 10°C/min.

At 55°C, the quenched PTHP crystallized very slowly. After 1000 h of annealing, a very heterogeneous material was obtained. Glass transition similar to the one shown in Figure 3(b) was observed and also four small endothermic peaks with peak temperatures at 72, 96, 112.5, and 116°C (Fig. 4). The origin of the two very small low-temperature peaks is not known; the two other peaks between 100 and 120°C can be attributed to the beta and delta modifications of the additive.<sup>12</sup>

Annealing the glassy material at 80°C resulted

in a much faster crystallization and recrystallization. As crystal nucleation is a random process,<sup>15</sup> the rate of crystallization could not be controlled. In some cases, crystallization started after a very short time (less than 2 h), and in others, only after 50 h. First, the less stable crystals were formed that recrystallized with increasing annealing time. After a relatively short treatment, glasslike material could be simply separated from the more opaque crystalline phase. The former gave a glass transition at 48°C and two small melting peaks at 72 and 96°C. The



**Figure 5** Melting endotherms of Irganox 1010 melted, quenched, and annealed at 80°C. Annealing time: (a) 24 h; (b) 620 h. Rate of heating: 10°C/min.

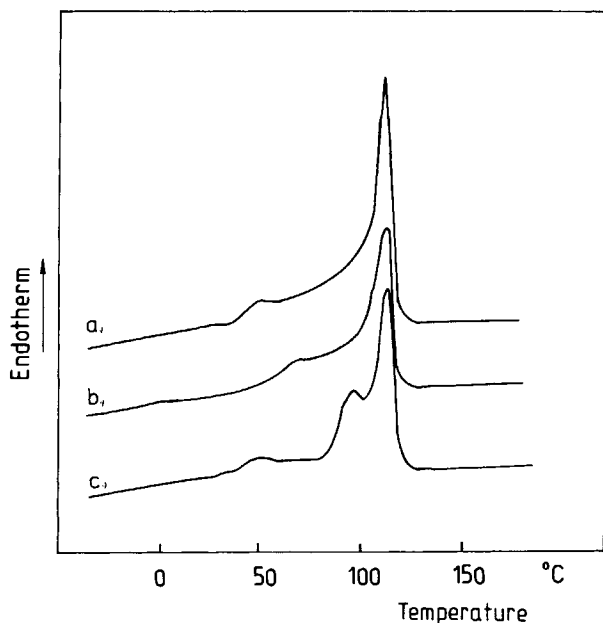
latter had a transition range between 100 and 130°C with a double peak, as can be seen from Figure 5 (a). With increasing time, the lower-temperature transitions disappeared and the amount of the delta crystal modification increased. From the asymmetric shape of the melting peak in Figure 5 (b) measured after 680 h, it can be concluded that the material contained at least two crystal modifications.

### Characterization of the Polymer

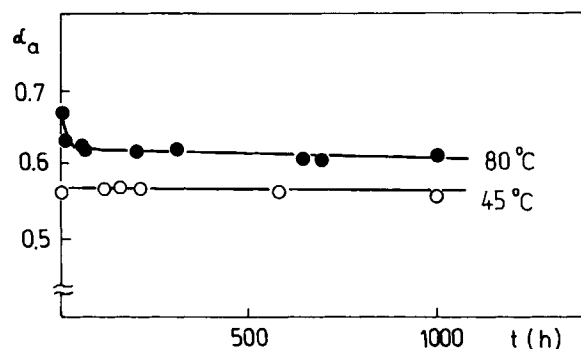
Transport properties of PTHP were investigated in additive-free LDPE,  $d = 0.921 \text{ g/cm}^3$  (Tipolen PB 2212; TVK, Hungary) that was processed into 70–80  $\mu\text{m}$ -thick film by extrusion blow molding.

The physical structure of the polymer was studied by DSC with a heating rate of 10°C/min. Crystallinity and the amorphous fraction were calculated by using a specific heat of fusion of 293 J/g.<sup>16,17</sup> The crystallinity of LDPE at room temperature was 43%.

