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# DIFFUSION OF ORGANIC COMPOUNDS IN SATURATED POLYOLEFINS

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**Abstract**—The diffusion of 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-*n*-butoxybenzophenone, 2-hydroxy-4-*n*-octoxybenzophenone, 2-hydroxy-4-*n*-dodecoxybenzophenone, 2-hydroxy-4-*n*-octadecoxybenzophenone has been studied. The polymers examined were: stereoblock polypropylene (between 70° and 85°) high density polyethylene (between 80° and 110°), low density polyethylene (between 70° and 90°). Also the diffusion of dimethyl-3, 3′-thiodipropanoate and di-*n*-hexyl-3, 3′-thiodipropanoate in low crystalline polypropylene was studied between 20° and 40°. The diffusion coefficients are reported. The effect of mutual compatibility between penetrant and polymer upon the diffusion process is discussed. The linear relation $\ln D_0 = -14{\cdot}8 + 0{\cdot}43\, E_d/T$ is obtained for the diffusion in saturated polyolefins using these and other published data.

IN A PREVIOUS paper[1] we reported on the diffusion of thiodipropionic esters and hydroxybenzophenones in isotactic polypropylene. The presence of crystallinity in the polymer allows these large molecules to diffuse with different rates, the energies of activation for diffusion being smaller than the energy for the self-diffusion of polymer segments. In order to study more fully the behaviour of large molecules in the diffusion process, the diffusion of a series of 2-hydroxy-4-alkoxy-($C_1$—$C_{18}$)-benzophenones and esters ($C_1$—$C_6$) of 3,3′-thiodipropionic acid in saturated polyolefins with different structures and crystallinities, was investigated. These compounds are of practical interest being used as additives in polymers.

## EXPERIMENTAL

The radioisotopic technique and the apparatus employed for diffusion measurements, were similar to those used earlier.[1] The polymer samples (6 mm thick, $\phi = 14$ mm) were prepared from sheets obtained by melting and annealing. After diffusion, the samples of stereoblock polypropylene were sectioned by a microtome (slices 0·1 mm thick).

The measurements of mutual compatibility were carried out according to Ref. (2) by determination of the crystallization kinetics performed on mixtures of polymer and hydroxy-alkoxy-benzophenones. The concentration of compounds (mole of penetrant for weight of polymer) was kept constant.

## MATERIALS

(1) Stereoblock polypropylene; crystallinity = 24 ± 4 per cent; intrinsic viscosity $[\eta] = 0{\cdot}59$ (tetrahydronaphthalene at 135°). The material was obtained according to Natta, Mazzanti, Crespi and Moraglio.[3] The *n*-heptane soluble fraction of a Zeigler–Natta polypropylene was extracted by boiling ethyl ether and the residue was extracted by boiling *n*-hexane. The *n*-hexane extractable fraction was used in our experiments.

(2) Low crystallinity polypropylene; crystallinity = 16 ± 4 per cent; intrinsic viscosity $[\eta] = 0{\cdot}3$ (tetrahydronaphthalene at 135°); solubility in boiling ethyl ether = 90 per cent. The material was obtained extracting the Ziegler–Natta polypropylene with boiling *n*-heptane.

(3) Isotactic polypropylene; crystallinity = 63 ± 4 per cent; intrinsic viscosity $[\eta] = 3{\cdot}0$ (tetrahydronaphthalene at 135°); solubility in boiling *n*-heptane = 3·2 per cent.

(4) High pressure, branched, low density polyethylene, FERTENE Q/1, manufactured by Montecatini–Edison S.p.A.; crystallinity = 59 ± 4 per cent; intrinsic viscosity $[\eta] = 0{\cdot}96$ (tetrahydronaphthalene at 135°).

(5) Linear, high density polyethylene, ROTENE 10 Q, manufactured by Montecatini–Edison S.p.A. with the Ziegler–Natta catalytic system; crystallinity = 70 ± 4 per cent; intrinsic viscosity $[\eta] = 1{\cdot}40$ (tetrahydronaphthalene at 135°).

