Diffusion of High Molecular Weight, Sterically Hindered Amines in Polypropylene

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ABSTRACT: The diffusion of sterically hindered amines with molecular weight 1364, 1393, 2286, and 2758 was studied in polypropylene between 60 and 130°C. The diffusion coefficient changes with time and plots log D vs $1/T$ are given as broken lines for additives with molecular weight 2286 and 2758. IR data show that changes in the polymer structure during diffusion occurs. Slow diffusion of the additives in PP at elevated temperatures and high activation energies indicate that no migration at room temperature should take place. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 890–896, 2000

Key words: diffusion; sterically hindered amines; stabilizers; polypropylene

INTRODUCTION

Additives used to prevent thermo- and photooxidation of polymers must be effective as stabilizers and at the same time remain in the polymer during the whole service life of the polymer. A rapid diffusion of stabilizers facilitates their reaction with macroradicals formed during polymer oxidation, but on the other hand, this may result in their loss from the polymer.[1,2] The increase in molecular weight of stabilizers reduces their loss, but it leads to a decrease in their compatibility with the polymer.[2–7] It has been shown that the efficiency of acrylic derivatives of hindered amines depends on their molecular weight. The maximum efficiency corresponds to additives with molecular weights of about 2700.[8] Oligomeric stabilizers with molecular weights higher than 13,000 do not prevent oxidation efficiently due to their poor distribution inside the polymer.[8–10]

The process of dissolution and diffusion of additives in a polymer comprises their passing through zones containing a free volume.[11–14] As has been shown in our previous studies,[15,16] the dissolution of high molecular weight hindered amines in polypropylene (PP) differs from that of additives with low molecular weight: the solubility of the additives at 100°C changes with time and increases with increasing additive molecular weight due to rearrangement of the polymer structure.

In this work, the diffusion of four sterically hindered amines with molecular weights 1364, 1393, 2286, and 2758 in PP was studied.

EXPERIMENTAL

Materials

Polypropylene films 50–70 μm were prepared by heating PP powder (Moplen FLF20 Montell) to 200°C. Stabilizers:

N',N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-2,9,15,22-tetrakis(2,2,6,6-tetramethyl-4-piperidinyl),2,9,11,13,15,22,24,26,27,28-decaazatricyclo[21.3.1.1.10.14]-octacosa-1(27),10,12, 14(28),23,25-hexaene-12,25-dibutylamine (HAS-1), MW 1364. N,N'-bis[2,4-bis[N-(2,2,6,6-tetramethyl-4-piperidinyl)butylamino]-1,3,5-triazine-6-yl]-N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl]-1,6-hexanediamine (HAS-2), MW1393.

1,3,5-Triazine-2,4,6-triamine,N,N'''-1,2-ethanediylbis[N-[3-[[4,6-bis(butyl(1,2,2,6,6-pentamethyl-4-piperininyl)amino]-1,3,5-triazine-2-2-yl]methylamino]propyl]-N',N''-dibutyl-N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) (HAS-3), MW 2286.
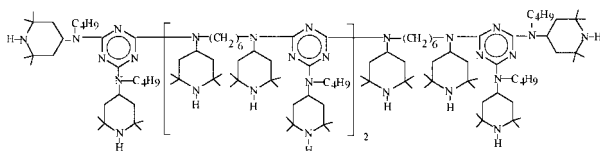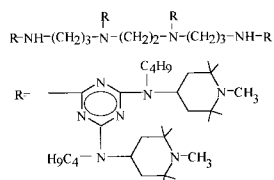
N^{III},N^{IV}-bis(2,2,6,6-tetramethyl-4-piperidinyl)-N^{III},N^{IV}-bis[N,N'-dibutyl-N^{II}[6-[[4-[butyl-(2,2,6,6-tetramethyl-4-piperidinyl]-amino]-6-yl-1,3,5-triazine-2-yl]-(2,2,6,6-tetramethyl-4-piperidinyl)-amino]-hexyl]-$N,N^{I}.N^{II}$-tris(2,2,6,6-tetramethyl-4-piperidinyl)-1,3,5-triazine-2,4,6-triamine]-1,6-hexanediamine (HAS-4), MW 2758.
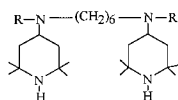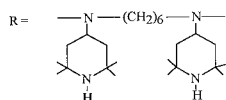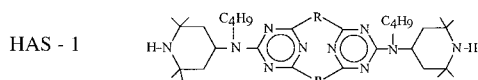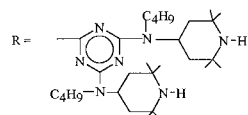
Diffusion Experiments

