Solubility of High Molecular Weight, Sterically Hindered Amines in Polypropylene

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ABSTRACT: The dissolution of four sterically hindered amines with molecular weights from 1364 to 2758 was studied in polypropylene in the interval, 60–130°C. The solubility of the additives at 100°C passes through a maximum during time and the maximum solubility increases with increasing additive molecular weight. The rearrangement of the polymer structure during additives dissolution is discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 883–889, 2000

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

INTRODUCTION

Hindered amine stabilizers (HAS) are widely used for UV and thermal stabilization of polyolefins. The efficiency of stabilization depends not only on the chemical structure of the stabilizers but also on physical factors, including their compatibility, and loss due to migration from the polymer and washing-out by liquids.[1–7] The increase in molecular weight of the stabilizer reduces its loss but on the other hand it gives rise to a decrease in its solubility inside the polymer. In spite of the many publications concerning the behavior of HAS in polymers, only few data exist on their solubility in polymers.[4–6]

It is known that[8–13] additives during dissolution in the polymer occupy zones with lower density packing that contain a free volume sufficient for additive molecules. Such zones have either a relaxed[10–13] or topological structure [8, 9] The latter are formed around knots and other polymer chain entanglements, and are stable due to the length of the macromolecules. If this free volume is less than that necessary for sorption of additive, dissolution can occur only in the case of rearrangement of this center resulting in changes of the polymer structure. This could be important when large-sized additive molecules are considered. So, one can expect that the behavior of high molecular weight additives in a polymer will differ from that of additives with an average molecular weight.

In this work, the solubility of four sterically hindered amines with molecular weights from 1364 to 2758 in polypropylene (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, was prepared according to the method described in the literature.[14] 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), MW 1393, was prepared according to the method described in the literature.[15]

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-triazin-2-2yl]methylamino]propyl]-N',N''-dibutyl-N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl) (HAS-3), MW 2286, was prepared according to the method described in the literature.[16]

N^{III},N^{IV}-bis(2,2,6,6-tetramethyl-4-piperinyl)-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-hexadiamine (HAS-4), MW 2758, was prepared according to the method described in the literature.[17]

HAS -1

HAS -2

HAS -3

HAS -4
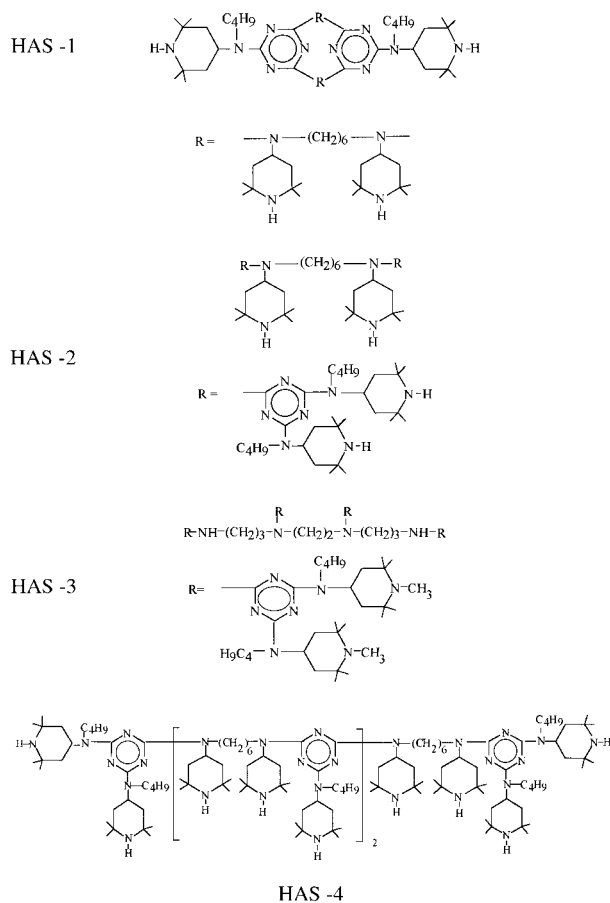
Solubility Experiments

The additive dissolved in heptane was placed on both sides of the polymer film and after solvent evaporation, was put in a glass tube, sealed under vacuum, and kept at a fixed temperature for different periods of time. At the end of the experiment the samples were washed with cold ethanol to remove the additive from the surface and the additive content in the film was analyzed by UV spectroscopy of the film itself or of the solution after dissolution of the film in hot decane followed by extraction with methanol (Uvicom 941 Plus UV-VIS; the extinction coefficients of HAS-1, HAS-2, HAS-3, and HAS-4 at 230 nm are 1.28×10^5, 1.23×10^5, 1.88×10^5, and 2.26×10^5 l mol^{-1} cm^{-1}, respectively.

