Diffusion of Methyl Esters of Higher Fatty Acid in Polypropylene

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SYNOPSIS

Diffusion coefficients of several methyl esters of linear higher fatty acid ($C_{10} \sim C_{18}$) into polypropylene (PP) were determined, over the temperature range of 50 to 110°C, using a mass uptake technique. The relations between an amount of mass uptake and $t^{1/2}$ were linear within 10 min, indicating Fickian diffusion. The diffusion coefficients were in the range of 4.6×10^{-8} to 6.2×10^{-12} cm^2 sec^{-1}, increased with temperature, and decreased with increasing n-alkyl chain length of fatty acid. The plots of ln D vs. the molecular weight of methyl esters were approximately linear. The temperature dependence of diffusion followed an Arrhenius relationship, and the activation energies were in the range of 133 $\sim$ 147 KJ mol^{-1} and increased with an increase in n-alkyl chain length of corresponding fatty acid. The diffusion coefficients were discussed with the interaction between methyl esters of higher fatty acid and PP. The diffusion coefficients of methyl esters, at the simultaneous diffusion process, were always higher than that derived from the single diffusion process, except for methyl decanoate with lower molecular weight. The difference in diffusion coefficients in single and simultaneous diffusion was discussed thermodynamically. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In polypropylene (PP), molding products are widely used as not only one-way, but also long-lived. Long-lived lunchware is used repeatedly, being washed to remove odors and soil and being sterilized by heating. PP decomposes readily to produce polymer radicals, leading to the cleavage of the polymer chain because hydrogens, attached to the tertiary carbons in polymer chains, are unstable. Many kinds of phenolic hydroxy compounds are added to PP for the inhibition of autooxidation.

In previous articles,[1,2] authors reported that 2,6-di-tert-butyl-p-cresol (BHT), which is one of the antioxidant additives that is widely used, showed the concentration distribution in PP and vaporized from the surface by heating. Furthermore, the authors[2] and other workers[8] found that the coexistent oils lowered the specific rate of the vaporiza-

tion of BHT by heating. However, the content of 0.2 wt % in PP was not sufficient to lower the specific rate of the vaporization. Consequently, it was necessary to ascertain the diffusion behavior of oils in PP in detail, involving in the influence of the BHT vaporization.

Polypropylene shows a high resistance to chemicals because it has high crystallinity. Parrini[4] reported that, when PP is immersed in olive oil, it absorbs the oil at $0 \sim 1.5\%$ at $20 \sim 70°C$ and 1.5 $\sim 5\%$ at 100°C. However, the detailed mechanism of the penetration of oils in PP was not clarified. Since the composition of higher fatty acids, which are contained in fats and oils, depends largely on the species of source material and on the place of origin, it is difficult to obtain reproducible data on the diffusion of fatty acids in PP. Furthermore, as highly sensitive methods for the detection of fats and oils have not been yet developed, the work performed on this topic was only done by use of the gravimetric method.

Preliminary experiments revealed that the amount of mass uptake is too low to determine it

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gravimetrically. Consequently, it is difficult to examine the diffusion behavior of fats and oils in PP accurately and closely. The lack of information on the detailed behavior of fats and oils in PP promoted this investigation.

In this work, the authors examined methyl esters of higher fatty acids, which are the chief ingredients in fats and oils. The methyl esters have a similar molecular structure and property as does the source material. The determination of the esters can be carried out accurately and sensitively by a gas–liquid chromatograph, equipped with a flame ionization detector.

The authors report on the time course of mass uptake of methyl oleate in PP that was immersed for a long periods of time, and on the diffusion coefficients and activation energies of several methyl esters of straight-chain fatty acids in PP, immersed during a sufficiently short amount of time. The mass uptake technique, also applied to the mixture, consisted of an equimolecular amount of esters in order to ascertain the influence of a coexistent homologue to the diffusion of each component. The authors, moreover, report on the influence of crystallinity on the diffusion behavior of these esters in PP.

EXPERIMENTAL

Material and Reagents

The PP homopolymer, 0.03 cm in thickness, was purchased from Tokyo Cellophane Co. Ltd. The X-ray profile of this sheet did not show any orientation. The crystallinity of the sheet was estimated to be 0.64 by the density measurement method. All methyl

esters of higher fatty acid, of commercial grade, that were used in the present work, were purchased from Wako Pure Chemicals Co. Ltd., and the properties of esters and those acronyms used herein were listed in Table I. All esters were methyl esters of linear higher fatty acid ($C_{10} \sim C_{18}$), without branchings in the alkyl chains. These esters were saturated compounds, except for methyl oleate, with one double bond in a molecule. The purities of those were 65% for MO and over 95% for others. These were used without further purification.