Figure 6 shows the melting curves of LDPE films untreated and annealed at 45 and 80°C. At 80°C, secondary crystallization takes place.<sup>13</sup> The effective amorphous fraction ( $\alpha_a$ ) of the polymer at the annealing temperatures was determined from the melting endotherms and it is plotted as a function of annealing time in Figure 7.  $\alpha_a$  decreased significantly at 80°C, while at 45°C, hardly any change was obtained.



**Figure 6** Melting endotherms of LDPE: (a) untreated extruded film; (b) annealed at 45°C; (c) annealed at 80°C. Rate of heating: 10°C/min.



**Figure 7** Amorphous fraction of LDPE at the annealing temperature as a function of annealing time measured by DSC.

### Diffusion of PTHP in LDPE

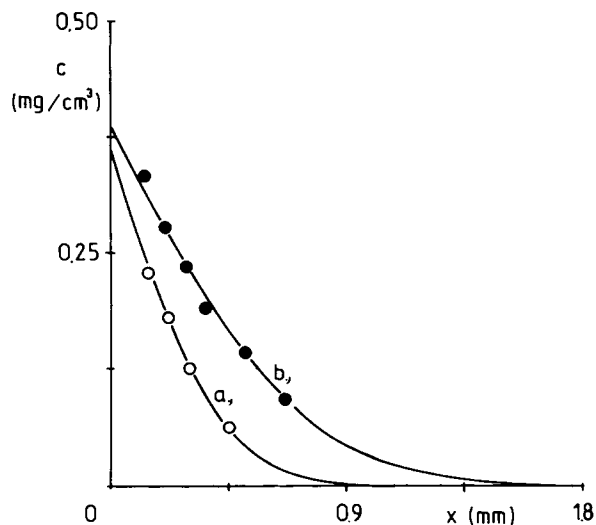
For the diffusion measurements, additive sources were prepared by three methods. Irganox 1010 was

- used in the form of fine crystalline powder as received (“crystalline”);
- melted at 150°C for 10 min in aluminum foil, then quenched in liquid nitrogen (“quenched”);
- mixed with LDPE (Tipolen PB 2212; TVK, Hungary) in melt in 5% at 150°C and granulated. The obtained pellets were compression-molded twice at 150°C in argon atmosphere into 1 mm-thick plates, then cooled by running water (“mixed”).

Before the experiments, the surface of the additive-free polymer films was cleaned with ethanol then dried in air.

Diffusion measurements were carried out using the system described by Roe et al.<sup>3</sup> A stack of 50 additive-free polymer films was placed between two additive sources. The “sandwich system” was placed into a diffusion cell, compressed by 2 N/cm<sup>2</sup>, and put into a vacuum oven of controlled temperature. The diffusion process was terminated before the additive reached the central layer of the stack of films. Additive concentration in the polymer films was determined directly by UV spectroscopy. Calibration was made in *n*-octane solution. To avoid mistakes caused by the additive adsorbed on the surface contacting the additive source, concentration of the film next to the additive source was not used in the calculation.

The diffusion coefficient was determined using the principle given by Moisan.<sup>6,7</sup> This method treats the process as a one-dimensional diffusion problem.



**Figure 8** Concentration distribution of Irganox 1010 in LDPE measured after diffusion at 45°C: (a) “quenched” additive source, 1000 h; (b) “mixed” additive source, 50 h.

It is assumed that at the start of the experiment ( $t = 0$ ) the additive concentration is  $c = 0$  at any distance from the additive source ( $x > 0$ ) and that during the experiment ( $t > 0$ ) concentration of the additive in the additive source ( $x \leq 0$ ) remains constant and equals the solubility ( $c = S$ ). The concentration at position  $x$  and time  $t$  is described by

$$c(x, t) = S[1 - \operatorname{erf}(x/K)] \quad (1)$$

where  $K$  is determined by the time and the diffusion coefficient  $D$  and can be given by

$$K = 2\sqrt{Dt} \quad (2)$$

For calculation of the parameters  $D$  and  $S$  from the

concentration profile, an interactive least-squares curve-fitting program was used. The solubility is given directly by this calculation.