## RESULTS

The measured concentrations of radioactive compounds in polymer slices were used to obtain the diffusion coefficient, $D$, along the axis normal to the section, by the equation:

$$C(x, t) = \frac{C_0}{(\pi Dt)^{\frac{1}{2}}} \exp\left(-\frac{x^2}{4\,Dt}\right). \tag{1}$$

It is supposed here that at time $t = 0$, the total amount $m$ of diffusing substance is concentrated in the plane $X = 0$.[4] If $S$ is the cross section of the cylinder, $C_0$ is $\frac{m}{S}$. The quantity $m$ was kept constant for every experiment, and was sufficiently small for total solution to be obtained in a time (about half an hour) substantially less than that needed in the diffusion experiments (20–30 hr). Thus the involved parameters may be referred, to a first approximation, to diffusion alone. The concentration of the penetrant in the polymer is very small (less than 1–2 per cent) during the diffusion, so that, probably, the values of $D$ are little affected by small variations in the concentration around this figure.[8]

The activation energy $E_d$ and the pre-exponential constant $D_0$ were calculated from the equation:

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right). \tag{2}$$

In the explored range of temperatures, at least twelve diffusion experiments were made for each compound. For the high crystallinity polymers, the experimental temperatures were kept below those at which the crystallinities begin to decrease with approach towards the melting point.

The values of the parameters of the diffusion coefficients for the studied compounds and the ranges of temperatures are summarized in Table 1.

The dependence of the logarithm of the pre-exponential constant $D_0$ upon the number of carbon atoms present in the alcoholic radical of hydroxy-benzophenones is shown in Fig. 1 for stereoblock polypropylene and in Fig. 3 for the two polyethylenes.

TABLE 1. VALUES OF $D_0$ AND $E_d$ FOR THE DIFFUSION OF 2-HYDROXY-4-ALKOXY-BENZOPHENONES AND ESTERS OF 3, 3′-THIODIPROPIONIC ACID IN SATURATED POLYOLEFINS

| Polymer | Range of temperatures (°C) | Penetrant | $D_0$ (cm²/sec) | In $D_0$ | $E_d$ (kcal/mole) |
|---|---|---|---|---|---|
| Stereoblock polypropylene | 70–85 | 2-hydroxy-4-methoxybenzophenone | 1·2 | 0·2 ± 1·64* | 12·1 ± 1·3* |
| Stereoblock polypropylene | 70–85 | 2-hydroxy-4-*n*-butoxybenzophenone | 3·8 . 10 | 3·65 ± 3·27 | 14·9 ± 2·3 |
| Stereoblock polypropylene | 70–85 | 2-hydroxy-4-*n*-octoxybenzophenone | 5·9 . $10^3$ | 6·39 ± 4·11 | 16·7 ± 2·9 |
| Stereoblock polypropylene | 70–85 | 2-hydroxy-4-*n*-dodecoxybenzophenone | 1·2 . $10^5$ | 11·67 ± 1·89 | 20·0 ± 1·2 |
| Stereoblock polypropylene | 70–85 | 2-hydroxy-4-*n*-octadecoxybenzophenone | 2·6 . $10^3$ | 7·86 ± 1·83 | 18·2 ± 1·3 |
| High density polyethylene | 80–110 | 2-hydroxy-4-methoxybenzophenone | 3·0 . $10^2$ | 5·73 ± 3·17 | 17·4 ± 2·3 |
| High density polyethylene | 80–110 | 2-hydroxy-4-*n*-butoxybenzoylphenone | 8·3 . $10^3$ | 6·72 ± 1·92 | 18·5 ± 1·4 |
| High density polyethylene | 80–110 | 2-hydroxy-4-*n*-octoxybenzophenone | 4·0 . $10^4$ | 10·60 ± 2·00 | 21·6 ± 1·5 |
| High density polyethylene | 80–110 | 2-hydroxy-4-*n*-dodecoxybenzophenone | 4·4 . 10 | 3·78 ± 2·76 | 16·8 ± 2·0 |
| High density polyethylene | 80–110 | 2-hydroxy-4-*n*-octadecoxybenzophenone | 2·7 . 10 | 3·31 ± 1·67 | 17·0 ± 1·2 |
| Low density polyethylene | 70–90 | 2-hydroxy-4-methoxybenzophenone | 1·9 | 0·65 ± 1·22 | 12·0 ± 0·8 |
| Low density polyethylene | 70–90 | 2-hydroxy-4-*n*-butoxybenzophenone | 5·8 . $10^3$ | 6·36 ± 2·35 | 16·4 ± 1·6 |
| Low density polyethylene | 70–90 | 2-hydroxy-4-*n*-octoxybenzophenone | 8·4 | 2·12 ± 1·86 | 13·5 ± 1·3 |
| Low density polyethylene | 70–90 | 2-hydroxy-4-*n*-dodecoxybenzophenone | 13·4 | 2·59 ± 1·84 | 14·0 ± 1·2 |
| Low density polyethylene | 70–90 | 2-hydroxy-4-*n*-octadecoxybenzophenone | 6·7 | 1·91 ± 0·66 | 13·6 ± 0·4 |
| Low crystalline polypropylene | 20–40 | dimethyl-3, 3′-thiodipropanoate | 2·4 . $10^5$ | 12·4 ± 2·0 | 19·1 ± 1·2 |
| Low crystalline polypropylene | 20–40 | di-*n*-hexyl-3, 3′-thiodipropanoate | 1·8 . $10^5$ | 12·1 ± 0·9 | 19·2 ± 0·5 |

