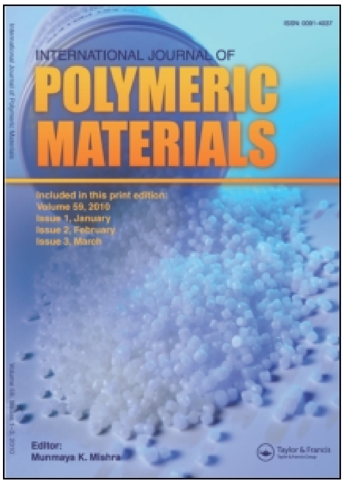

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Physical Chemistry of Topological Disorder in Polymeric Substance: Rearrangement of Additive Sorption Centers

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Low-molecular compounds present in the melt of isotactic polypropylene in concentrations exceeding a certain limit, transform some elements of disordered domains into additional sorption centers for the same compounds. These centers can persist after the removal of the low-molecular compound leading to a post-plasticizing effect. This effect slowly disappears at elevated temperatures (80–100°C). The theory of sorption centers rearrangement is discussed.

KEY WORDS Topological disorder, additive solubility, plasticizing, post-plasticizing, structure.

THEORY

The studying of physico-chemical processes in a polymer matrix require a quantitative description of the polymer structure. To solve this problem a two-component model of polymeric substance was proposed by one of the present authors.[1-3] According to this model, a bulk polymer is considered as a two-component mixture, the main component of which is the system of ordered polymer chains, and the second includes a multitude of various units of disorder (UODs): knots, folds and various entanglements of the polymer chains. Because these structures are the parts of long polymer chains they are stable even in the polymer melt where they behave as relatively mobile particles. UODs prevent complete crystallization of crystalline polymers and participate in some other processes. Being the sites of decreased density, they are the stable elements of free volume present in the polymer.

Despite the great variety of UODs, they can be divided in respect of any process into two groups: participating and non-participating.

The molecules of a compound dissolved in the polymer require the presence of free volume elements. These elements may either pre-exist in the polymer or be formed by the penetrating molecules. In this study we tried to find the relation between these two ways of dissolution of a low-molecular compound.

As postulated in dual mode sorption model,[4] the dissolution the additive A in a polymer includes the formation of true solution obeying the Henry law:

$$[A] = \gamma[A]_m \tag{1}$$

This step is followed by sorption at sorption centers. This process may be considered as complex formation:

$$A + Z_i \overset{K_{ai}}{\rightleftharpoons} AZ_i \tag{2}$$

Here $[A]$ is the concentration of truly dissolved A, and $[A]_m$ = of the same additive in surrounding medium (in vapor phase or in low-molecular solvent). According to two-component model, these centers are formed by some UODs containing enough space for A molecules.

It follows from (2) that the total additive concentration in the polymer $[A]_p = [A] + \Sigma[AZ_i]$ or:

$$[A]_p = [A] + \sum_i \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \tag{3}$$

It has been shown in Reference 5 that if $[A] << \Sigma[AZ_i]$, the isotherm (3) is practically indistinguishable from Langmuir-type one and we may substitute the formula (3) with the simple one:

$$[A]_p = + \frac{K_a\gamma_a[Z_a][A_m]}{1 + K_a\gamma_a[A]_m} \tag{4}$$

where $[Z_a] = \Sigma[Z_i]$ for all centers participating in A sorption, and K_a is a certain average value of K_{ai}.

Numerous experiments had shown that the concentration of centers participating in sorption of any additive A $[Z_a]$ does not depend on temperature in a wide range sometimes exceeding 180°C.[5]

If the concentration of A in the medium surrounding the polymer $[A]_m$ is in equilibrium with excess of pure A, $[A]_p$ will be equal to S_A—the additive solubility in it. It has been shown in Reference 6 that, unlike the solubility in non-mixing liquids, S_A depends on the composition of medium surrounding the polymer because the molecules of solvent compete with the additive for some sorption centers ($AZ_i + Lq \leftrightarrow LqZ_i + A$), where Lq is the molecule of liquid solvent.

