Rearrangement of the Polymer Structure in the Presence of High Molecular Weight Additives

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REARRANGEMENT OF THE POLYMER STRUCTURE IN THE PRESENCE OF HIGH MOLECULAR WEIGHT ADDITIVES

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ABSTRACT

The solubility, diffusion, and washing-out of four new sterically hindered amines was studied in polypropylene. It was shown that dissolution induces a strong change in polymer structure: the additives solubility at 100°C passes through a maximum during time and increases with additive molecular weight. The diffusion coefficients of the additives also depend on time. The stabilizers leak from the polymer in heptane and the residual concentration remaining in the polymer depends on the additive molecular weight.

INTRODUCTION

The efficiency of stabilizers in polymers depends not only on their chemical structure but also on physical factors, including their solubility, diffusion, and

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washing-out by liquids [1–5]. The increase in molecular weight of the additive reduces its loss due to diffusion in the polymer; on the other hand it gives rise to a decrease in its solubility inside the polymer.

According to previous works [6–11], additives during dissolution in the polymer occupy zones with a lower packing density which contain a free volume sufficient for additive molecules. Such zones have either a relaxed [8–11] or topological structure [6, 7]. The latter are formed around knots and other polymer chain entanglements and are stable due to the length of the macromolecules. 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 with the formation of an immobile complex AZ_i (Equation 1):

$$A + Z_i \rightleftharpoons AZ_i \tag{1}$$

Sorption centers Z_i should contain an excess volume large enough to locate the additive molecule. If this volume is less than that necessary for sorption of A, dissolution can occur only if rearrangement of this center takes place resulting in changes of the polymer structure as shown in Equation 1a:

$$A + Z_i \longrightarrow AZ_i^* \rightleftharpoons A + Z_i^* \tag{1a}$$
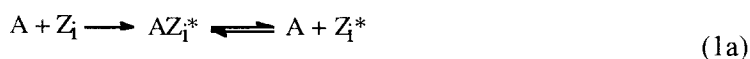
This could be important when large sized additive molecules are considered. So, one can expect that the behavior of high molecular weight additives in a polymer will differ from that of additives with a lower molecular weight.

In this work, the solubility, diffusion and washing-out of four new sterically hindered amines with molecular weights from 1364 to 2758 in PP were 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 (SHA–1), m.w. 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–hexane
diamine (SHA–2), m.w.1393;

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–piperidininyl)amino]–1,3,5–triazin–2–
yl]methylamino]propyl]–N′,N″–dibutyl–N′,N″–bis(1,2,2,6,6–pentamethyl–4–
piperidinyl) (SHA–3), m.w. 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–
hexadiamine (SHA–4), m.w. 2758.

All stabilizers were prepared in the laboratories of Ciba Specialty
Chemicals.

Block

SHA-1

SHA-2

R-NH-(CH$_2$)$_3$-N-(CH$_2$)$_2$-N-(CH$_2$)$_3$-NH-

R=

SHA-3

SHA-4
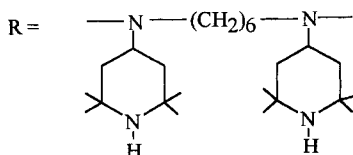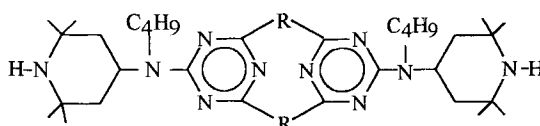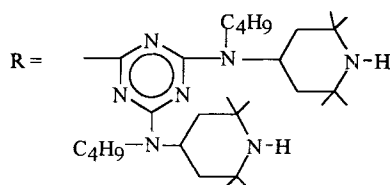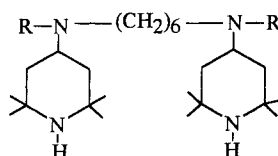
Solubility Experiments

