Physical Chemistry of Topological Disorder in Polymers: Some Remarks on Polymer Memory

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ABSTRACT: The long-term structural memory of a polymeric substance is determined by the concentration, size, and space distribution of the elements of topological disorder present in it. The short-term structural memory is the result of the reversible reconstruction of existing elements. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4208–4211, 2006

Key words: polymer memory; topological disorder; solubility; polyethylene; polypropylene

INTRODUCTION

It is well known that the properties of a polymer may depend on the prehistory of a polymer sample.[1–3] We show that there are two types of structural memory: long-term memory, which preserves many influences on it, and short-term memory, which disappears with time or slight heating.

According to the theory discussed in refs. 4 and 5, a polymer may be considered an ideally ordered substance composed from chain-like molecules in which various elements of disorder (ξ_i's) are distributed. The content of these elements may be expressed in units of concentration:[4]

$$[\xi_i] = \xi_i(m_s N_A)^{-1}(\text{mol/kg}) \qquad (1)$$

where m_s is the mass of the sample and N_A is Avogadro's number ($N_A = 6.02 \times 10^{23}$). The total concentration of the elements of disorder ($[\xi]$) is the sum of the $[\xi_i]$'s:

$$[\xi] = \sum_i [\xi_i] \qquad (2)$$

There are several ways to change these elements and their distribution and with which one may try to increase or decrease $[\xi]$ and its distribution in size or shape. However, first, one must be able to evaluate both.

To investigate these ξ_i's, the method of sorption of low-molecular-mass additives may be used. The long,

chain-like macromolecules are virtually immobile, and to form the solvent shell, the additive molecule A must find the element containing a free volume sufficient for the A molecule, the shape of which must be easily changed to fit it. Such experiments were performed with several modifications by saturation of polymer with A from the gas or liquid phase. With the dual sorption model, we assumed that the molecules of compound A dissolved in the polymer divided into two groups: those truly dissolved in the ordered part of the polymer and present as complexes with certain centers (Z_i's):

$$\text{A} + \text{Z}_i \leftrightarrow \text{AZ}_i \qquad (3)$$

If the concentration of A outside the Z_i's is neglected, we may write

$$[\text{AZ}_i] = \frac{K_{ai}[\text{Z}_i][\text{A}]}{1 + K_{ai}[\text{A}]} \qquad (4)$$

where K_{ai} is the constant of equilibrium (3) and the total concentration of A in the polymer ($[\text{A}]_p$) will be

$$[\text{A}]_p = [\text{A}] + \sum_i [\text{AZ}_i] = [\text{A}] + \sum_i \frac{K_{ai}[\text{Z}_i][\text{A}]}{1 + K_{ai}[\text{A}]} \qquad (5)$$

If the real solubility of A in the ordered part of polymer is assumed to be negligibly small compared to that in the sorption centers, we may neglect [A] compared with the second term of the sum in eq. (5). It was shown in refs. 5 and 6 that this second term at various assumptions of [Z_i] distribution may be approximated with a Langmuir-type formula:

$$[\text{A}]_p = \frac{K_a[\text{Z}_a][\text{A}]}{1 + K_a[\text{A}]} \qquad (6)$$
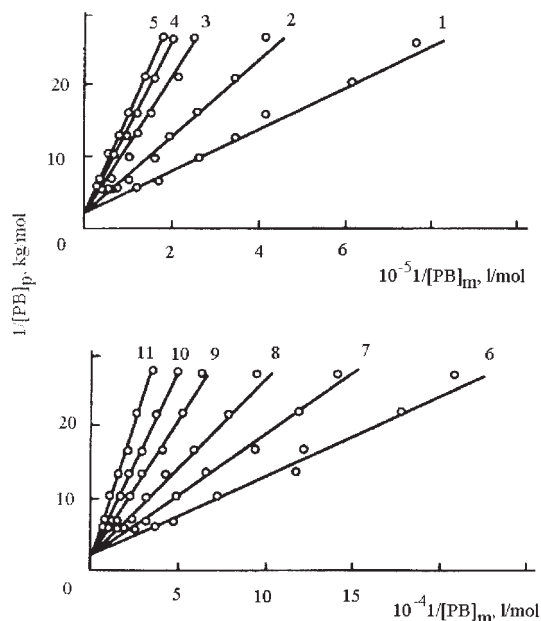
Figure 1 Sorption isotherms of phenyl benzoate by polyethylene from the gas phase in the coordinates $1/[PB]_p$ versus $1/[PB]_m$ at the following temperatures: (1) 80, (2) 90, (3) 100, (4) 110, (5) 120, (6) 130, (7) 140, (8) 150, (9) 160, (10) 170, and (11) 180°C.