The stacks (10 mm width and 30 mm long) containing 8 films (each 50–70 μm thick) were prepared by pressing the films ($P = 50$ atm) at 100°C for 3 min. Two different types of "additive source" were used: (1) the additive dissolved in heptane was placed on the surface of the stack and the solvent was evaporated; (2) PP film (100 μm thick) containing 5–10% wt of the stabilizer were prepared by heating PP powder with the additive at 200°C followed by rapid cooling, and pressed with the stack at 100°C for 2 min. The stacks were then put into glass tubes, sealed under vacuum, and kept at a fixed temperature for different periods of time. At the end of the experimental period the stack was washed with cold ethanol, the films were separated from each other, and the additive content was analyzed by UV spectroscopy directly of the film or of the solution after dissolution of the film in hot decane followed by extraction with methanol. The diffusion coefficient (D) was calculated by using the solution of Fick's law for semidefinite media[3] and curve fitting,

$$Q_x/Q_1 = 1 - \frac{\sqrt{\pi}}{\sqrt{\pi}\,\exp(x/k)^2 - x/k + (x/k)\mathrm{Erf}(x/k)} \tag{1}$$

where Q_1 is the total amount of the additive which passed in the stack during the period of time t; Q_x is the amount of the additive that passed to distance x from the surface; $k = 2\sqrt{Dt}$.

IR Studies

A Nicolet 20SX FT-IR spectrometer was used to monitor changes in the polymer structure after diffusion. The ratio of the peaks area at 1218 and 1255 cm^{-1} (S_{1218}/S_{1255}) was taken as a characteristic of polymer crystallinity[17]; the peak area at 1155 cm^{-1} corresponding to C—CH$_3$ stretching and CH$_2$ rocking modes in the amorphous zone[17, 18] referred to the sample thickness.

RESULTS AND DISCUSSION

Diffusion of HAS-4, having the highest molecular weight, was studied in the temperature range 60–130°C. The method used does not measure the concentration dependence of the diffusion coefficient but does permit calculation of an effective

Table I Diffusion of HAS in PP[a]

T (°C)	HAS-4		HAS-3		HAS-2		HAS-1	
	Time (h)	$D \times 10^{10}$ (cm² s⁻¹)	Time (h)	$D \times 10^{10}$ (cm² s⁻¹)	Time (h)	$D \times 10^{10}$ (cm² s⁻¹)	Time (h)	$D \times 10^{10}$ (cm² s⁻¹)
130	27	60						
130	27	59						
130	31	47						
115	65	4.5						
115	65	6.6						
115	139	11						
115	139	9.1						
115	139	11						
115	165	8.2						
115	165	5.5						
105	285	3.6						
105	285	3.6						
105	452	3.5						
100	720	1.6	1080	1.0	20.1	20	89.5	12
100	720	1.7	1080	1.28	83.5	9.2		
100	840	1.9	2200	1.1[b]	94.5	11		
100	840	1.9	2200	1.3[b]				
100	1180	0.94	2200	0.98				
100	1680	1.5	2200	1.2				
90	1440	(0.32)	2200	0.086[b]	500	4.9	500	4.5
90	2230	0.38	2200	0.084[b]	500	4.4	500	3.2
90	3650	0.38	3650	0.06	720	2.2[b]	720	3.3
90	3650	0.28[b]	3650	0.168[b]	720	2.4[b]	720	5.1
90	5100	0.22					720	1.5[b]
90							720	1.2[b]
90							720	1.1[b]
80	2930	0.037	3650	0.09	1800	0.62	1800	0.68
80	4370	0.034	3650	0.035[b]	1800	0.57	1800	0.57
80			3650	0.039	2520	0.15	2520	0.28[b]
80					2520	0.13	2520	0.19[b]
80					2520	0.40[b]		
80					2520	0.41[b]		
70	4370	(0.0026)	5850	0.06	3670	0.12	3670	0.036
70	13140	(0.0009)	5850	0.03[b]				
60			5850	(0.036)	5850	0.013	5850	0.0068
60			5850	(0.03)	8760		8760	