Apparatus

The gas chromatograph, used in this study, was a Shimadzu model GC-8A gas chromatograph, equipped with a flame ionization detector.

Density Measurement

The measurement of diffusion coefficient by the mass uptake technique requires knowledge of the densities of esters at a given temperature. Densities of all esters were determined with the use of a pycnometer at various temperatures in the range of 40–80°C. The relations between density and temperature were linear. The density of an ester at a given temperature was obtained from the first-order equation.

Preparation of Mixture Consisted of Equimolecular Esters

One-hundred eighty-six g of MD, 214 g of ML, 242 g of MM, 270 g of MP, and 298 g of MS were mixed and were stirred sufficiently to mix with each other.

Table I Methyl Esters of Higher Fatty Acids Investigated

Name	Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	Density
Methyl Decanoate (MD)	$C_{11}H_{22}O_2$	186.3	228[5] (758 mm Hg)	−10--11[5]	0.8730 (20°C)[5]
Methyl Laurate (ML)	$C_{13}H_{25}O_2$	214.4	261.5–262[5] (766 mm Hg)	+4.8[6]	0.8695 (20°C)[6]
Methyl Myristate (MM)	$C_{15}H_{30}O_2$	242.4	295[7] (751 mm Hg)	+18[7]	0.8671 (20°C)[8]
Methyl Palmitate (MP)	$C_{17}H_{34}O_2$	270.5	415–418[9] (747 mm Hg)	+29.5–30[9]	0.8520 (37.8°C)[10]
Methyl Stearate (MS)	$C_{19}H_{38}O_2$	298.5	214–215[11] (15 mm Hg)	+39.7–40[11]	0.8498 (40°C)[12]
Methyl Oleate (MO)	$C_{19}H_{36}O_2$	296.5	218.5[13] (20 mm Hg)	−19.6–20.4[13]	0.8739 (20°C)[13]

The concentrations of each ester in the mixture, which were necessary to calculate the diffusion coefficient at the simultaneous diffusion process, were determined by eqs. (1) and (2), as follows:

$$C_i = M_W/V_T \tag{1}$$

$$V_T = \left(\frac{M_W}{d_o}\right)_{MD} + \left(\frac{M_W}{d_o}\right)_{ML} + \left(\frac{M_W}{d_o}\right)_{MM}$$
$$+ \left(\frac{M_W}{d_o}\right)_{MP} + \left(\frac{M_W}{d_o}\right)_{MS} \tag{2}$$

where C_i is the concentration of ester (g/cm^3) in the mixture, M_W is the molecular weight, V_T is the total molar volume of a mixture containing each gram mol at a given temperature, d_o is the density of each respective ester. Here the additivity of volume of each component is assumed for V_T.

Diffusion Measurement

Square disks, 5 × 5 cm, were cut off from a PP sheet of 0.03 cm in thickness. Five to six disks per run were individually weighed and placed together in each ester, held at a constant temperature, within 0.5°C. The inside of the beaker was divided into eight compartments with wirework to allow free contact of the ester with both sides of a disk.

After 0.5, 1, 2, 3, 4, and 5 min, each respective disk was taken out of the beaker and was immersed into a large quantity of acetone at a room temperature for two or three seconds to cool and to remove roughly the excess amounts of ester adhered to the surface of the PP disk. The disk was then wiped to remove acetone and adhered ester. The disk was immersed in 50 mL of n-hexane for 24 h at 50°C to extract completely the imbibed ester. The extract was condensed under the vacuum until just before the solvent completely disappeared at a temperature below 35°C, and the extract was then dissolved in 5 mL of n-hexane.

The content of ester in the solution was determined by gas–liquid chromatography, the operating conditions of which were denoted as follows.

A column, 3 mm i.d. × 2000 mm, of glass tubing, packed with 5% Advance DS on Shinchrom A (80–100 mesh), was isothermally operated at a constant temperature in the range of 160–190°C. The injector was maintained at 230°C. Nitrogen, as a carrier gas, was allowed to flow at a pressure of 1.8 kg/cm². The typical gas–liquid chromatogram of the sample solution is shown in Figure 1.

The change in concentration, due to imbibed ester, was recorded for each disk as a function of contact time with ester.