In Figure 8, additive concentration ( $c$ ) is plotted as a function of penetration depth ( $x$ ) measured at 45°C using different additive sources. Curve a corresponds to the values obtained after 1000 h of diffusion from the quenched additive source; curve b was obtained after 50 h of diffusion from the mixed one. Diffusion coefficients ( $D$ ) calculated from the plots are given in Table I. The results suggest that the additive diffused much faster from the mixed system than from the quenched additive source. From the crystalline additive source, no material entered into the polymer at 45°C even after 1000 h.

Plots of concentration vs. penetration depth measured after 20 h of diffusion at 80°C are shown in Figure 9. Concentration was very small when pure crystalline material was used as the additive source. Larger values were obtained for the originally amorphous material and even larger ones for the mixed blend. In the latter case, the penetrant reached the middle layers of the polymer film stack. For the quenched additive source, the concentration profile does not correspond to the shape characteristic for Fickian diffusion.

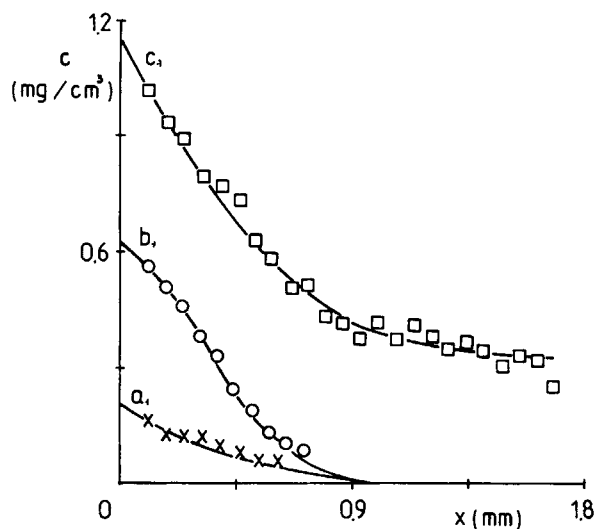
Diffusion coefficients measured at 80°C are given also in Table I. Similar values were obtained for every additive source. The only exception was the mixed system where the effect of the additive source preparation resulted in differences in the results.  $D$  increased with the storing time of the pellets.

#### Solubility of PTHP in LDPE

Solubility of the additive in LDPE was determined by two methods:

**Table I** Apparent Diffusion Coefficient of Irganox 1010 in LDPE

Temperature (°C)	Film Preparation	Additive Source	$D \times 10^9$ (cm <sup>2</sup> /s)	Ref. No.
45	Extruded film	Crystalline	0.0	This work
45	Extruded film	Quenched	0.1	This work
45	Extruded film	Mixed	7.1	This work
80	Extruded film	Crystalline	23.0	This work
80	Extruded film	Quenched	13.4	This work
80	Extruded film	Mixed	22.8	This work
			59.6	
67	Melted, quenched	Mixed	3.2	3
45	Not defined	Mixed	0.1	6, 7
80	Not defined	Mixed	7.9	6, 7



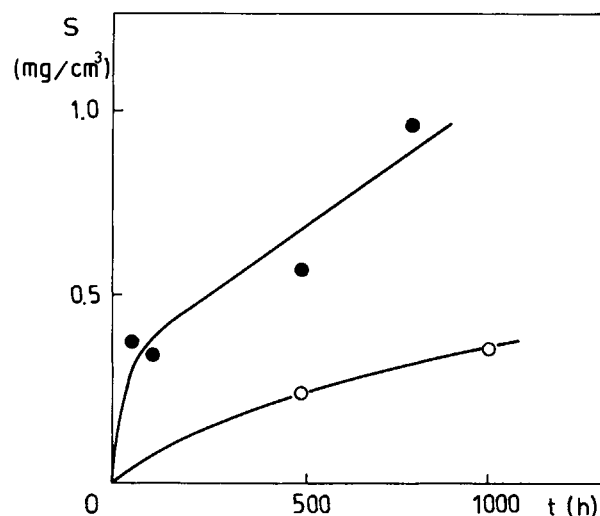
**Figure 9** Concentration distribution of Irganox 1010 in LDPE measured after 20 h of diffusion at 80°C. Additive source: (a) "crystalline"; (b) "quenched"; (c) "mixed."