* Limit of reliability for a 50 per cent probability.

The effect of the number of carbon atoms on the activation energy for diffusion, $E_d$, is shown in Fig. 2 for stereoblock polypropylene and in Fig. 4 for polyethylenes. These correlations may be made because the concentration of diffusing substance is similar for all compounds.

An idea of the mutual compatibility between penetrant and polymer may be given by the ratios, $C$, between the half-time of crystallization of the mixtures studied and the half-time of crystallization of the pure polymer.[2]

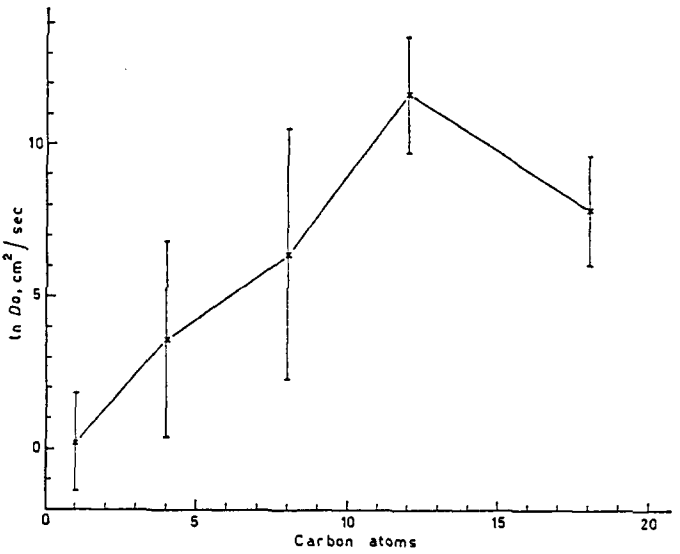


FIG. 1. Ln $D_0$ vs. number of carbon atoms in the alcoholic radical for diffusion of hydroxy-alkoxy-benzophenones in stereoblock polypropylene at 70°–85°.

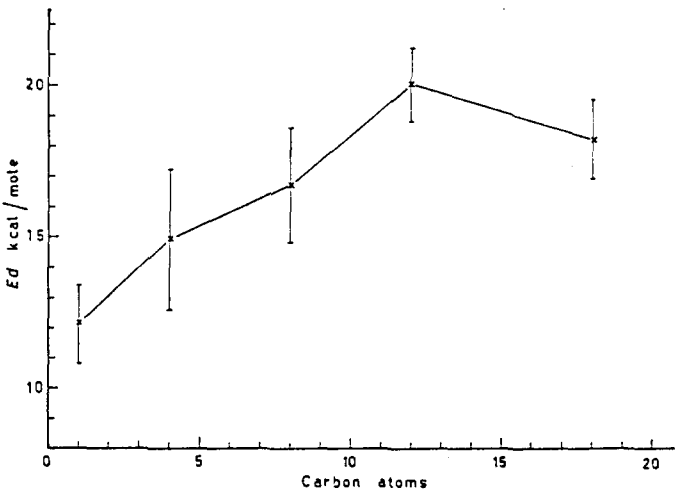


FIG. 2. Energy of activation for diffusion of hydroxy-alkoxy-benzophenones in stereoblock polypropylene at 70°–85° vs. number of carbon atoms in the alcoholic radical.