Calculation of the Diffusion Coefficient and Activation Energy

In order to calculate the diffusion coefficients of esters into PP by mass uptake technique, the following eq. (3), which was given by Crank[14] and is used for the calculation of the diffusion coefficients of plasticizers into PVC,[15,16] was applied conveniently.

$$D = \frac{\pi M_t^2}{16 S^2 C_o^2 t} \tag{3}$$

where D is diffusion coefficient; S is the area of one side of the disk, C_o is the density of a methyl ester at a given temperature,[15,16] t is time, and M_t is the total amount of mass uptake.

Equation (3) indicates that the diffusion coefficient is readily calculated by knowing S, C_o, and the slope of the straight line of the plot of M_t against $t^{1/2}$ for a sufficiently short time.
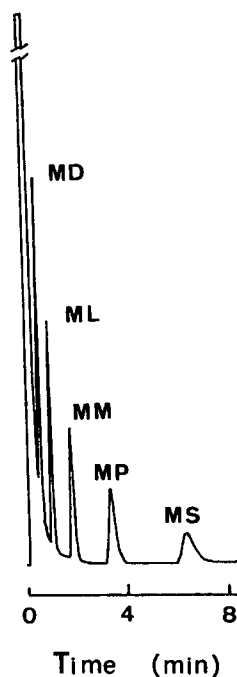
Figure 1 The typical gas–liquid chromatogram of the sample solution containing several methyl esters of higher fatty acid. GLC-operating condition: Column, 3 mm i.d. × 2000 mm, glass tubing packed with 5% Advance DS on Shinchrom A (80–100 mesh); Temp, inj. 230°C, oven. 190°C; carrier gas, N₂, 1.8 kg/cm².

The activation energy E in diffusion and D are usually combined as in eq. (4).
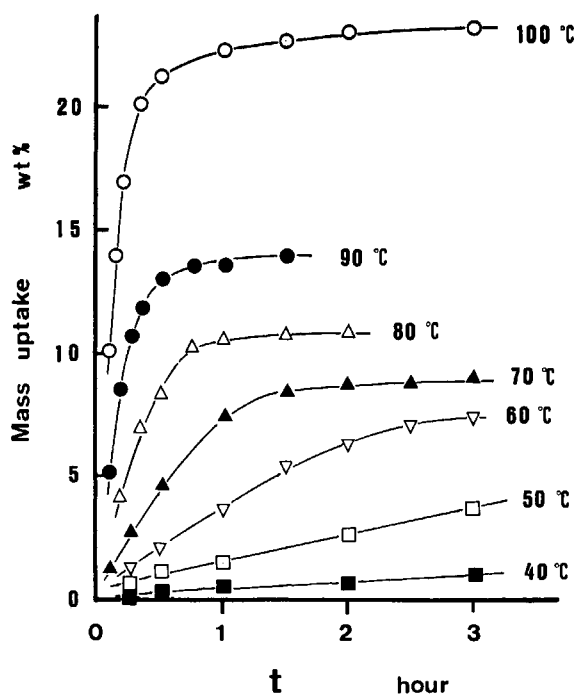
$$D = D_o e^{-E/RT} \tag{4}$$

$$\ln D = \ln D_o - E/RT \tag{5}$$

where D is the diffusion coefficient, D_o is a constant, E is the activation energy, R is the gas constant, and T is the absolute temperature.
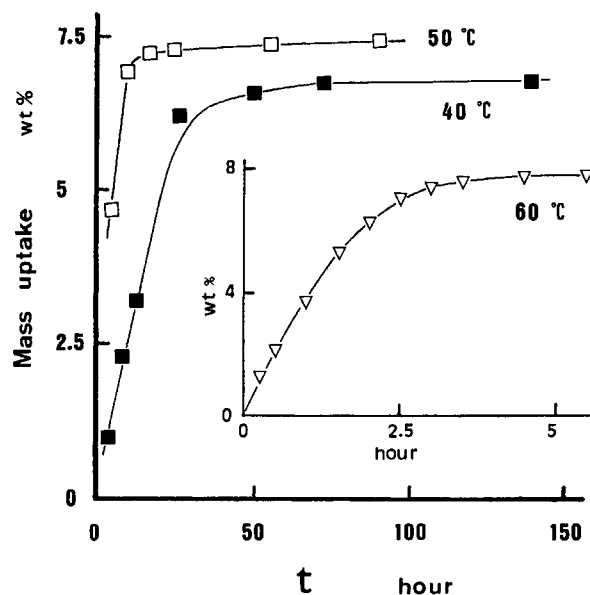
RESULTS AND DISCUSSION