- (a) "Extrapolating method":  $S$  was calculated from the diffusion measurements as described above.
- (b) "Equilibrium method": 20 additive-free polymer films were held between two additive sources in a vacuum oven for long times. After that, equal concentration was obtained in each film.

In Figure 10, extrapolated solubility values of the additive measured at 45°C are plotted as a function of diffusion time. Equilibrium concentration could not be reached even after a very long period. At a given diffusion time, larger  $S$  values were obtained for the mixed additive source than for the quenched one.

Results also showed that the measured solubilities depend on the storing time and the thermal history of the pellets used for the preparation of the mixed additive source. This indicates that homogenization takes place during storage at room temperature, resulting in an increase of  $S$ . Studying additive diffusion in polypropylene, Ryan and Calvert<sup>18</sup> showed that the additive initially rejected from the spherulites subsequently diffuses back into them.

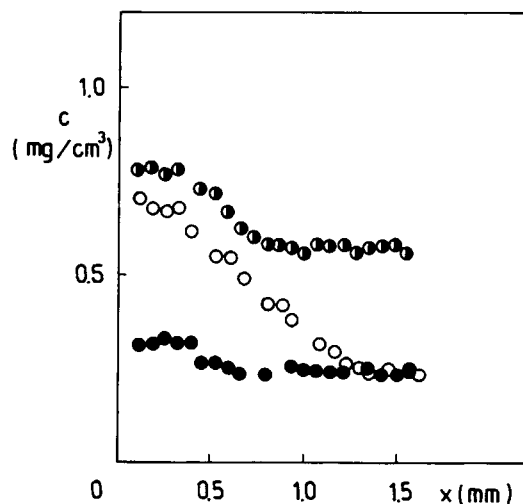
Diffusion curves measured at 80°C after 210 h are presented in Figure 11. Concentrations in the films close to the additive source were very similar for the quenched and mixed additive sources, whereas in the middle of the polymer stack, i.e., farthest from the source, the same concentrations for



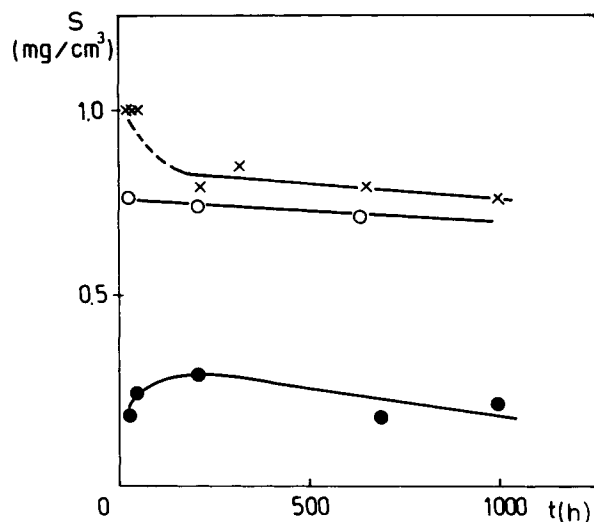
**Figure 10** Measured solubility of Irganox 1010 in LDPE at 45°C as a function of diffusion time. Additive source: (○) "quenched"; (●) "mixed."

the quenched and crystalline additive sources were obtained.

Solubility values obtained at 80°C in LDPE are plotted as a function of diffusion time in Figure 12. Values under 300 h were calculated by extrapolation; for longer times, the equilibrium method was used. Similarly to the tendency obtained at 45°C, the smallest concentrations were measured for the crystalline additive source and the largest ones for the mixed system. Changes of  $S$  with diffusion time de-



**Figure 11** Concentration distribution of Irganox 1010 in LDPE measured after 210 h of diffusion at 80°C. Additive source: (●) "crystalline"; (○) "quenched"; (●) "mixed."