IR Studies

A Nicolet 20SX FT-IR spectrometer was used to check the changes in polymer structure on additive dissolution. The ratio of the peak areas at 1218 and 1255 cm^{-1} (S_{1218}/S_{1255}) was taken as a characteristic of polymer crystallinity[18]; the peak intensity at 1155 cm^{-1} corresponding to C—CH$_3$ stretching and CH$_2$ rocking modes in amorphous zone[18, 19] referred to the sample thickness.

RESULTS AND DISCUSSION

To determine the solubility of an additive in a polymer, it is necessary to keep the polymer sample with the additive for a sufficient length of time in order to reach the equilibrium concentration of the additive in the polymer. Usually, it corresponds to some *plateau* on the curve "concentration of additive in the polymer *vs* time."

Figure 1 shows the kinetics of dissolution of HAS-4 in PP in the temperature range 60–130°C: at low temperatures (60–90°C) the concentration of HAS-4 in PP reaches a constant value after 500–1000 h and then it does not change; while at higher temperatures (100°C) the concentration of HAS-4 passes through a maximum with time. The same phenomenon is observed in the case of dissolution of HAS-3 (Fig. 2). It is interesting to point out that the final solubility of HAS-3 at 80–100°C practically does not change with temperature, equal to about 0.5% wt. In the case of HAS-1 and HAS-2 having lower molecular weights, their solubility in the polymer passes through a maximum at temperatures above 60°C, and the time, corresponding to the maximum of
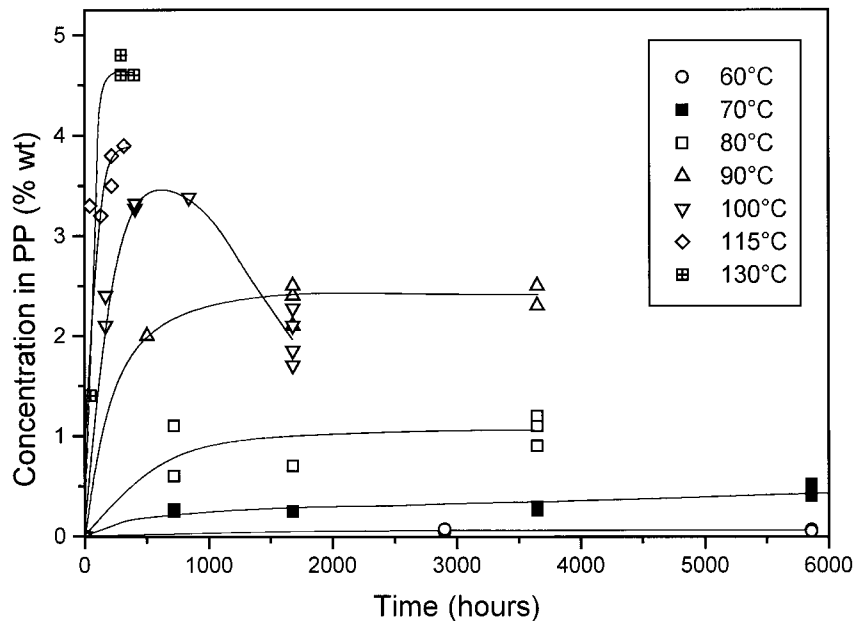
Figure 1 Kinetics of dissolution of HAS-4 in PP at various temperatures.

solubility shifts in less time on increasing the temperature (Figs. 3 and 4). Comparing the kinetic curves corresponding to the different additives at the same temperature (100°C), one could point out that the value of the maximum solubility in the polymer depends on the molecular weight of the stabilizer: the higher the molecular weight of the stabilizer the higher its solubility in