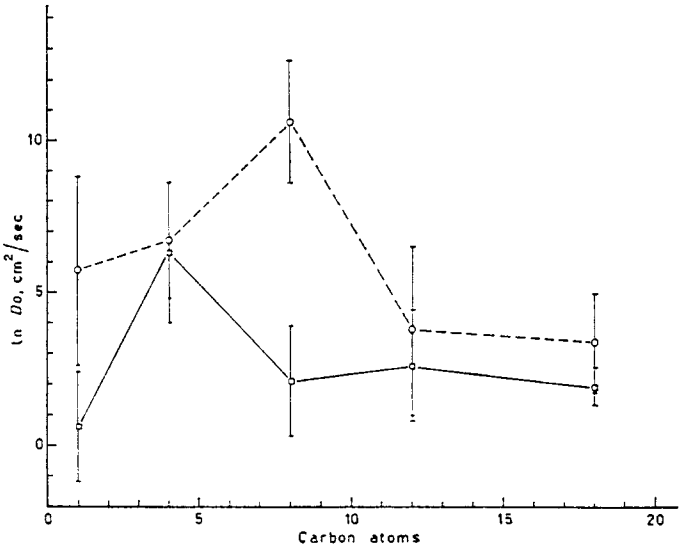


FIG. 3. Ln $D_0$ vs. number of carbon atoms in the alcoholic radical for diffusion of hydroxy-alkoxy-benzophenones in high density polyethylene (○) at 80°–110° and in low density polyethylene (□) at 70°–90°.

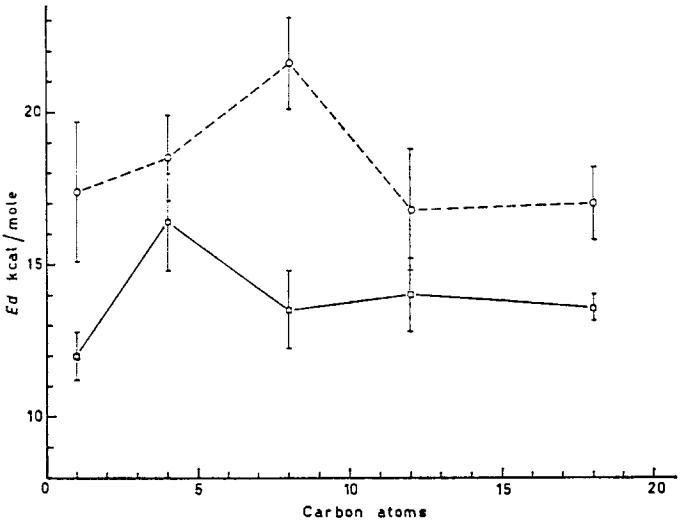


FIG. 4. Energy of activation for diffusion of hydroxy-alkoxy-benzophenones in high density polyethylene (○) at 80°–110° and in low density polyethylene (□) at 70°–90° vs. number of carbon atoms in the alcoholic radical.

Mixtures of 2-hydroxy-4-alkoxy ($C_1$—$C_{18}$)-benzophenones (4,4 m-moles for 100 g of polymer) and isotactic polypropylene or high density polyethylene were tested. The values of ratio $C$ are reported in Table 2. The compatibility of hydroxy-alkoxy-benzophenones with isotactic polypropylene is very low as the ratio $C$ is almost constant and close to unity even by changing the number of carbon atoms in the