At high additive concentrations and at temperatures above T_g the simple law (1) is violated and the additive concentration in the polymer becomes greater than $[Z_a]$ calculated at moderate A concentrations.[3,7,8] To explain this phenomenon we consider the energy of the sorption center formation.

The elements of disorder are in the same time the sites in which the polymer density is decreased, therefore, they represent the elements of free (excess) volume. To form an excess volume v_i in the polymeric matrix a certain energy is needed.

We assumed that this energy is directly proportional to the volume formed, i.e.[9] that:

$$\varepsilon_i = qv_i \tag{5}$$

for all meanings of i. The dimension of coefficient q is energy/volume or pressure. In the presence of low-molecular compound A the value of q will decrease by the value of energy of interaction between the molecules of A and surrounding polymer q_a. Therefore, q must be substituted with $q - q_a$.

It follows from (5) that $\Delta\varepsilon_i/\Delta v_i = q - q_a$ depends neither on v_i nor Δv_i values. Consider that the center Z_i already exists and its volume is less than that necessary for the sorption of A molecules v_a. To increase the volume v_i to v_a and rearrange this center, a certain minimal (threshold) value of osmotic pressure of the additive $P_A = q - q_a$ is needed which does not depend on the size of v_i. In the polymer melt, where the entire volume of the polymer sample is accessible for the mobile part of the additive, this osmotic pressure P_A is related to the concentration of A around the polymer $[A]_m$ by expression:

$$P_A = RT[A] = RT\phi[A]_p \tag{6}$$

where $\phi = [A]/[A]_p$ = the variable coefficient which may be calculated from expression (5). When $[A]_p << [Z_a]$ $\phi = (K_a[Z_a])^{-1}$, but deviates from this when $[A]_p$ is comparable with $[Z]_a$. It follows from (6) that the minimal additive concentration is needed above which the sorption centers will rearrange. If $q_a \geq q$, $P_A \leq 0$ and the polymer will be swelling at any concentration of A.

The transformation of the element of disorder ζ_i into a new sorption center Z^*_{ai} may be written as:

$$\zeta_i + A \rightarrow Z^*_{ai}A \tag{7}$$

Because of low translational mobility in solid polymer these new centers must exist as relatively stable structures even after removal of A. Therefore, we studied the effect of high concentrations of phenyl-β-naphthylamine, $C_{10}H_7$—NH—C_6H_5, and phenyl benzoate, C_6H_5—CO—O—C_6H_5, dissolved in isotactic polypropylene melt, on the solubility of additives in the solid polymer prepared from this melt. Considering that the additives producing the changes of the polymer structure are called plasticizers, we propose that the changes of the polymer structure remaining after removal of this additive be called the post-plasticizing effect.

EXPERIMENTAL

Isotactic polypropylene ProFax 6501 produced by Himont Co (U.S.A.), having the molecular mass M_w = 164 400, M_w/M_n = 38, was washed with heptane from atactic fraction. The additives: phenyl benzoate (PB), molecular mass M = 198.2 and phenyl-β-naphthylamine (PNA), M = 219.3, crystallized from heptane, were used. The samples were prepared by heating the mixtures of polypropylene with phenyl benzoate to 220–230° between two polished plates of stainless steel with subsequent pressing into 0.005 cm thick films and rapid cooling to room temperature. For analysis of additive concentration, the additives were extracted with alcohol (48 hours, 40°C), and their quantity determined spectrophotometrically.[10]

The experiments relative to additives solubility were performed at 40°C.

RESULTS AND DISCUSSION

Variation of concentrations of PNA and PB in the polypropylene samples with various initial concentrations of these compounds kept in the saturated vapors of the same compound at 40° is shown in Figures 1 and 2. As seen from these figures, the concentrations of both compounds in untreated polypropylene increases reaching the limits equal to 0.008 mol/kg for PNA and 0.055 mol/kg for PB, but the concentrations of both compounds in the samples prepared from polypropylene melt containing various concentrations of PNA and PB, decreased approaching the limits depending on additive concentration in the polymer melt.