Diffusion of Several Methyl Esters of Higher Fatty Acid

Figures 2 and 3 show the time course of the mass uptake of PP disks, immersed in methyl oleate, in the temperature range of 40–100°C. In the early stage, the amounts of the mass uptake increased linearly with the square root of time t. Mass uptake equilibrium was established after a certain period of time, which depended on the temperature. The amount of mass uptake in equilibrium increased with the rise in temperature (Fig. 4). On the other hand, the uptake decreased with the increase in the mo-

lecular weight of esters; as an example, the values at 50°C were 9.24% for MD, 8.78% for ML, 8.52% for MM, 7.89% for MP, and 7.49% for MS.

Figure 5 shows the representative mass uptake plots for a model straight chain methyl ester of higher fatty acid without the carbon–carbon double bond in a molecule at various temperatures. The


Figure 3 Time course of mass uptake for diffusion of methyl oleate in PP disks at 40–60°C. Temperature: (- ■ -) 40°C, (- □ -) 50°C, and (- ▽ -) 60°C.

Figure 2 Time course of mass uptake for diffusion of methyl oleate in PP disks at 40–100°C. Temperature: (- ■ -) 40°C, (- □ -) 50°C, (- ▽ -) 60°C, (- ▲ -) 70°C, (- △ -) 80°C, (- ● -) 90°C, and (- ○ -) 100°C.
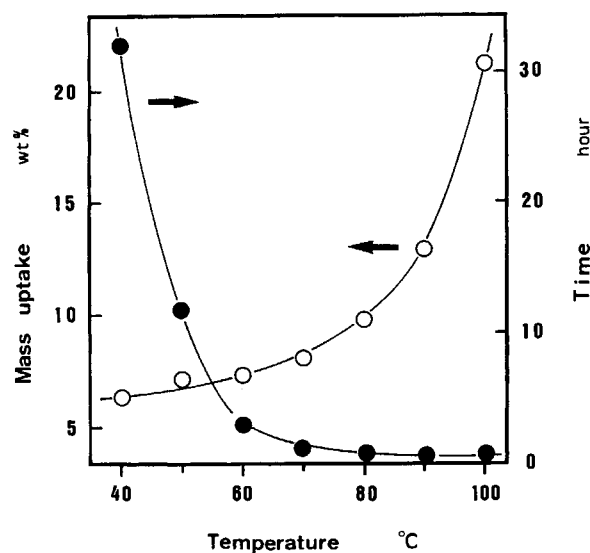
Figure 4 Correlations between temperature and the time required for the arrival of equilibrium and amount of mass uptake in equilibrium for diffusion of methyl oleate in PP disks.
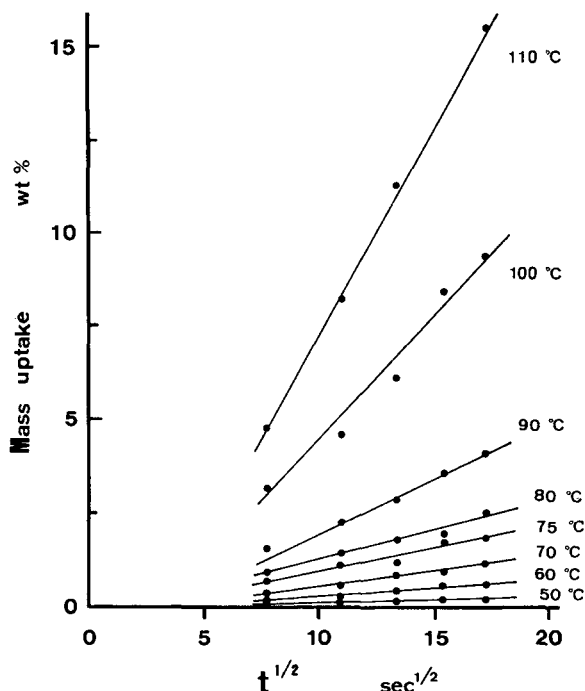
Figure 5 Mass uptake plots for diffusion of methyl stearate in PP disks at various temperatures of 50–110°C, in the absence of other methyl esters of higher fatty acids.

plots are linear with respect to $t^{1/2}$, in the range within 400 seconds of a short period of time. The amount of mass uptake at the same immersing period of time increased with a rise in temperature, and the slope also increased steeply at higher temperatures. Similar relations were always observed for the other five kinds of methyl esters that are listed in Table I. From the comparison of all the mass uptake plots drawn for these experiments, the amount of mass uptake appears to decrease at the longer, unbranched chain of carbon atoms, as is shown in Figure 6. Therefore, the change in molecular chain length of methyl ester, of the straight chain fatty acid, was found to influence the rate of penetration into the inside of the PP disks.