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 directly in the film or in methanol solution after dissolution of the film in hot decane followed by extraction with methanol.
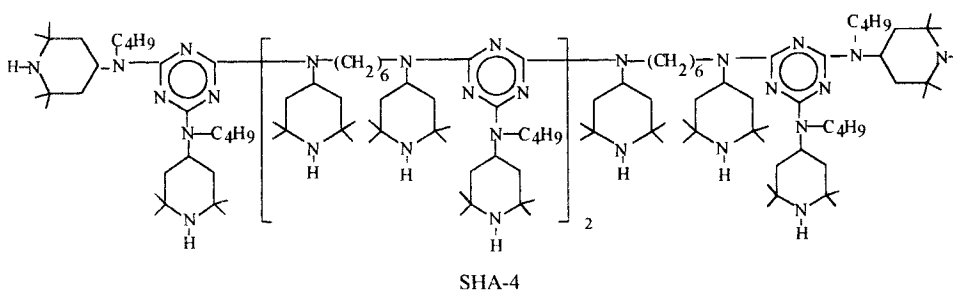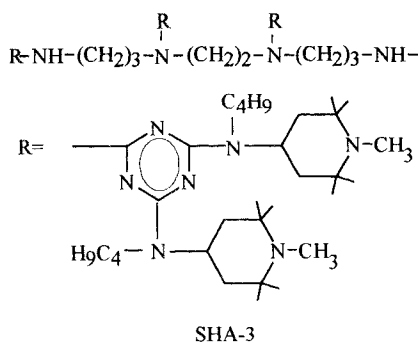
Diffusion Experiments

For diffusion, 8 films were pressed together at 100°C for 3 minutes, then a heptane solution of the additive was immersed on the surface of the stack; after solvent evaporation samples were put into glass tubes, sealed under vacuum and kept at a fixed temperature for different periods of time. The stack then was washed with cold ethanol, the films were separated from each other, and the content of additive was analyzed in the same way as in the solubility experiments. The diffusion coefficient (D) was calculated by using the solution of Fick's law for semi-infinite media (Equation 2) and curve fitting

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

where Q_l 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 which passed to distance x from the surface and $k = 2\sqrt{Dt}$

Washing-out Experiments

Films of 70 μm thickness containing additives were kept in heptane at room temperature (T=22–24°C); the amount of additive released from the polymer was measured by UV spectroscopy carried out directly on film and on heptane solution during the experiment.

IR Sudies

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} (A_{1218}/A_{1255}) was taken as a characteristic of polymer crystallinity [12]; the peak intensity at 1155 cm^{-1} corresponding to C–CH$_3$ stretching and CH$_2$ rock-ing modes in amorphous zone [12, 13] 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 amount of time in order to reach the equilibrium concentration of additive in the polymer. Usually, it corres-ponds to some *plateau* on the curve "the concentration of additive in the polymer *vs* time". Figure 1 shows the kinetics of dissolution of SHA–2 and SHA–4 in PP at 70°C: one can see that the concentration of SHA–4 in PP reaches a constant value after 700 hours and then does not change; the concentration of SHA–2 having a lower molecular weight is considerably higher than SHA–4 and passes through a maximum with time. A more complicated kinetics are observed on dissolution at 100°C (Figure 2): the concentration of all the stabilizers in PP passes through a maximum with time and the value of the maximum concentration in the polymer depends on the molecular weight of the stabilizer: the higher the molecular weight of the stabilizer the higher its maximum concentration in PP.
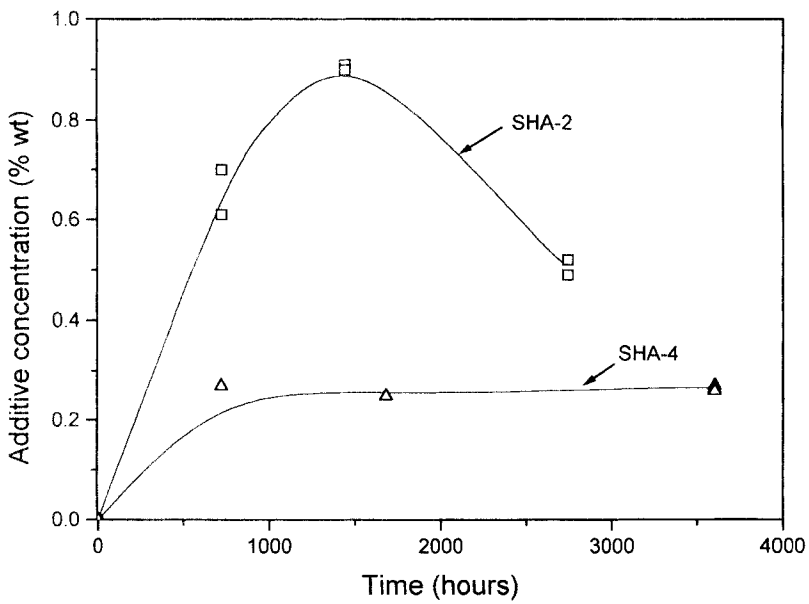
Figure 1. Kinetics of the additives dissolution in PP at 70°C.
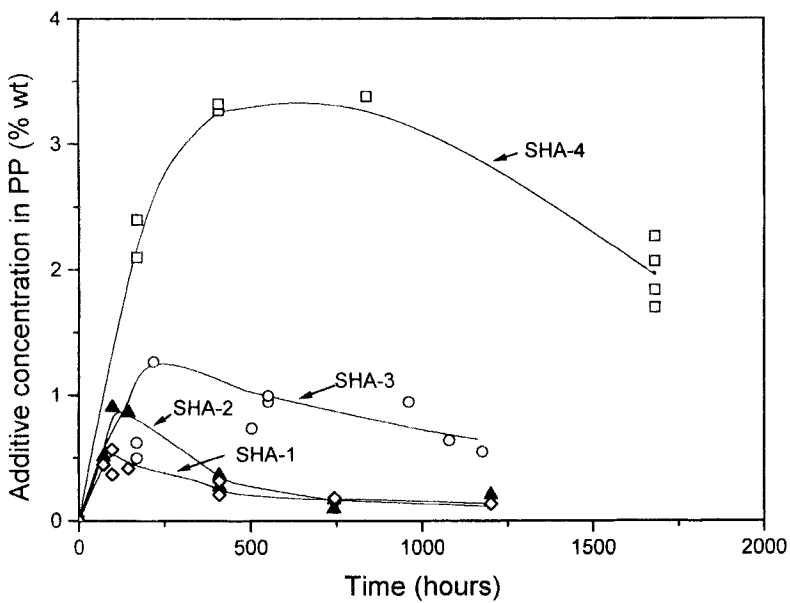
Figure 2. Kinetics of the additives dissolution in PP at 100°C.