[a] In parentheses are given the approximate values.
[b] Additive source—PP film containing 5–10% wt of the additive.

diffusion coefficient at different periods of time. As can be deduced from Table I, the diffusion coefficient of HAS-4 decreases (at 130, 90, and 70°C) or passes through a maximum (at 115 and 100°C) with time, similar to the changes in its solubility with time.[15,16] This shows that high solubility facilitates faster diffusion. The temperature dependence of the diffusion coefficient in coordinates log$D$ vs $1/T$ is shown as a broken line for both straight and curved sections: a slow change of D in the range 100–115°C and a considerably higher change of D in the ranges 70–90°C and 115–130°C occur (Fig. 1, line 1). The activation energy of the diffusion is about 65 kcal mol⁻¹ in the temperature interval 70–90°C. At 60°C it was difficult to calculate D of HAS-4 due to low depth of additive penetration in the stack (less than 50 μm after 1.5 year).

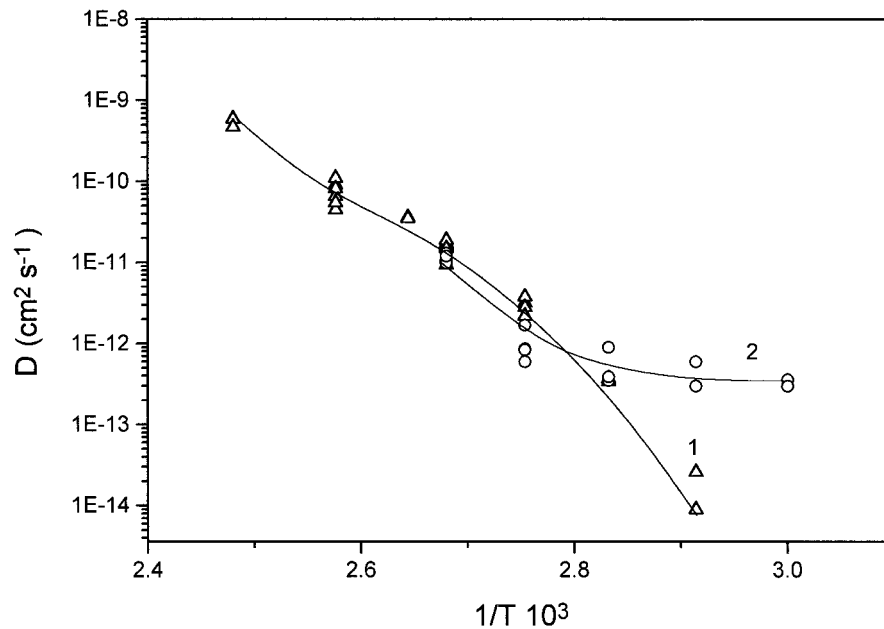The value of D for HAS-3 (MW 2286) shows only slight changes with time at all the tempera-

Figure 1 Temperature dependence of the diffusion coefficients of HAS-3 and HAS-4 in PP.