Variation of additive concentration in the sample is the result of the additive diffusion from the sample surface to its inside or, vice versa, from inside the sample to its surface. The result of diffusion in uniform media is the equalization of diffusant

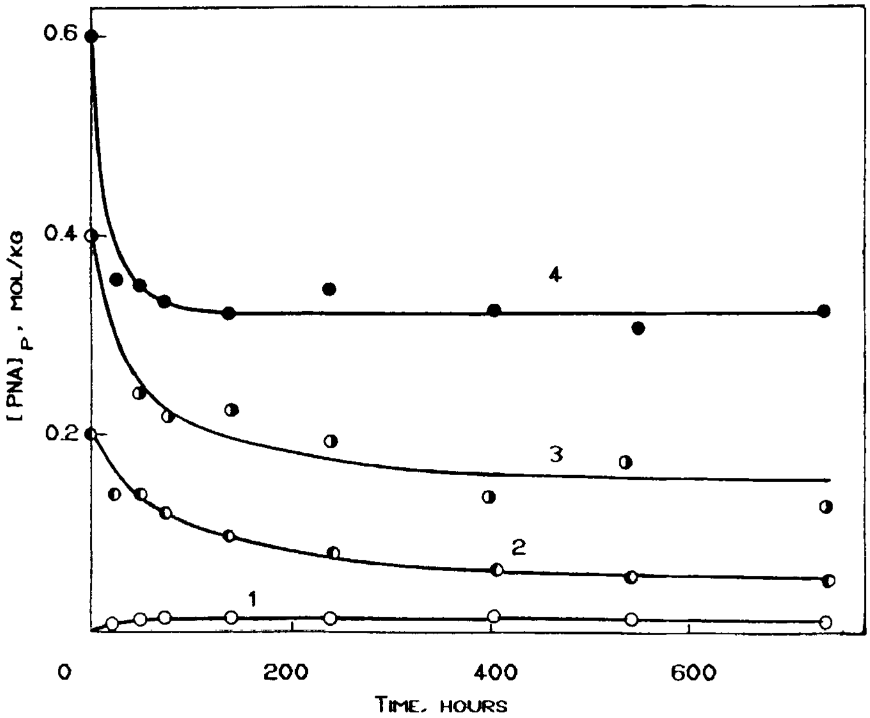

FIGURE 1 Variation of concentration of PNA $[PNA]_p$ in non-treated polypropylene (1) and in polypropylene samples, prepared from melts containing PNA, 0.2 (2), 0.4 (3) and 0.6 mol/kg (4) 40°C.