As already mentioned previously, an additive molecule during dissolution occupies zones containing elements of free volume which may be rearranged them in case the volume is not large enough for additive sorption. To form an excess volume in the polymeric matrix a certain energy is required. One may assume that this energy is directly proportional to the volume formed:

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

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

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

To change the volume of sorption center by ΔV_i, according to Equation 3a, 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 higher the size of the molecule, the greater should be the value of ΔV_i and the greater energy needed 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 respectively; ϕ is a coefficient expressed by the ratio $[A]/[A]_p$ and can be easily calculated. Taking into account that

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

we get

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

According to Equation 6, a certain minimal concentration of additive $[A]_p$ is necessary to change the sorption center. As the segmental mobility of polymer

TABLE 1. Solubility of Additives in PP

Additive	Solubility (wt%)	
	at 100°C	at 70°C
SHA–1	0.5	0.11
SHA–2	0.95	0.9
SHA–3	1.0- 1.3	–
SHA–4	2.4 - 3.3	0.25

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 features in kinetics of SHA–2 and SHA–4 dissolution at 70°C we may assume that only SHA–2 being a smaller molecule (m.w. 1393), is able to affect considerably the polymer structure because the free volume needed for its dissolution is less than that for SHA–4 (m.w. 2758). At a high temperature (100°C), the macromolecular mobility is enough high to permit that large molecules such as SHA-4 can influence the polymer structure. Of course, molecules of larger size are able, to a greater extent, to change the polymer structure than those of smaller size. 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 (Figures 1 and 2) is probably due to annealing of the polymer in the presence of additives.

Table 1 shows the maximum solubility of the additives at 70°C and 100°C. The difference in solubility at these temperatures indicates that the heats of solution of SHA–1 and SHA–2 are less than that of SHA–4.