PP (Table I). We may suppose that changes in the polymer structure take place during additive dissolution at high temperatures. Table II shows the changes in the ratio S_{1218}/S_{1255}, which is proportional to the PP crystallinity, with time at 100°C in vacuum. Although some difference in the initial ratio of S_{1218}/S_{1255} between various samples is observed, the following comments can be made:
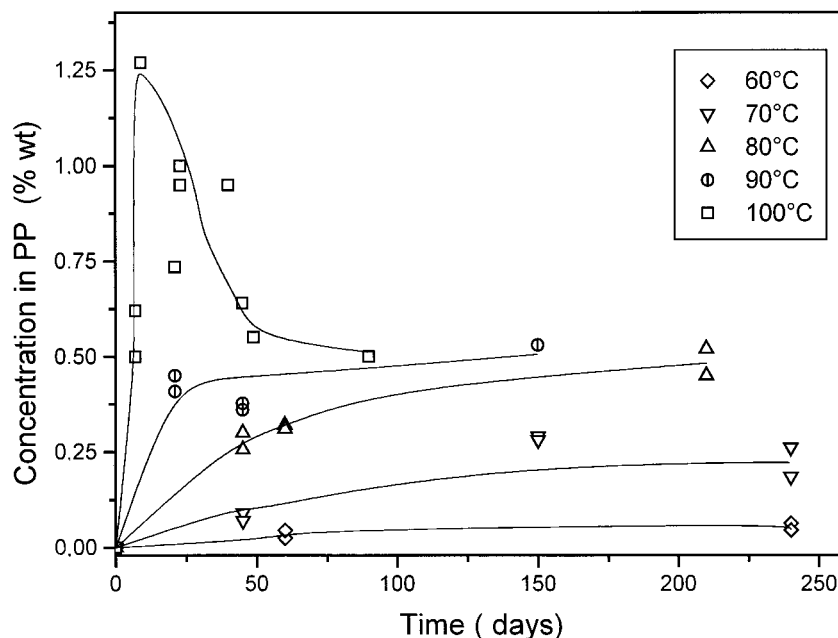

Figure 2 Kinetics of dissolution of HAS-3 in PP at various temperatures.
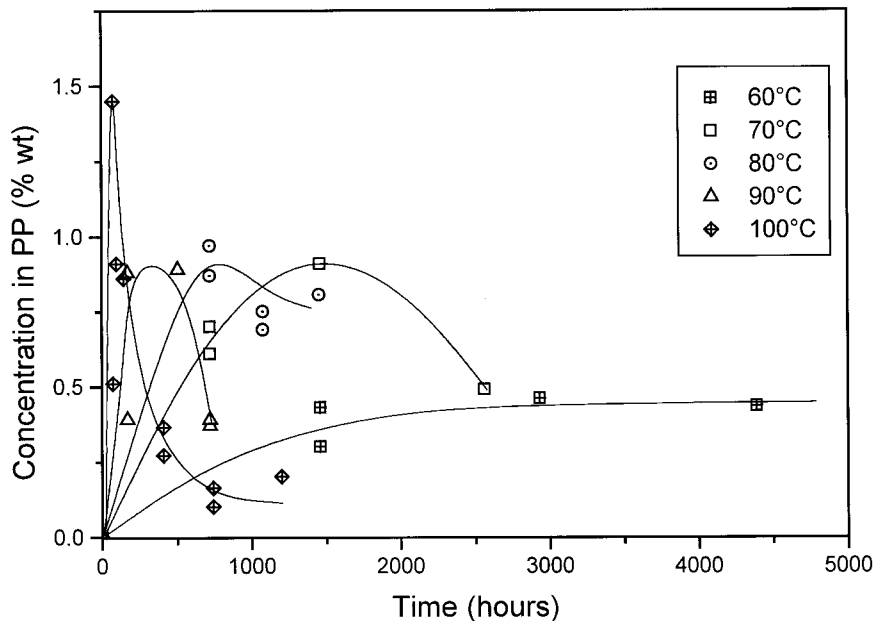
Figure 3 Kinetics of dissolution of HAS-2 in PP at various temperatures.