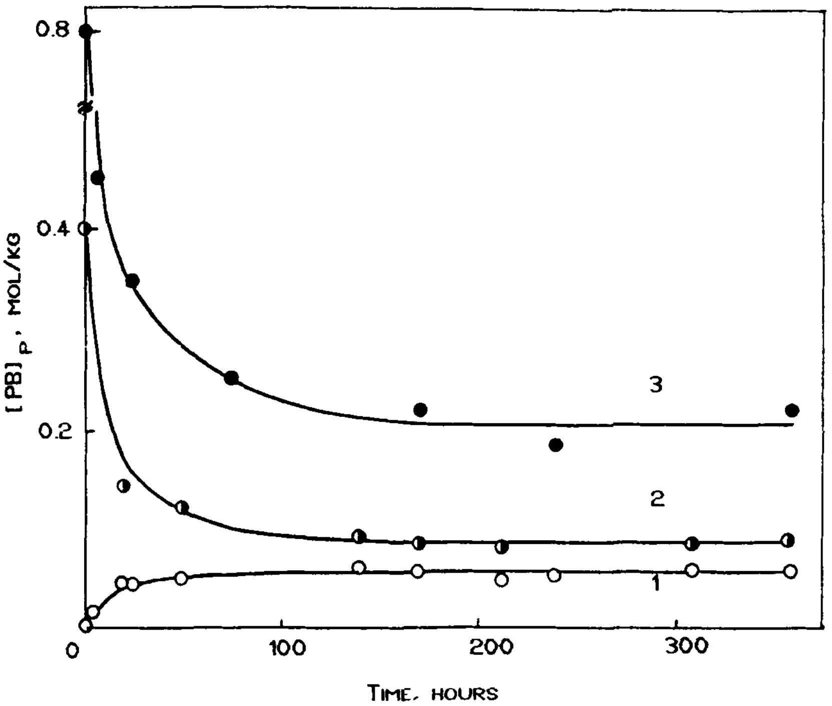

FIGURE 2 Variation of concentration of PB $[pb]_P$ in non-treated polypropylene (1) and in polypropylene samples, prepared from melts containing PB, 0.4 (2), and 0.8 mol/kg (3) 40°C.

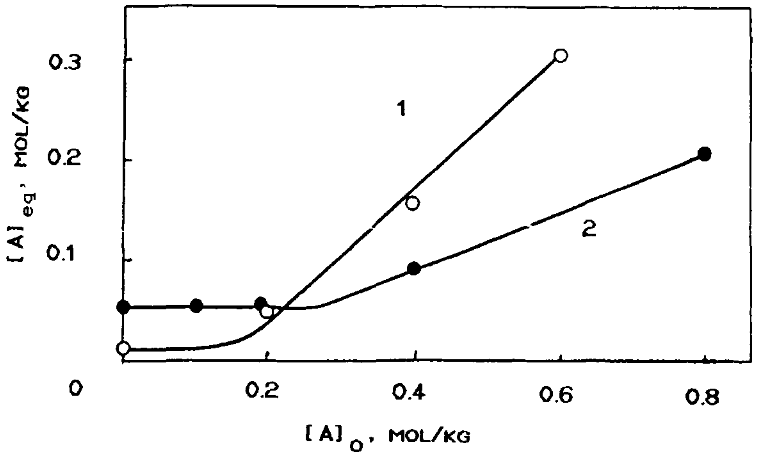

FIGURE 3 Equilibrium additive concentrations in isotactic polypropylene at 40°C $[A]_p$ as function of its concentration in the polymer melt $[A]_0$. A = PNA (1), and A = PB (2).

concentration in the medium. When the average additive concentration in the sample becomes constant its concentration through the sample is the same and is in equilibrium with the additive vapors around the sample.

As seen from Figure 3, to increase the additive solubility the concentration of this additive in the polymer melt must exceed the certain limiting value. This is in the good agreement with the theory considered above according to which the certain minimal additive concentration is needed to rearrange the sorption center. These data allow us to predict these limiting concentration values.

The increase in additive solubility may be due to increase of sorption centers concentration $[Z_a]$, or to increase in the value of the equlibrium constant K_a (or of the product $\gamma_a K_a$). To distinguish between these possibilities we studied the sorption isotherms of both PNA and PB of non-treated and treated polypropylene from heptane solutions of the additives. The results of these experiments are presented in Figures 4 and 5.

All the isotherms presented in Figures 4 and 5 can be described by formula (4). The values of $[Z_a]$ and $\gamma_a K_a$ calculated from data presented in these figures were: for A = PB $[Z_a] = 1.3 \cdot 10^{-2}$ mol/kg, $\gamma_a K_a = 64$ l/mol in non-treated polypropylene and $[Z_a] = 1.8 \cdot 10^{-2}$ mol/kg, $\gamma_a K_a = 47$ l/mol in polypropylene treated in the molten state with PB, 0.8 mol/kg; for A = PNA $[Z_a] = 2.3 \cdot 10^{-2}$ mol/kg, $\gamma_a K_a = 101$ l/mol in non-treated and $[Z_a] = 12.0 \cdot 10^{-2}$ mol/kg, $\gamma_a K_a = 32$ l/mol in poly-