tures studied except at 80°C and 90°C (Table I). Probably, this is because the diffusion experiments of HAS-3 were performed at time intervals in which its solubility did not change considerably. At 90 and 100°C the migration of HAS-3 proceeds slower than that of HAS-4 at these temperatures, but at 70 and 80°C the inverse is observed (Table I). The temperature dependence of D of HAS-3 is shown in Figure 1, line 2: a lower slope of the plot is observed in the case of HAS-3 compared with that of HAS-4 at the interval 60–90°C. This could be due to the fact that a much
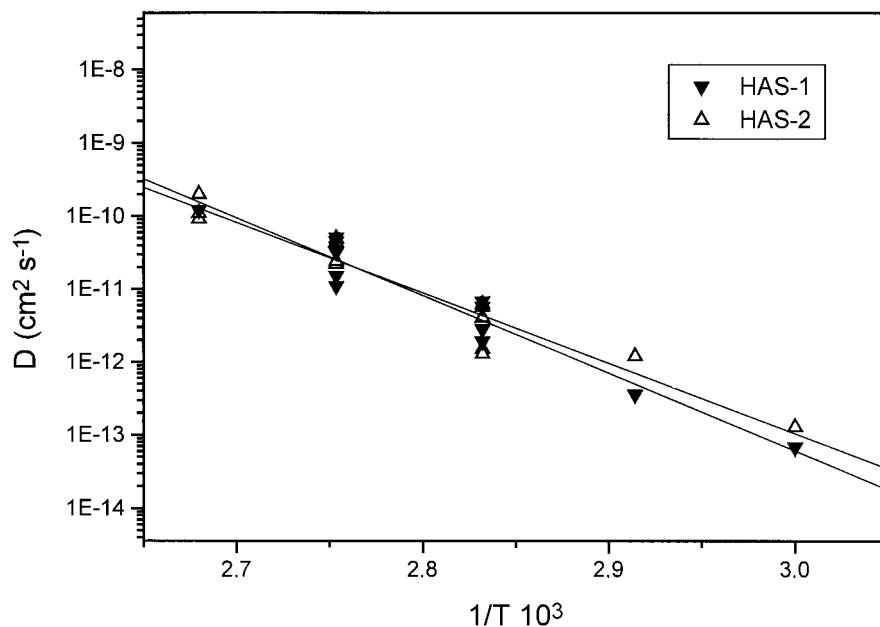

Figure 2 Temperature dependence of the diffusion coefficients of HAS-1 and HAS-2 in PP.
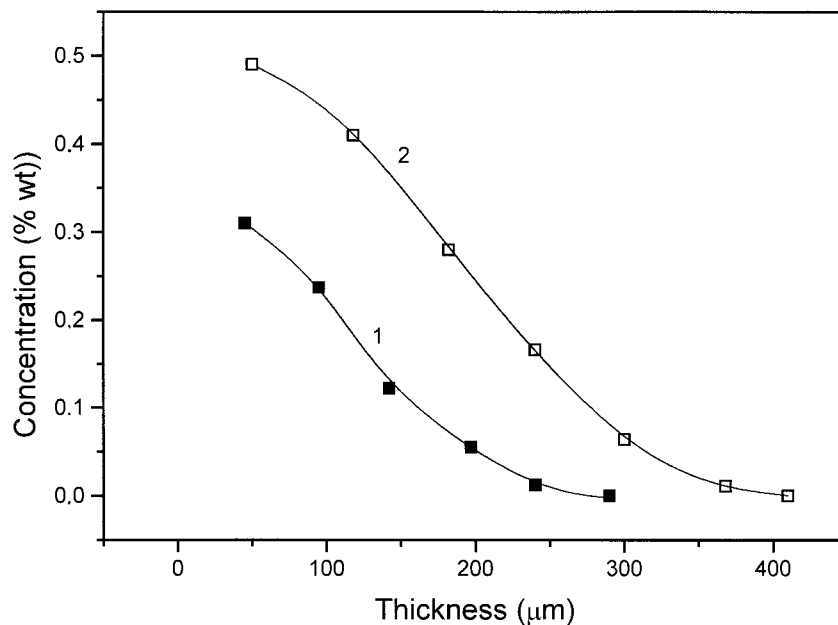
Figure 3 Concentration distribution of HAS-2 in PP after diffusion for 1 month at 90°C: additive free source (1) and additive contained film source (2).

rearrangement of the polymer structure in the presence of HAS-3 takes place.