As shown in Figure 3, the absorption ratio A_{1218}/A_{1255} which is directly proportional to the crystallinity of PP, as stated above, only slightly decreases in the presence of SHA–2, but it changes considerably in the presence of SHA–3 and SHA–4. Figure 4 shows that even at small concentrations of stabilizers, the content
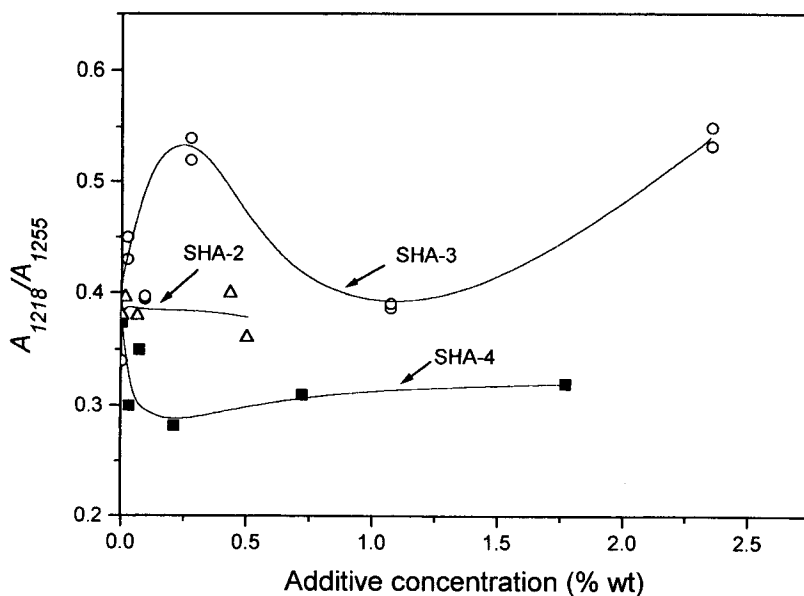
Figure 3. Changes of ratio A_{1218}/A_{1255} of PP as function of the additive concentration in the polymer.
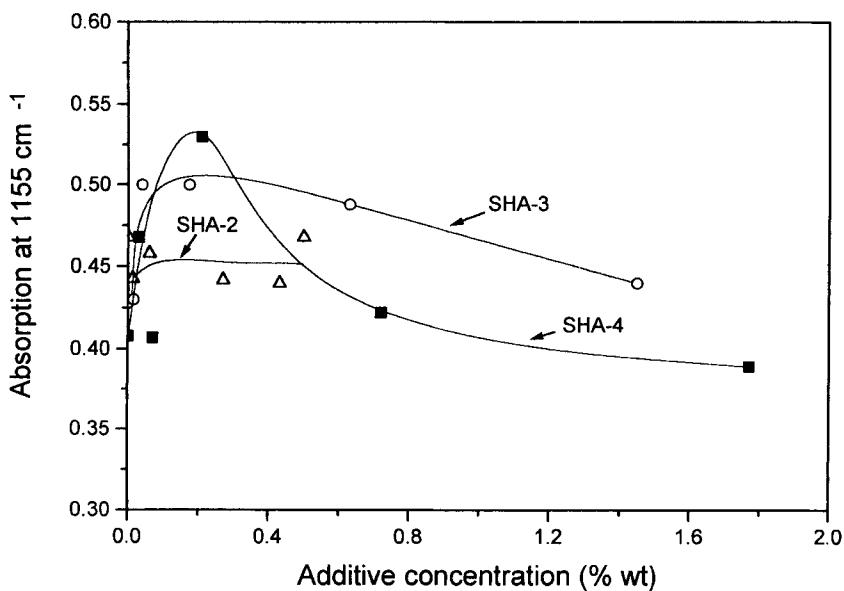
**Figure 4.** Changes of absorption at 1155 cm^{-1} of PP as function of the additive concentration in the polymer.

TABLE 2. Diffusion Coefficients of the Additives in PP at 100°C

Additive	Time, hours	$D \ 10^{11} \ cm^2 \ s^{-1}$
SHA–2	20	20
	20	21
	83	10
	95	11
SHA–3	1080	1.3
	1080	1.0
	2160	1.2
	2160	1.0
SHA–4	720	1.6
	720	1.6
	840	1.9
	840	2.0
	1180	1.0
	1180	1.2

of irregular conformations in the amorphous zone of PP (absorption at 1155 cm^{-1}) increases; it is noteworthy that at the same additive concentration in PP (0.2%), the higher the molecular weight of the additive the higher the concentrations of conformations observed. When SHA–4 is used at high concentrations (more than 1%), a considerable decrease in the absorption at 1155 cm^{-1} it can be observed showing a greater annealing effect of the polymer.