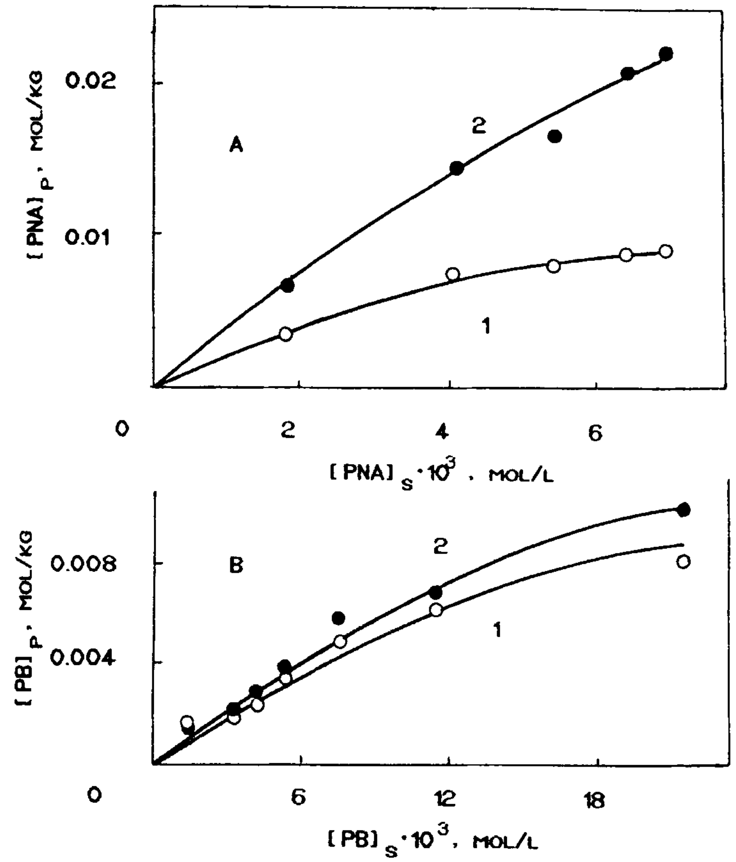

FIGURE 4 Sorption isotherms of PNA (A) and PB (B) from heptane solutions by non-treated polypropylene (1) and polypropylene samples prepared from melts, containing PNA, 0.6 mol/kg, and PB, 0.8 mol/kg 40°C. $[\mathrm{PNA}]_s$ and $[\mathrm{PB}]_s$ = the concentrations of additive in heptane solution.

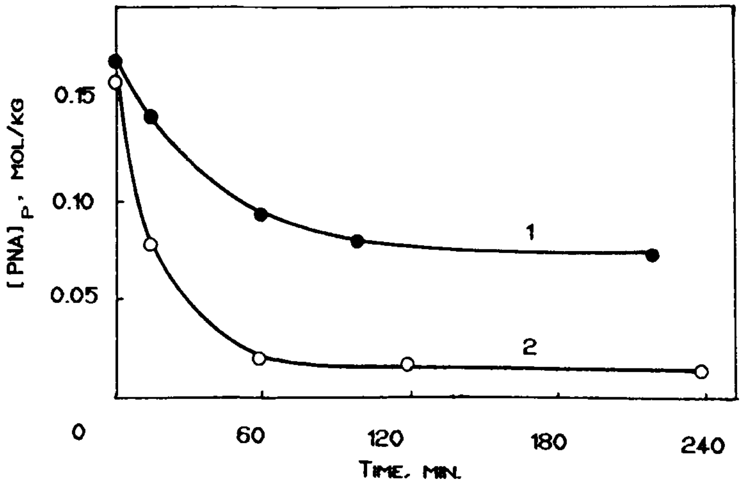

FIGURE 5 Variation of PNA solubility $[PNA]_p$ in polypropylene samples prepared from melt containing PNA, 0.6 mol/kg, as function of time of heating at 80° (1) and 100°C (2).