The diffusion coefficients of HAS-1 and HAS-2 at higher temperatures (70–100°C) are considerably higher than HAS-3 and HAS-4 and decrease with time of migration. The temperature dependencies of D of these compounds are shown in Figure 2. The activation energy of the diffusion calculated from the slopes are 49 and 44 kcal mol^{-1} for SHA-1 and SHA-2, correspondingly.
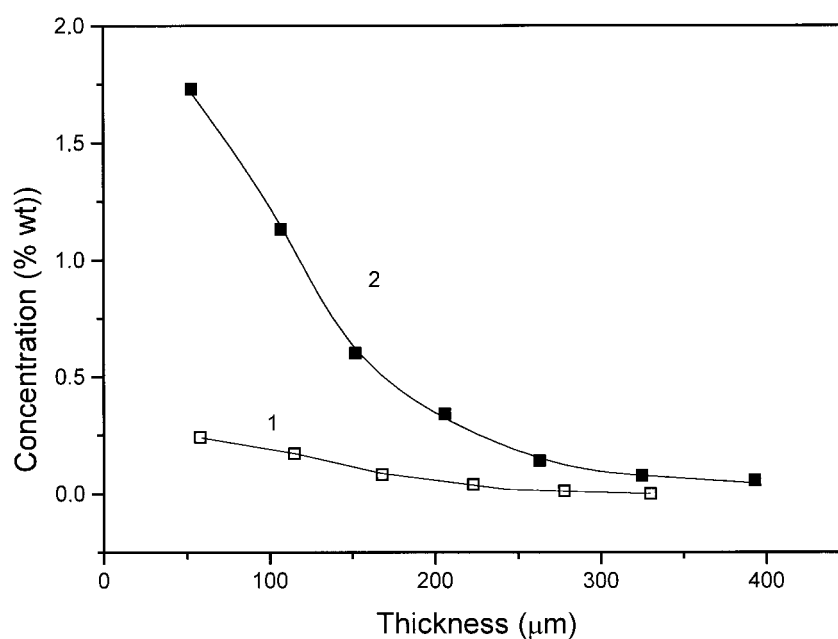

Figure 4 Concentration distribution of HAS-3 in PP after diffusion for 3 months at 100°C: additive free source (1) and additive contained film source (2).

Table II Changes in PP Structure After Diffusion of HAS-4 at 90°C for 5 Months

Concentration in the Layer (% wt)	S_{1217}/S_{1254}	$S_{1153/l}$	Crystallinity (%)
0	0.37	8.1	68.5
0.03	0.3	9.3	63.4
0.22	0.28	10.6	62.1
0.72	0.31	8.4	64
1.77	0.32	7.7	64.7

In the case of diffusion of HAS-2 and HAS-3 at 90 and 100°C, we observed that the concentration profile measured does not obey Fick's law of diffusion (Figs. 3 and 4).

There is no perceptible effect of the type of additive source on the value of D (Table I). The type of additive source affects the surface concentration: usually a higher surface additive concentration is observed in the case of film source compared to free additive (Fig. 4), while in the case of HAS-2 (Fig. 3), a higher surface additive concentration is observed when free additive is used. One of the reasons for these differences is connected with the additive solubility and its distribution inside the source. Besides, a supersaturated solution of the additive inside the source is present and no true equilibrium exists.

To check the changes in the polymer structure during additive migration we performed IR measurements on different layers of the stack after diffusion (Tables II–IV). The content of irregular conformers in the amorphous zone of PP (absorption at 1155 cm^{-1}) passes through a maximum with increasing concentration of HAS-3 and HAS-4 (Tables II and III) and only slightly de-

Table III Changes in PP Structure After Diffusion of HAS-3 in PP at 100°C for 1.5 Months

Concentration in the Layer (% wt)	S_{1217}/S_{1254}	$S_{1153/l}$	Crystallinity (%)
0	0.32	8.5	64.7
0.014	0.43	8.6	72
0.04	0.40	10	70
0.174	0.52	10	78.5
0.63	0.39	9.7	69.4
1.45	0.53	8.7	79