TABLE 2. RATIO OF MUTUAL COMPATIBILITY

| Polymer | Penetrant | $C$ $(t_{1/2}/t_{0\ 1/2})$ |
|---|---|---|
| Isotactic polypropylene | 2-hydroxy-4-methoxybenzophenone | 1·00 |
| Isotactic polypropylene | 2-hydroxy-4-*n*-butoxybenzophenone | 1·00 |
| Isotactic polypropylene | 2-hydroxy-4-*n*-octoxybenzophenone | 0·95 |
| Isotactic polypropylene | 2-hydroxy-4-*n*-dodecoxybenzophenone | 0·90 |
| Isotactic polypropylene | 2-hydroxy-4-*n*-octadecoxybenzophenone | 0·98 |
| High density polyethylene | 2-hydroxy-4-methoxybenzophenone | 1·08 |
| High density polyethylene | 2-hydroxy-4-*n*-butoxybenzophenone | 1·15 |
| High density polyethylene | 2-hydroxy-4-*n*-octoxybenzophenone | 1·20 |
| High density polyethylene | 2-hydroxy-4-*n*-dodecoxybenzophenone | 1·94 |
| High density polyethylene | 2-hydroxy-4-*n*-octadecoxybenzophenone | 1·88 |

Test conditions:
for polypropylene — $T_f = 220°$, $t_f = 60$ min, $T_c = 140°$;
for polyethylene — $T_f = 200°$, $t_f = 60$ min, $T_c = 128°$.
Concentration of penetrant = 4·4 m-moles for 100 g of polymer.
$t_{\frac{1}{2}}$ = half time of crystallization of the mixture.
$t_{0\frac{1}{2}}$ = half time of crystallization of the pure polymer.
$T_f$ = temperature of annealing of the melt.
$T_c$ = temperature at which the polymer has been allowed to crystallize.
$t_f$ = length of the period of annealing of the melt.

alcoholic radical from $C_1$ to $C_{18}$. As may be seen in Fig. 5, the mutual compatibility of hydroxy-alkoxy-benzophenones with high density polyethylene slightly increases with the number of C atoms of alcoholic radical up to the $C_8$-term, then it rises abruptly for the $C_{12}$ and $C_{18}$ terms.

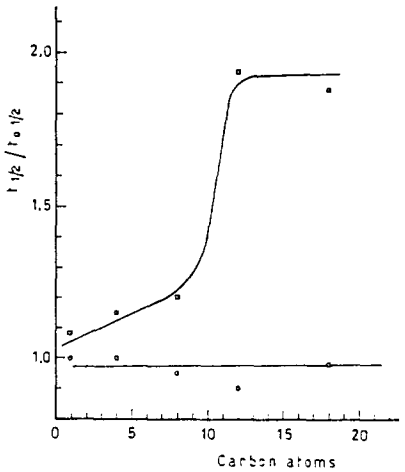


FIG. 5. Ratio of mutual compatibility between hydroxy-alkoxy-benzophenones and isotactic polypropylene (○) or high density polyethylene (□) vs. number of carbon atoms in the alcoholic radical.

## DISCUSSION

The practically equal values of $E_d$ for diffusion of 3,3′-thiodipropionic esters in low crystallinity polypropylene (Table 1) are in good agreement with that ($E_d = 19{\cdot}8$ kcal/mole) found by Frensdorff[5] for diffusion of benzene in low crystallinity polypropylene at about the same range of temperature (14°–40°). This means that the diffusion process is regulated by the self-diffusion of the polymer segments;[6–8] the value of $E_d$ should be of the same order of magnitude as the activation energy for self-diffusion.

As found for isotactic polypropylene, the value of $E_d$ tends to increase linearly with the molecular dimensions of the diffusing hydroxy-alkoxy-benzophenones in stereo-block polypropylene (Fig. 2), before approaching the activation energy for self-diffusion of the polymer segments. The curves, ln $D_0$ and $E_d$ vs. C atoms of residue, show a flat maximum just before the asymptotic value. The occurrence of a maximum in the $E_d$ vs. C atoms plot is more evident in Figs. 3 and 4, referring to the diffusion of hydroxy-alkoxy-benzophenones in polyethylenes. Although a greater diffusivity is found for the high pressure polymer, the dependence of the diffusion constants upon the molecular weight of penetrant is similar for the two polyethylenes. The presence of this maximum may be explained by considering that the coefficient for self-diffusion of polymer segments is influenced by the mutual compatibility between penetrant and polymer so that, by increasing the number of C atoms of alcoholic radical, the energy of self-diffusion, $E_v$, of the polymer decreases.