When the plots, shown in Figure 5, were extrapolated to zero of mass uptake, the times t were estimated at 3–10 seconds, which times are not zero. Therefore, it appears that there is an induction time that does not obey Fick's law at the initial stage in the time course of mass uptake. This induction time is regarded as the time required to loosen all the polymer chain to achieve the long-range segment movement at a newly established higher temperature. The decrease in induction time, with the increase in temperature, which was mentioned by Storey et al.[16] on the diffusion of plasticizers in PVC,

could not be observed in our work, because the times obtained by the extrapolation of the plots at different temperatures varied too irregularly in the experimental errors to ascertain the relations. The diffusion coefficients, calculated according to eq. (3) for a single diffusion process of all esters, are listed in Table II. The diffusion coefficients ranged from 4.6 $\times$ 10^{-8} to 6.2 $\times$ 10^{-12} cm^2 sec^{-1}, increased with a rise in temperature, and decreased with increasing alkyl chain length of 50–100°C. For example, the diffusion coefficients of MD, with 10 carbon atoms in a corresponding fatty acid at 100°C and 50°C, were two and six times higher than those of MS with 18 carbon atoms in it, respectively.

The reasons for the increase in the diffusion coefficients, with a rise in temperature, is due to voids of sufficient size, which accomodate the ester molecules with increasing temperature and also the promotion of the mobility of the ester molecules itself thermally at the same time.

The method for ascertaining the influence of temperature on the diffusion coefficient can be derived by plotting the logarithm of the diffusion coefficient against the reciprocal of the absolute temperature by means of eq. (5). These Arrhenius plots, as shown in Figure 7, were linear for all esters investigated in the temperature range of 50–110°C above the melting points of each ester, as are shown in Table I. The values of E_{act}, calculated from the slope, are listed in Table III. The values found were in the range of 133–146 KJ mol^{-1}, and tended to
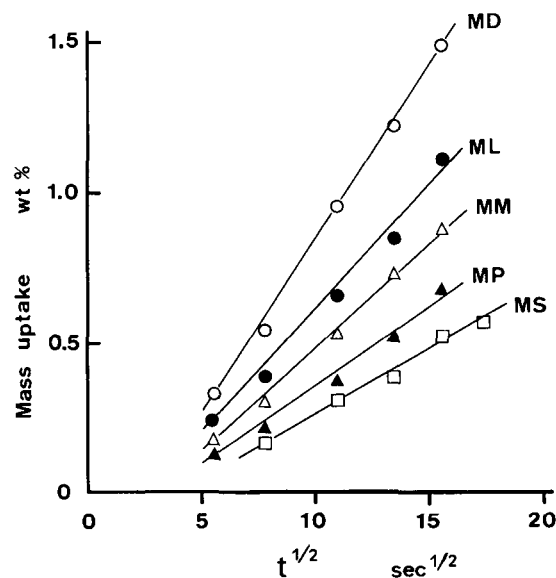
Figure 6 Mass uptake plots for diffusion of methyl esters of higher fatty acids into PP disks at 60°C.

Table II **Diffusion Coefficients D of Several Methyl Esters of Higher Fatty Acids Through Polypropylene Disks in the Case of Single Diffusion at 50–110°C by Mass Uptake Technique**