(1) The crystallinity of PP without additives (ratio S_{1218}/S_{1255}) increases with time, this is probably due to the fact that annealing of PP occurs at high temperature. (2) The crystallinity of PP in the presence of HAS-2 during its dissolution decreases, while that in the presence of HAS-3 and HAS-4 decreases at the beginning and then slightly increases with time, showing that proba-bly two processes are taking part simultaneously: disorganization of the polymer structure during additives dissolution and polymer annealing. It is interesting to point out that the final crystallinity of PP (after 860 h) containing the additives is less than that without additives. The absorption of the band at 1155 cm^{-1} corresponding to irregular conformation decreases with time for samples
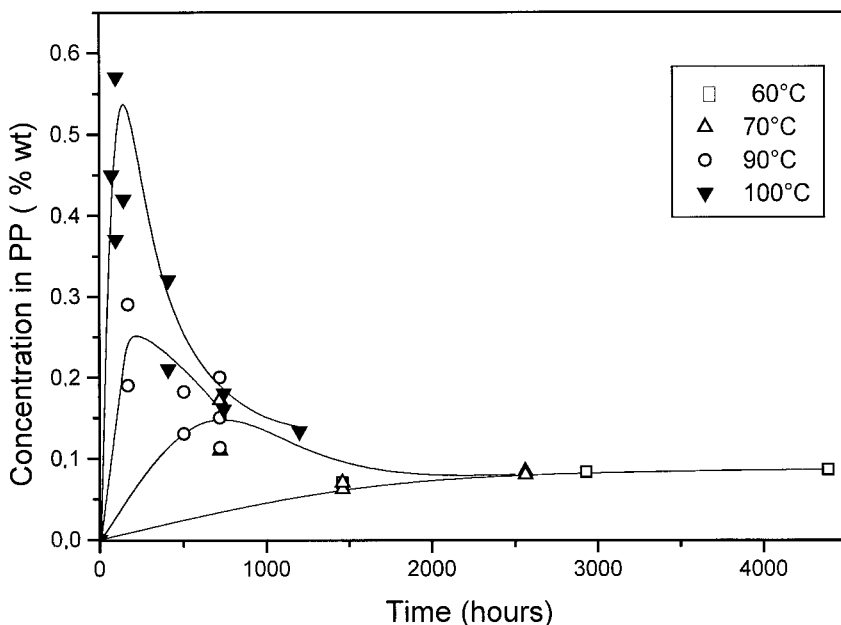

Figure 4 Kinetics of dissolution of HAS-1 in PP at various temperatures.

Table I   Solubility Parameters of Additives in PP

| Additive	MW	Solubility (% wt)		ΔH (kcal mol^{-1}) (60–70°C)
		100°C[a]	60°C	
HAS-1	1364	0.57	0.08	12
		0.42	0.086	
HAS-2	1393	1.45	0.43	9
		0.91	0.46	
HAS-3	2286	1.27	0.063	35
			0.045	
HAS-4	2758	3.32	0.05	43
		3.27	0.068	

[a] Corresponds to maximum solubility.

without additives; it does not change in the presence of HAS-2 and it slightly decreases in the presence of HAS-3 and HAS-4 (Table III).

The dissolution of additive A in the polymer can formally be considered as a reversible interaction with sorption centers Z_i around chain entanglements and the formation of immobile complex AZ_i[8]:

$$A + Z_i \rightleftharpoons AZ_i \qquad (1)$$

If dissolution of A is accompanied by rearrangement of this center, it may be considered as

$$A + Z_i \rightarrow AZ_i^* \rightleftharpoons A + Z_i^* \qquad (2)$$
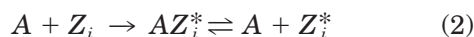
where Z_i^* is the new center formed after Z_i rearrangement.

To form an excess volume in the polymeric matrix, a certain energy is required. One may

Table II   Changes in Ratio S_{1218}/S_{1255} of PP Films in the Absence and in the Presence of HAS During Their Dissolution in the Polymer; 100°C, Vacuum Sealed Tubes

Time (h)	S_{1218}/S_{1255}			
	Without Additives	HAS-2	HAS-3	HAS-4
0	0.34	0.50	0.5	0.35
170	0.47	0.48	0.33	0.32
360	0.49	0.40	0.34	0.37
860	0.44	0.35	0.37	0.38

Table III   Changes of Absorption at 1156 cm^{-1} of PP Films in the Absence and in the Presence of HAS During Their Dissolution in the Polymer; 100°C, Vacuum Sealed Tubes

Time (h)	S_{1156}			
	Without Additives	HAS-2	HAS-3	HAS-4
0	8.0	5.4	5.4	5.8
170	5.2	5.8	4.5	5.3
360	6.0	5.6	4.2	5.2
860	5.0	5.8	5.2	5.0

assume that this energy is directly proportional to the volume formed, i.e.,

$$\Delta E_i = q\Delta V_i, \qquad (3)$$

where ΔV_i is the difference between the final and initial volume of the sorption center. The dimension of the coefficient q in eq. (3) is energy/volume or pressure. In the presence of additive, the value of q will decrease by the value of the energy of interaction between additive molecule and surrounding medium, i.e., q in eq. (3) must be substituted with $q - q_a$.

$$\Delta E_i = (q - q_a)\Delta V_i \qquad (3a)$$

According to eq. (3a), to change the volume of sorption center by ΔV_i, molecule A has to possess an energy (ΔE_a) equal or higher than ΔE_i ($\Delta E_a \geq \Delta E_i$). It is clear that the greater the size of the molecule, the higher should be the value of ΔV_i and the greater the energy required for this process.