Diffusion of the additive includes its dissolution in the polymer, so one should expect that the diffusion coefficient of the additive will not be constant and will change with time and with additive concentration in the polymer. Unfortunately, the method used does not allow to measure the concentration dependence of the diffusion coefficient but allows to calculate an effective diffusion coefficient at different periods of time.

Table 2 shows the values of diffusion coefficient of SHA–2, SHA–3 and SHA–4 in PP at 100°C. It can be noted that the diffusion coefficient of SHA–2 decreases by a factor of 2 with diffusion time; D of SHA–3 at the interval of time
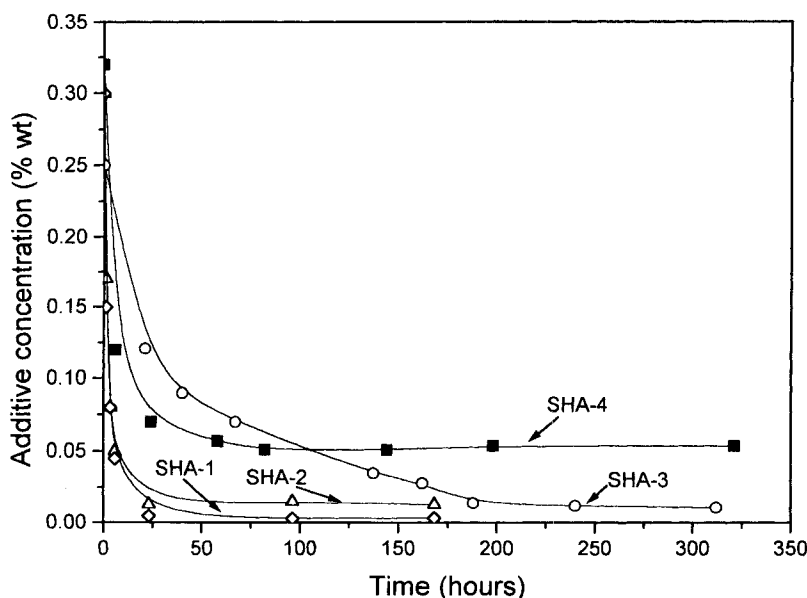
Figure 5. Washing–out of the additives from PP in heptane solution; T=22–24°C, film thickness:70 μm, the initial additives concentration 0.25–0.32 wt%.

measured does not change considerably whereas D of SHA–4 passes through a maximum with time, similar to the change in its solubility with time (Figure 2). So a high solubility facilitates a faster diffusion. The decrease in the diffusion of SHA–2 is probably due to annealing of the polymer which in the case of SHA–2 takes place even at small time intervals. The diffusion of SHA–3 was performed during a period of time in which its solubility does not change considerably.

The studied additives in spite of their high molecular weight leak from the polymer in heptane solution. Figure 5 shows that there is no simple correlation between the loss of the stabilizers and their molecular weight: the rate of loss of SHA–4 with m.w. 2758 is higher than that of SHA–4 (m.w. 2286) (Figure 5, Table 3). One of the possible reason for the fast release of additives is that the solvent facilitates their migration. On the other hand, high molecular weight stabilizers are only slightly soluble at room temperature. So the majority of them are present in a polymer in a meta-stable state or form a separate phase and they can be lost quickly.

Another feature is that stabilizers are not released completely. Some residual concentration of the stabilizers remains in PP (Table 3) and its value increases with

TABLE 3. Release of the Stabilizers from PP in Heptane

Additive	$\tau_{1/2}$, hours	Residual concentration in PP, wt%
SHA–1	1.1	0.008–0.01
SHA–2	1.5	0.013
SHA–3	14–20	0.013
SHA–4	3.5–4.0	0.053

$\tau_{1/2}$ corresponds to half the initial concentration of the additive in the polymer

the molecular weight of the additive. This is probably due to the fact that the dissolved additive rearranges the sorption centers making them more suitable to keep the additive molecules; this process, as stated above, depends on the size of the molecule.

CONCLUSION

The dissolution of high molecular weight additives in PP is accompanied by a polymer rearrangements, which are facilitated by a high temperature, conse-quently solubility and diffusion coefficient of the additives are a function of time. The additive with a large sized molecule is capable of changing the polymer struc-ture to a greater extent, resulting in an increase of the additive solubility. The studied additives leak from the polymer in heptane but not completely and the residual concentration depends on the molecular weight of the additive.

ACKNOWLEDGEMENT

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