Methyl Ester	Molecular Weight (M_w)	Diffusion Coefficient D (cm^2 sec^{-1})						
		50°C	60°C	70°C	80°C	90°C	100°C	110°C
Methyl Decanoate	186	5.09 $\times 10^{-11}$	3.05 $\times 10^{-10}$	1.08 $\times 10^{-9}$	3.33 $\times 10^{-9}$	1.28 $\times 10^{-8}$	4.64 $\times 10^{-8}$	
Methyl Laurate	214	3.19 $\times 10^{-11}$	1.70 $\times 10^{-10}$	6.73 $\times 10^{-10}$	2.26 $\times 10^{-9}$	9.88 $\times 10^{-9}$	2.56 $\times 10^{-8}$	
Methyl Myristate	242	1.62 $\times 10^{-11}$	1.15 $\times 10^{-10}$	6.35 $\times 10^{-10}$	1.48 $\times 10^{-9}$	6.11 $\times 10^{-9}$	2.39 $\times 10^{-8}$	
Methyl Palmitate	270	9.61 $\times 10^{-12}$	6.82 $\times 10^{-11}$	2.07 $\times 10^{-10}$	9.47 $\times 10^{-10}$	3.23 $\times 10^{-9}$	1.43 $\times 10^{-8}$	
Methyl Stearate	298	6.23 $\times 10^{-12}$	4.19 $\times 10^{-11}$	1.62 $\times 10^{-10}$	6.67 $\times 10^{-10}$	2.17 $\times 10^{-9}$	1.17 $\times 10^{-8}$	2.89 $\times 10^{-8}$

increase with increasing alkyl chain length of the corresponding fatty acid.

A decrease in the amount of mass uptake at equilibrium and in the rate, and an increase in E_{act} with increasing molecular weight, are considered to be due to the decrease in the interaction between an ester and PP with increasing molecular weight.

In order to investigate further whether the sorption mechanism follows the Fickian mode or not, the sorption results for the short time, $Q_t / Q_\infty < 0.5$, were fit to the following empirical expression.[17]

$$Q_t / Q_\infty = Kt^n \tag{6}$$
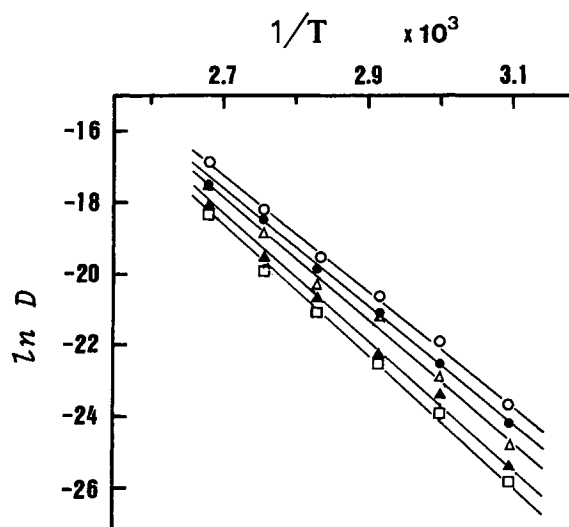
Figure 7 Relations between ln D and reciprocal of absolute temperature $1/T$ for several methyl esters at single diffusion process: (- □ -) methyl stearate, (- ▲ -) methyl palmitate, (- △ -) methyl myristate, (- ● -) methyl laurate, and (- ○ -) methyl decanoate.

where Q_t is the mass uptake of ester at time t, Q_∞ is the mass uptake at equilibrium, and K is a constant characteristic of the polymer–ester system.

The value $n = 0.5$ indicates the Fickian mode of transport and a value of $n = 1.0$ implies a case II transport. Values of n, between these limits, are indicative of anomalous transport behavior.[18] In this study, the mean values of n lie between 0.69 and 0.74, indicating the considerable deviation from the Fickian mode, and are clearly classified as anomalous transport. Penetrants are considered to diffuse, interacting with polymer segments.

Simultaneous Diffusion of Several Methyl Esters of Higher Fatty Acid

The relationship between $t^{1/2}$ and the mass uptake of each ester was obtained satisfactorily by immersing the PP disks in the mixture containing equimolecular amounts of the five kinds of esters,

Table III **Activation Energies E_{act} of Single (Sg) and Simultaneous (Sm) Diffusion Processes of Methyl Esters of Higher Fatty Acids Through Polypropylene Disks by Mass Uptake Technique**

| Methyl Ester	Molecular Weight (M_w)	E_{act} (KJ mol^{-1})	
		Sg	Sm
Methyl Decanoate	186	133	129
Methyl Laurate	214	135	136
Methyl Myristate	242	141	141
Methyl Palmitate	270	143	144
Methyl Stearate	298	146	147

Table IV   Diffusion Coefficients D of Several Methyl Esters of Higher Fatty Acids Through Polypropylene Disks in the Case of Simultaneous Diffusion at 50–100°C by Mass Uptake Technique