Table IV Changes in PP Structure After Diffusion of HAS-2 in PP at 90°C for 1 Month

Concentration in the Layer (% wt)	S_{1217}/S_{1254}	$S_{1153/l}$	Crystallinity (%)
0	0.38	8.3	68.9
0.012	0.39	8.8	69.4
0.064	0.38	9.1	68.9
0.43	0.41	8.7	70.8
0.5	0.34	9.3	66

pends on the concentration of HAS-2. That is probably because a small HAS-2 concentration is present in the layers (Table IV). At higher concentrations (more than 0.7%), HAS-4 having the highest molecular weight, decreases the absorption at 1155 cm^{-1} to a higher extent than HAS-3. The ratio S_{1218}/S_{1255} and the crystallinity that is directly proportional to this ratio, only slightly decreases in the presence of HAS-2 but changes considerably in the presence of HAS-3 and HAS-4. Although it is difficult to draw certain conclusions regarding the reason for crystallinity changes in different layers, we could suppose that two processes may occur at the same time: (1) disorganization of the polymer structure during additive penetration and (2) annealing of the polymer, which could be facilitated by high additive concentration in the polymer.

CONCLUSION

The results obtained show that migration of the studied HAS in PP due to the large size of the molecules occurs slowly and is accompanied by rearrangement of the polymer structure. Taking into account the experimental values of activation energy of the diffusion of the additives in PP, we may expect no diffusion or very slow diffusion at room temperature. In fact, the calculations show that the diffusion coefficients of HAS-1, HAS-2, and HAS-4 in PP at 25°C are 1×10^{-17}, 4×10^{-17}, and 1×10^{-20} cm^2 s^{-1}, respectively.

REFERENCES

1. Mar'in, A. P.; Shlyapnikov, Yu. A.; Mametov, E. S.; Dzhalilov, A. T. Polym Degrad Stab 1992, 35, 141.

2. Billingham, N. C. In Oxidation Inhibition of Organic Materials; Pospisil, J., Klemchuk, P. P., Eds.; CRC Press: Boca Raton, FL, 1990; v 2, p 249.

3. Moisan, J. Y. Eur Polym J 1980, 16, 979.

4. Billingham, N. C.; Calvert, P. D.; Mank, A. S. J Appl Polym Sci 1981, 26, 3543.

5. Gedraitite, G. B.; Mar'in, A. P.; Shlyapnikov, Yu. A. Eur Polym J 1989, 25, 39.

6. Malik, J.; Hrivik, A.; Tomovà, E. Polym Degrad Stab 1992, 35, 61.

7. Dudler, V.; Muinos, C. Adv Chem Ser (Polym Durab) 1996, 249, 441.

8. Gugumus, F. Research Disclosure 1981, 209, 357.

9. Chmela, S.; Hrdlovich, P. 11th Discussion Conference on Chemical and Physical Phenomena in the Ageing of Polymers, Prague, 1988, p. 9.

10. Malik, J.; Ligner, G.; Avàr, L. Angew Makromol Chem 1997, 247, 147.

11. Barrer, R. M.; Barrie, J. A.; Slater, J. J Polym Sci 1958, 27, 177.

12. Vieth, W. R.; Tam, R. M.; Michaels, A. S. J Coll Interface Sci 1966, 22, 360.

13. Paul, D. R.; Koros, W. J. J Polym Sci Polym Phys Ed 1976, 14, 675.

14. Shlyapnikov, Yu. A., Mar'in, A. P. Eur Polym J 1987, 23, 623.

15. Mar'in, A. P.; Borzatta, V.; Bonora, M.; Greci, L. J Macromol Chem Pure Appl Chem 1988, A35, 1299.

16. Mar'in, A. P.; Borzatta, V.; Bonora, M.; Greci, L. J Appl Polym Sci 2000, 75, 883.

17. Kissin, Y. V. J Polym Sci Polym Phys Ed 1983, 21, 2085.

18. Zerbi, G.; Piseri, L. J Chem Phys 1968, 49, 3840.