TABLE I

Solubilities of various compounds in isotactic polypropylene, non-treated and treated with phenyl benzoate in the melt (mol/kg) 40°C

	Compound			
	Phenyl benzoate	Diphenylamine	Dibenzylsulfide	Phenyl-β-naphthylamine
Non-treated	0.055	0.11	0.35	0.008
Treated with PB, 0.6 mol/kg	0.15	0.27	0.83	0.032

propylene treated with PNA, 0.6 mol/kg. It must be noted that increase in sorption centers concentrations is accompanied with the decrease in the values of constants of sorption equilibrium. Hence, the sorption centers Z_a^* formed in the polymer melt according to the process (6) are less "convenient" than the pre-existing centers in the polymer. Thus not changing the number of UODs but changing the structures of some of them we can change the level of disorder in the polymer.[11]

From the Table I, it follows that the centers formed by the treatment of polymer with one additive can also sorb some other additives. The solubilities of diphenylamine, dibenzylsulfide and PNA in isotactic polypropylene prepared from melt containing PB were markedly greater than in non-treated polymer.

Contrary to the centers existing in non-treated polymer, the new-formed centers Z_a^* are unstable and disappear at the moderate heating of the sample. Figure 6 shows the decrease of solubilities of PB and PNA, measured at 40°C, as functions of the heating time at 80° and 100°C. Before the heating, all samples were washed to remove the additives. These data show that the heating at 80°C decreases the solubilities of both additives to values markedly differing from their solubilities in non-treated polymer. The heating at 100° results, however, in nearly complete

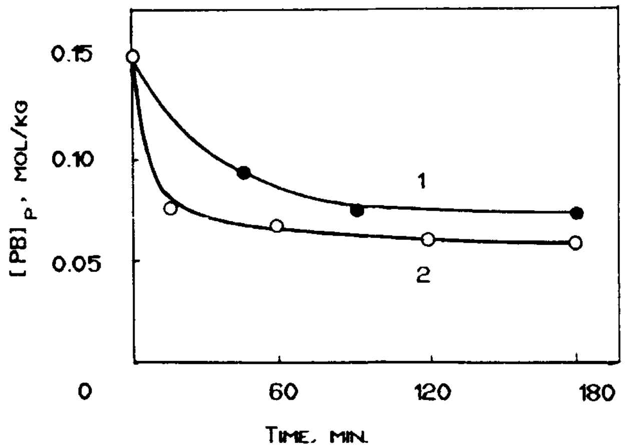

FIGURE 6 Variation of PB solubility $[PB]_p$ in polypropylene samples prepared from melt containing PB, 0.8 mol/kg, as function of time of heating at 80° (1) and 100°C (2).

disappearance of new-formed centers due to relaxation of the substance surrounding UOD. The process can be formally described by equation:

$$Z_a^* \rightarrow \zeta_i \tag{8}$$

It follows from (4), that the concentration of mobile molecules of the additive A at $[A]_p << [Z_a]$ is $[A] = [A]_p/K_a[Z_a]$ or, if the polymer sample was prepared from melt containing a high concentration of A, $[A] = [A]_p/K_a^*[Z_a]$. The mobility of the additive and, if A is antioxidant, the apparent rate constant of its interaction with relatively immobile macroradicals which, besides other factors, is proportional to the ratio $\phi = [A]/[A]_p$. The additive mobility and its action, therefore, depends on the way the additive was incorporated into the polymer.

As shown in this paper, some elements of polymer structure may be reversibly changed without changing UOD topology and concentration. When these newly formed centers contain molecules of an additive A, polymer may be considered as plasticized by A, but the changes preserved after removal of this additive may be considered as post-plasticizing.

As shown in Reference 12, the concentration and composition of UODs in a polymer and, as a sequence, the properties of the polymer can be varied by varying the condition of the polymer consolidation. The difference between samples prepared from different solvents remains even in the polymer melt.

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