The osmotic pressure created by an additive A is connected with its concentration in the polymer by the expression:

$$P_a = RT[A] = RT\phi[A]_p \qquad (4)$$

where $[A]$ and $[A]_p$ are the additive concentrations outside the sorption centers and the total concentration in the polymer; $\phi = [A]/[A]_p$ is a coefficient that can be calculated. Taking into account that

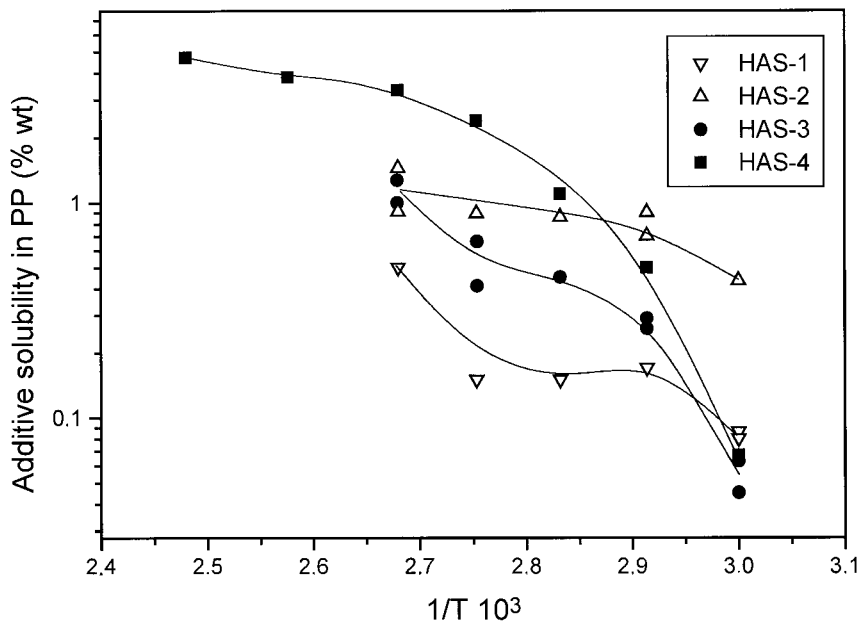$$E_a = P_a\Delta V_i = RT\phi[A]_p\Delta V_i, \qquad (5)$$

we get

Figure 5 Temperature dependence of solubility of the stabilizers in PP.

$$RT\phi[A]_p \geq (q - q_a) \qquad (6)$$

According to eq. (6), a certain minimal concentration of additive ($[A]_p$) is necessary to change the sorption center. As the segmental mobility of polymer chains increases with temperature, less energy is required for the rearrangement of centers at high temperature and parameter $q - q_a$ will decrease with temperature.

To explain the difference in kinetics of the dissolution of HAS-1 and HAS-2 from HAS-3 and HAS-4 at 70°C, we may assume that only additives with smaller molecules (MW 1368 and 1393) are able to affect considerably the polymer structure because the free volume needed for their dissolution is less than that for HAS-3 and HAS-4 (MW 2286 and 2758). At high temperature (100°C), the macromolecular mobility is sufficient for large molecules of HAS-3 and HAS-4 to affect the polymer structure. Naturally, one can assume that larger sized molecules are able to change the polymer structure more than smaller sized ones, so the apparent solubility may increase with the molecular weight of the additive as observed experimentally. Thus, the process of dissolution of high molecular additives gives rise to a certain "destruction" of the initial polymer structure. The decrease in additives solubility with time (Figs. 1–4) is probably due to annealing of the polymer in the presence of additives.

Table I shows the maximum solubility of the additives at 60 and 100°C. The temperature dependencies of the maximum solubility of additives in PP in coordinates $\log S$ vs $1/T$ show nonstraight lines (Fig. 5). The heat of solution in the temperature interval from 60 to 70°C (which may be only approximately calculated) strongly increases with increasing molecular weight of the additive (Table I), indicating that solubility of high molecular weight additives should be very low at room temperature, i.e., solubility of HAS-3 and HAS-4 at 25°C is about 1×10^{-4} and 3×10^{-5} %, respectively.

CONCLUSION

From the results obtained one may conclude that the dissolution of high molecular weight additives in PP at high temperature is accompanied by change in the polymer structure; as a result (1) the solubility of the additives passes through a maximum with time and increases with increasing additive molecular weight; and (2) the solubility depends only slightly on the temperature in the interval 80–100°C while it sharply decreases in the interval 60–70°C showing that additives solubility at room temperature is very low.

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