The experimental curves (Figs. 2 and 4) can be considered as the resultants of two lines (Fig. 6): the curve (a) represents the dependence of the energy of diffusion of the penetrant in the polymer on the molecular volume of the penetrant; the curve (b) shows what could be the decrease of $E_v$ with the increase in compatibility between penetrant and polymer.

This hypothesis fits well with the data reported in Fig. 5 concerning the compatibility between hydroxy-alkoxy-benzophenones and high density polyethylene: during the diffusion experiment and the compatibility measurement the $C_{12}$ and $C_{18}$ terms show behaviour different from the other homologous compounds. On the other hand,

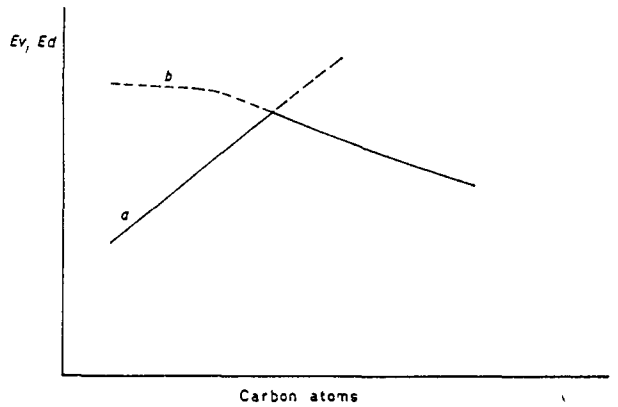


FIG. 6. (a) Variation of $E_d$ with the molecular volume of penetrant; (b) Variation of $E_v$ with the mutual compatibility between penetrant and polymer.

the incompatibility between isotactic polypropylene and hydroxy-alkoxy ($C_1$—$C_{18}$)-benzophenones is in agreement with the behaviour of these compounds on diffusion.[1]

The contribution of each $=CH_2$ group of the alcoholic radical to the energy of activation for the diffusion of hydroxy-alkoxy-($C_1$—$C_{12}$)-benzophenones in stereo-block polypropylene can be calculated. The value of

$$\frac{E_d}{CH_2} \text{ is } 686 \text{ cal},$$

which is higher than that found by us for diffusion of the same compounds in isotactic polypropylene:

$$\left(\frac{E_d}{CH_2} = 302 \text{ cal } [1]\right).$$

These values suggest that, in a homologous series of compounds, the molecular volume of penetrant has a larger influence on the diffusion when the polymer has a higher diffusivity.

An empirical correlation, like that of Barrer and Chio,[9] between ln $D_0$ and $E_d/T$ for elastomers, can be obtained for saturated polyolefins using the data reported in Table 3. The resulting linear relation (Fig. 7) can be expressed as:

$$\ln D_0 = -14{\cdot}8_4 + 0{\cdot}43_9 E_d/T. \quad (3)$$

TABLE 3. DIFFUSION OF ORGANIC COMPOUNDS IN SATURATED POLYOLEFINS

| Polymer | Penetrant | $\ln D_0$ ($cm^2/sec$) | $\frac{E_d}{T}$ (cal $mole^{-1}$ $°K^{-1}$) | References |
|---|---|---|---|---|
| Isotactic polypropylene | 2-hydroxy-4-methoxybenzophenone | 6·52 | 49·57 | (1) |
| Isotactic polypropylene | 2-hydroxy-4-*n*-butoxybenzophenone | 7·94 | 52·33 | (1) |
| Isotactic polypropylene | 2-hydroxy-4-*n*-octoxybenzophenone | 9·22 | 56·55 | (1) |
| Isotactic polypropylene | 2-hydroxy-4-*n*-dodecoxybenzophenone | 9·65 | 57·10 | (1) |
| Isotactic polypropylene | 2-hydroxy-4-*n*-octadecoxybenzophenone | 12·66 | 63·49 | (1) |
| Isotactic polypropylene | dimethyl-3, 3′-thiodipropanoate | 5·66 | 45·87 | (1) |
| Isotactic polypropylene | di-n-hexyl-3, 3′-thiodipropanoate | 7·04 | 49·76 | (1) |
| Isotactic polypropylene | di-n-dodecyl-3, 3′-thiodipropanoate | 8·66 | 54·37 | (1) |
| Isotactic polypropylene | di-n-hexadecyl-3, 3′-thiodipropanoate | 9·89 | 57·61 | (1) |
| Isotactic polypropylene | n-decane | 8·39 | 50·13 | (10) |
| Isotactic polypropylene | n-hexadecane | 8·84 | 51·50 | (10) |
| Isotactic polypropylene | 2, 6-di-*tert*-butyl-*p*-cresol | 15·44 | 64·25 | (11) |
| Isotactic polypropylene | phenothiazine | 27·65 | 91·38 | (11) |
| Stereoblock polypropylene | 2-hydroxy-4-alkoxy ($C_1$—$C_{18}$)-benzophenones | Table 1 | | this paper |
| Low crystallinity polypropylene | dimethyl and di-n-hexyl-3, 3′-thiodipropanoate | Table 2 | | this paper |
| Low crystallinity polypropylene | $C_{22}$—$C_{25}$ hydrocarbon | −0·42 | 28·60 | (6) |
| Low crystallinity polypropylene | benzene | 15·07 | 66·00 | (5) |
| Ethylene propylene copolymer: | | | | |
| propylene 72 mole-% | benzene | 8·47 | 51·00 | (5) |
| propylene 51 mole-% | benzene | 5·84 | 44·00 | (5) |
| propylene 31 mole-% | benzene | 2·09 | 35·60 | (5) |
| high density polyethylene | 2-hydroxy-4-alkoxy-($C_1$—$C_{18}$)-benzophenones | Table 1 | | this paper |
| low density polyethylene | 2-hydroxy-4-alkoxy-($C_1$—$C_{18}$)-benzophenones | Table 1 | | this paper |
| poly-isobutylene | *n*-butane | 7·83 | 53·10 | (12) |
| poly-isobutylene | *iso*-butane | 8·28 | 56·80 | (12) |
| poly-isobutylene | *n*-pentane | 6·46 | 51·90 | (12) |
| poly-isobutylene | *iso*-pentane | 9·22 | 58·70 | (12) |
| poly-isobutylene | tetramethylmethane | 8·07 | 58·50 | (12) |
| poly-isobutylene | $C_{22}$—$C_{25}$ hydrocarbon | 8·64 | 51·40 | (6) |

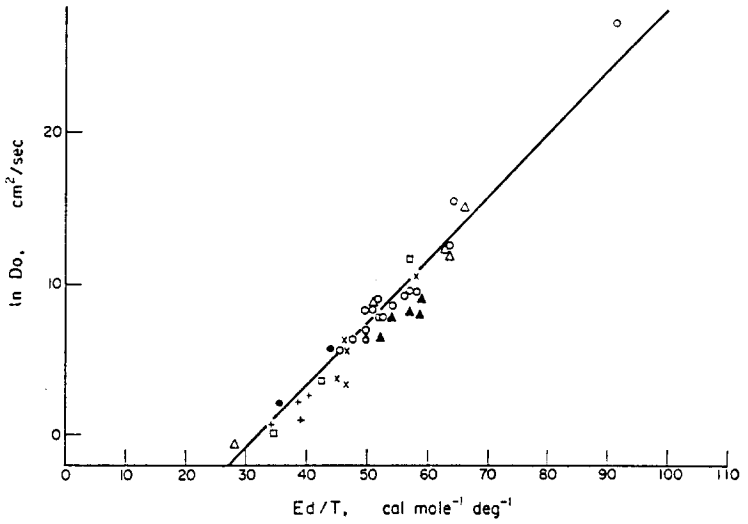


FIG. 7. Relationship between ln $D_0$ and $E_d/T$—Isotactic polypropylene (○). Stereoblock polypropylene (□). Low crystallinity polypropylene (△). Ethylene-propylene copolymer (●). High density polyethylene (×). Low density polyethylene (+). Polyisobutylene (▲).