Methyl Ester	Molecular Weight (M_w)	Diffusion Coefficient D (cm^2 sec^{-1})					
		50°C	60°C	70°C	80°C	90°C	100°C
Methyl Decanoate	186	5.23×10^{-11}	2.86×10^{-10}	1.18×10^{-9}	3.84×10^{-9}	1.37×10^{-8}	3.16×10^{-8}
Methyl Laurate	214	2.82×10^{-11}	1.81×10^{-10}	7.20×10^{-10}	2.41×10^{-9}	8.96×10^{-9}	2.69×10^{-8}
Methyl Myristate	242	1.81×10^{-11}	1.22×10^{-10}	4.95×10^{-10}	1.75×10^{-9}	6.74×10^{-9}	2.24×10^{-8}
Methyl Palmitate	270	1.36×10^{-11}	9.07×10^{-11}	3.78×10^{-10}	1.40×10^{-9}	5.57×10^{-9}	1.94×10^{-8}
Methyl Stearate	298	8.95×10^{-12}	6.19×10^{-11}	2.67×10^{-10}	1.01×10^{-9}	4.17×10^{-9}	1.56×10^{-8}

MD, ML, MM, MP, and MS, at 50–100°C. The plots were all linear with respect to $t^{1/2}$ in sufficient short times, within 10 min, as were those of the plots obtained at the single diffusion process, indicating Fickian diffusion with a constant diffusion coefficient. The values, calculated according to eq. (3), were listed in Table IV. Diffusion coefficients were in the range of 3.2×10^{-8}–9.0×10^{-12} cm^2 sec^{-1} and they increased with a rise in temperature and decreased with an increase in the number of carbon atoms in a molecule. The relationship between ln D and the molecular weight for single and simultaneous diffusion is shown in Figure 8. Ln D deceased linearly with increasing M_W for both diffusion processes and, in simultaneous diffusion, ln D depended highly on M_W. Both plots are apparently different in slope, although the values of ln D for MD are almost identical to each other. The values of ln D for simultaneous diffusion processes at various temperatures were always higher than that for single diffusion process, indicating the greater difference with the increase in molecular weight. An increase in the free volume of the polymer, brought about by the swelling with smaller molecules prior to others, due to its stronger interaction with an ester, is considered to enhance the segment mobility of the inner part and to lead to easier penetration of larger molecules.

The Arrhenius plots were also linear and the activation energies are included in Table III. The diffusion coefficients for the esters in PP at simultaneous diffusion were higher than those for single
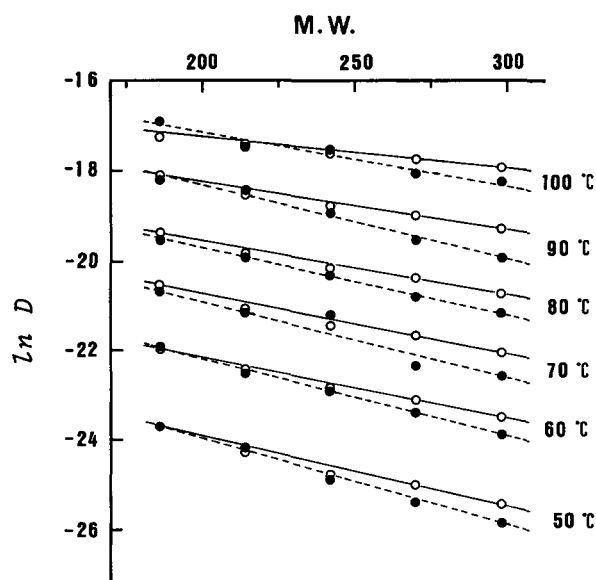
Figure 8   Relations between ln D and molecular weight of methyl esters of higher fatty acids: (– ● –) single diffusion process and (– ○ –) simultaneous diffusion process.
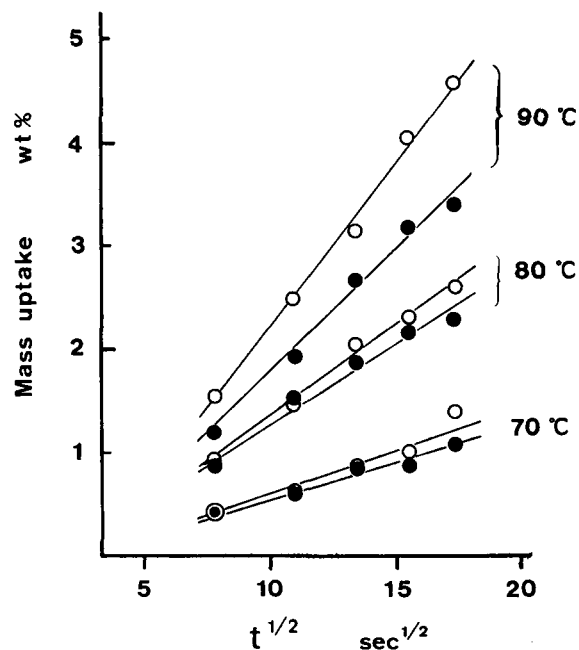
Figure 9   Mass uptake plots for diffusion of methyl oleate into PP disks with different crystallinity: (– ○ –) 64.1% and (– ● –) 70.1%.