**Figure 12** Measured solubility of Irganox 1010 in LDPE at 80°C as a function of diffusion time. Additive source: (●) "crystalline"; (○) "quenched"; (×) "mixed."

pend on the additive source. For the crystalline material, a curve with a maximum was obtained. In the two other cases, the measured solubility decreased with time. This latter effect was more pronounced when the mixed additive source was used.

As PTHP is not volatile in the temperature range of the measurements, the results were not influenced by evaporation of the additive.

## DISCUSSION

Material transport through a semicrystalline polymer solid can be considered exclusively diffusive when the swelling ratio is sufficiently low and its driving force as derived from the chemical potential of the diffusant is wholly based on the concentration gradient.<sup>19</sup> The penetrant diffuses exclusively through the amorphous phase,<sup>8,9,19</sup> which can be considered a highly viscous liquid.

Diffusion of a liquid in another homogeneous liquid is controlled macroscopically by the friction of the molecules.<sup>15</sup> In unoriented semicrystalline polymers, a "tortuosity factor" has to be also taken into account,<sup>19</sup> which represents the mechanical hindrance of the crystallites to the movement of the diffusant. Orientation of the amorphous component is another parameter that very much affects the sorption and diffusion of small molecules.<sup>19,20</sup>

Studying the transport of additives in polymers, the physical state of the penetrant in the additive source cannot be neglected. When it is a solid, the

enthalpy change accompanying the solution will contain two parameters<sup>4</sup>:

$$\Delta H = \Delta H_1 + \Delta H_2 \quad (3)$$

where  $\Delta H_1$  is the heat of the phase transition of the dissolving material and  $\Delta H_2$  is the heat of solvation. Generally,  $\Delta H_1$  is positive, and  $\Delta H_2$ , negative. When the same additive/polymer pair is investigated, changes in  $\Delta H$  will be controlled by  $\Delta H_1$ . At constant pressure, the heat of the phase transition depends on the temperature and the heat capacity of the material.<sup>15,21</sup>

PTHP is a relatively large symmetric molecule that crystallizes in different crystal modifications. When it is cooled from melt, supercooled liquid is formed and crystallization starts only above the glass transition range ( $> 50^\circ\text{C}$ ). The rate of crystallization and the type of crystal modification depend on the temperature and time. Close above  $T_g$ , the process is very slow, and even after a long time, the material is very heterogeneous morphologically. Close to the melting temperatures of the different crystal modifications, crystallization and recrystallization is much faster, and with annealing time, the system becomes more homogeneous with higher melting temperatures.

To compare literature data with those of this work, the diffusion coefficient and solubility values of PTHP in LDPE are presented in Tables I and II, respectively. The additive source types and film-preparation techniques are also given. In Table II, solubility data of this work were calculated using the actual amorphous and crystalline phase content values measured by DSC and specific volumes given by Ref. 22.

Our study conducted at 45°C, in the lower half of the glass transition range of PTHP and far below the melting temperatures of the different crystal modifications, revealed strong dependence of the measured solubility and diffusion coefficient values on the additive source type, i.e., on the physical state of the penetrant in the additive source. In case of the crystalline additive source, the heat needed for the phase transition far exceeds the available thermal energy; therefore, the molecules cannot detach themselves from the additive source.

It is very hard to interpret the result of Ref. 10 where a concrete solubility value is given for PTHP in LDPE at 25°C when the crystalline additive source was used. Most probably it is extrapolated data.