By combining Eqns. (3) and (2), we obtain the universal diffusion equation:

$$\ln D = -14{\cdot}8_4 - 0{\cdot}064\, E_d/T,$$

for organic compounds in saturated polyolefins. One possible use of this equation might be the calculation of an approximate value of the activation energy of diffusion from the measurement of $D$ at one temperature only.

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**Résumé**—On a étudié la diffusion de l'hydroxy-2-méthoxy-4-benzophénone, de l'hydroxy-2-*n*-butoxy-4-benzophénone, de l'hydroxy-2-*n*-octoxy-4-benzophénone, de l'hydroxy-2-*n*-dodecoxy-4-benzophénone et de l'hydroxy-2-*n*-octadecoxy-4-benzophénone dans les polymères suivants: polypropylène

stéréoséquencé (entre 70° et 85°), polyéthylène de haute densité (80°–110°) et polyéthylène de basse densité (70°–90°). On a étudié en outre la diffusion du diméthyl-3, 3′-thiodipropionate et du di-*n*-hexyl-3, 3′-thiodipropionate dans un polypropylène de faible taux de cristallinité (entre 20° et 40°). On donne les coefficients de diffusion obtenus. On discute l'influence exercée sur la diffusion par la compatibilité mutuelle entre la substance diffusante et le polymère. Pour la diffusion dans les polyoléfines saturées on a calculé la relation linéaire:

$$\ln D_0 = -14{\cdot}8 + 0{\cdot}43\, E_d/T$$

au moyen des données publiées et de celles obtenues dans le présent travail.

**Sommario**—E' stata studiata la diffusione del 2-idrossi-4-metossibenzofenone, del 2-idrossi-4-*n*-butossibenzofenone, del 2-idrossi-4-*n*-ottossibenzofenone, del 2-idrossi-4-*n*-dodecossibenzofenone, del 2-idrossi-4-*n*-ottadecossibenzofenone nei seguenti polimeri: polipropilene stereoblocchi (intervallo di temperatura 70°–85°), in polietilene ad alta densità (intervallo di temperatura 80°–110°) e in polietilene a bassa densità (intervallo di temperatura 70°–90°). Inoltre è stata studiata la diffusione del dimetil-3, 3′-tiodipropionato e del di-*n*-esil-3, 3′-tiodipropionato in polipropilene a bassa cristallinità (intervallo di temperatura 20°–40°). Sono riportati i coefficienti di diffusione. E' discussa l'influenza esercitata sulla diffusione dalla mutua compatibilità tra penetrante e polimero. Utilizzando i dati riportati in letteratura e quelli da noi trovati è stata calcolata la relazione

$$\ln D_0 = -14{\cdot}8 + 0{\cdot}43\, E_d/T$$

valida per la diffusione in poliolefine sature.

**Zusammenfassung**—Es wurde die Diffusion des 2-Hydroxy-4-methoxybenzophenons, des 2-Hydroxy-4-*n*-butoxybenzophenons, des 2-Hydroxy-4-*n*-octoxybenzophenons, des 2-Hydroxy-4-*n*-dodecoxybenzophenons und des 2-Hydroxy-4-*n*-octadecoxybenzophenons bei den folgenden Polymeren untersucht: Stereoblock-Polypropylen (Temperatur zwischen 70° und 85°), Polyäthylen hoher Dichte (Temperatur 80°–110°) und Polyäthylen niedriger Dichte (Temperatur 70°–90°). Es wurde ferner die Diffusion des Dimethyl-3,3′-thiodipropionates und des Di-*n*-hexyl-3,3′-thiodipropionates in ataktischem Polypropylen (Temperatur zwischen 20° und 40°) (geprüft).

Hierbei werden die Difffusionskoeffizienten angegeben. Es wird der Einfluß der gegenseitigen Verträglichkeit zwischen dem diffundierenden Stoff und dem Polymeren auf die Diffusion diskutiert.

Auf Grund der in der Literatur aufgeführten Angaben und denjenigen, die von uns gefunden wurden, wurde die folgende Gleichung für die Diffusion in gesättigten Polyolefinen aufgestellt:

$$\ln D_0 = -14{\cdot}8 + 0{\cdot}43\, E_d/T.$$