Table V Diffusion Coefficients D and Activation Energies E_{act} of Methyl Oleate Through Polypropylene Disks with Different Crystallinities

Aging[a] (h)	Crystallinity (%)	Diffusion Coefficient D (cm^2 sec^{-1})			E_{act} (KJ mol^{-1})
		70°C	80°C	90°C	
0	64.1	1.67×10^{-10}	7.01×10^{-10}	2.38×10^{-9}	143
7	65.9	1.78×10^{-10}	(4.18×10^{-10})	2.36×10^{-9}	134
50	68.0	1.49×10^{-10}	6.56×10^{-10}	1.36×10^{-9}	131
300	70.1	1.03×10^{-10}	5.00×10^{-10}	1.34×10^{-9}	134

[a] Aged at 120°C in oven.

ones, as in the case of larger molecules, as mentioned above, whereas both activation energies agreed well with each other for any ester and there was no influence of the coexistent homologue. Thus, the increase in D, for an ester in simultaneous diffusion, is due to the increase in the preexponential factor in $D = A \exp(-E/RT)$. Since A concern the entropy of activation for diffusion, the increase in A in the mixture is considered to be the principal reason for the increase in D in simultaneous diffusion process.

Influence of Crystallinity on Diffusion Behavior

The crystallinities of the PP disks, heated at 120°C for 0, 7, 50, and 300 h under air, and then cooled gradually at room temperature, were estimated as 64.1, 65.9, 68.0, and 70.1%, respectively, from the density obtained by means of the sink and float test.

The relations between $t^{1/2}$ and the amount of mass uptake of methyl oleate for both disks of 70.1% and 64.1% crystallinity at 70–90°C, are shown in Figure 9. The mass uptake plots are linear in a sufficiently short time, as are those of other experiments. The amount of mass uptake for each time, and the specific rate of mass uptake, $W_t/t^{1/2}$, for the disks with 70.1% of crystallinity, is always lower than those for the disks of 64.1% crystallinity. The differences were evident at higher temperatures.

The diffusion coefficients and the activation energies are listed in Table V. The diffusion coefficient tended to decrease with increasing crystallinity, as expected. Priority is given to the amorphous regions in crystalline polymer, in which the polymer segments move more easily.

The Arrhenius plots of the logarithm of the diffusion coefficient vs. the reciprocal of the absolute temperature are laid approximately on a straight line for each sample. The Es for the samples with crystallinities of 65.9, 68.0, and 70.1% are almost equal to each other, while the E for the original sample is higher than those mentioned above. The reason for

this difference is uncertain, however, the difference in microstructure would contribute to it.

The influence of the heat-treatment on the mass uptake behavior was also seen in the amounts of mass uptake in equilibrium. These amounts were 5.9% at 40°C, 7.0% at 60°C, and 9.5% at 80°C, for the disks with 70.1% of crystallinity, whereas those for the sample with 64.1% of crystallinity were about 10% higher, respectively.

CONCLUSION

Methyl esters of higher fatty acids, C_{10}–C_{18}, diffuse into PP, obeying Fick's law. Diffusion coefficients (D), ranging from 5.09×10^{-11}–6.23×10^{-12} cm^2 sec^{-1} at 50°C, decreased with increasing molecular weight. Mass uptake in equilibrium also depends on molecular weight (M_W) and decreased with increasing M_W. The diffusion coefficient (D) was considered to depend on the interaction of the esters with PP. In simultaneous diffusion, each ester diffuses obeying Fick's law. However, D is larger than that in single diffusion, and the discrepancy of D between both cases decreased with decreasing molecular weight. The increase in the entropy of activation for diffusion in the mixture was assumed, and D decreased with increasing crystallinity.

Further investigation on the basis of thermodynamics is necessary.

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