The measured rate of diffusion of PTHP at 80°C was independent of the additive source type. Dif-

**Table II Solubility of Irganox 1010 in LDPE**

Temperature (°C)	Film Preparation	Additive Source	Solubility (w/w %)	Ref. No.
45	Extruded film	Crystalline	0.00 <sup>a</sup>	This work
45	Extruded film	Quenched	0.04 <sup>a</sup>	This work
45	Extruded film	Mixed	0.11 <sup>b</sup>	This work
80	Extruded film	Crystalline	0.02 <sup>a</sup>	This work
80	Extruded film	Quenched	0.08 <sup>a</sup>	This work
80	Extruded film	Mixed	0.09 <sup>a</sup>	This work
56	Melted, quenched	Mixed	0.0029	3
66	Melted, quenched	Mixed	0.0091	3
76	Melted, quenched	Mixed	0.0111	3
40	Melted, quenched	Mixed	0.075	11
60	Melted, quenched	Mixed	0.055	11
80	Melted, quenched	Mixed	0.080	11
45	Not defined	Mixed	0.024	6, 7
80	Not defined	Mixed	0.246	6, 7
25	Extruded film	Crystalline	0.02	10
70	Extruded film	Crystalline	0.24	10

<sup>a</sup> After 1000 h.<sup>b</sup> After 800 h.

ferences in  $D$  obtained at 45°C and as an effect of the mixed additive source preparation can originate from the measuring technique and the used calculation. If the limiting condition  $c = S$  is not attained permanently on the surface of the additive source ( $x = 0$ ) during the experiment, eq. (1) used for the determination of  $D$  will not provide the correct value. In that case,  $D$  represents only an apparent diffusion coefficient, as its value depends also on the dissolution rate of the additive.

At 80°C, several processes take place at the same time. The most important ones are diffusion and phase transition—melting and recrystallization—of the penetrant, relaxation, and recrystallization of the polymer. The measured solubility values are determined by these cooperative processes. The small  $S$  values measured when the crystalline additive source was used suggest that only some part of the material is melted at this temperature. The decrease of  $S$  with time in all three cases and the concentration distributions measured after 210 h indicate the recrystallization of the additive during the experiment.

Also, LDPE recrystallizes slowly and the amorphous fraction decreases at 80°C. Relaxation of the polymer accompanies these processes. It was controlled by measuring the shrinkage of the extruded film at 80°C. After 20 h of annealing, a 1.5% decrease in length was obtained in the direction of extrusion.

Polyethylene films exhibit an increase of  $S$  and  $D$  with elongation in the elastic deformation range.<sup>19,20</sup> The diffusion coefficient increases with the strain in a short range of  $\epsilon$  (up to 2%), reaches a maximum, and, after that, steadily drops. Solubility increases to a rather high elongation and approaches a limiting value.

We can conclude that recrystallization of both the additive and the polymer and relaxation of the latter influence the measured rate of diffusion and solubility values. Arrhenius plots can only be calculated when the physical properties of the additive and the polymer remain constant during the experiment.

Considering the results presented above, variations in the literature data can be explained by the differences in the measuring conditions. For a correct correlation, not only the temperature dependence of the diffusion coefficient and solubility but also a detailed description of the measuring conditions and the structural changes of the materials would be needed.

## CONCLUSIONS

The aim of this work was to find the reason for the differences in the literature data given for the parameters describing transport properties of Irganox



1010 in LDPE. Changes in the morphology of the antioxidant with heat treatment was studied thoroughly. Irganox 1010 crystallizes in different crystal modifications. Morphology of the material strongly depends on the thermal history.

It was shown that the measured rate of diffusion and solubility values are determined by the physical state of the penetrant in the additive source. An essential condition of diffusion is that the penetrant must be brought into a dissolved or liquid state. It can be achieved by mixing the additive with polymer in melt or by melting it. When the available heat energy is not enough for the fusion of the penetrant, the molecules are immobile. At elevated temperatures, several processes take place simultaneously: diffusion and recrystallization of the additive and recrystallization of the polymer. When the diffusion is studied in slightly oriented polymer films, the relaxation process is another parameter that influences the transport. Consequently, when transport properties of Irganox 1010 are studied, experimental conditions have to be defined exactly, and in the evaluation of the results, all the influencing parameters have to be taken into account.

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