where K_a is the average constant of sorption equilibrium and Z_a is the total concentration of centers sorbing the compound A. Also, if it is assumed that the concentration of truly dissolved A in the polymer is directly proportional to that in the surrounding medium ($[A]_m$)

$$[A] = \gamma_a [A]_m \qquad (7)$$

we get a formula similar to eq. (6), in which K_a must be substituted with $\gamma_a K_a$ and $[A]$ must be substituted with $[A]_m$. This formula written in inverse coordinates ($1/[A]_p$ vs $1/[A]_m$) describes the straight line intersecting the ordinate axis in the point equal to $1/[Z_a]$ to the reciprocal concentration of centers sorbing compound A:

$$\frac{1}{[A]_p} = \frac{1}{\gamma_a K_a [Z_a]} \times \frac{1}{[A]_m} + \frac{1}{[Z_a]} \qquad (8)$$

To check this dependence, the sorption of two compounds absorbing UV light from their vapors, namely, phenyl benzoate and phenyl-β-naphthylamine, was studied. Concentrations of both compounds in the gas phase were measured from their UV spectra.

As shown in Figure 1, the sorption isotherms, that is, the equilibrium dependencies of $[A]_p$ on $[A]_m$ at the sorption of phenyl benzoate by polyethylene in the coordinates of eq. (8) were straight lines. The lines corresponding to various temperatures from 80 to 180°C intersected the ordinate axis at the same point,

that is, the limiting value of $1/[Z_a]$, and correspondingly, the meaning of the sorption centers concentration did not change with temperature, neither below nor above the melting temperature of the polymer (ca. 130°C). Such invariable structures can be only topological ones, that is, based on various knots and interlacements of the polymer chains.[4,5]

Some experiments were performed on the sorption of additives with polyethylene and isotactic polypropylene from solutions of these additives in various solvents. In some studies, the substitution of one additive with another, that is, the following process, was observed:[6]

$$AZ_i + B \rightarrow BZ_i + A \qquad (9)$$

In some experiments, instead of sorption isotherms, the limiting additive concentration, corresponding to the additive solubility ($[A]_s = \gamma_{as}[A]_m$) was measured. Similarly, the solvent molecules (S's) could substitute for the additive in the sorption centers:

$$AZ_i + S \rightarrow SZ_i + A \qquad (10)$$

In the absence of additive, the molecules of solvent, including water, penetrated into the sorption centers. This is why polymer density data obtained by hydrostatic weighing were not reliable.

The regularities of sorption from solution were the same as from the gas phase; only the values of $[Z_a]$ were considerably smaller because some centers occupied by the solvent molecules were inaccessible to the molecules of the additive. In these experiments, the polymer "remembered" from which solvent it was precipitated. Thus, the meanings of $[Z_a]$ for isotactic polypropylene precipitated from n-decane was nine times greater than that for the same polypropylene precipitated from chlorobenzene[7] (Fig. 2). Similarly, the polypropylene samples precipitated from the same solvent, p-xylene, by rapid cooling and by slow cooling differed markedly in their sorption capacities.[8]

Repeated melting with subsequent crystallization at 150°C led to a decrease in $[A]_s$; the greater the solubility was, the lower the molecular mass of the additive was.[9] To explain this, we had to assume that when the molecular mass was greater, which in compounds consisting of the light atoms H, C, N, and O meant that the volume of the molecule was greater, the more complicated the ξ_i sorbing it had to be, but at the same time, the more complicated the element was, the more stable it was in the course of polymer crystallization. In this process, the leading facets of the growing crystallites disentangled interlacements of the polymer chains and the easier and simpler this interlacement was. In another experiment, polypropylene was crystallized 12 times in vacuo (with the samples heated to 220°C and kept at this temperature 1.5 h, slow cooled to 150°C and kept at this temperature for 1.5 h, and
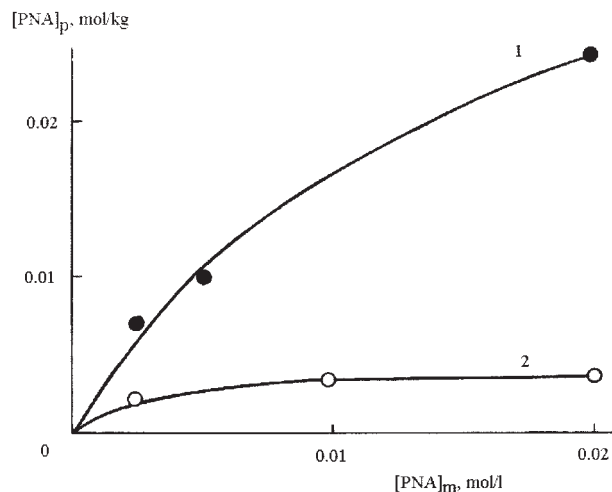
Figure 2 Sorption isotherms of phenyl-β-naphthylamine from heptane solutions by polypropylene precipitated from (1) *n*-decane and (2) chlorobenzene at 40°C.

Figure 4 Sorption isotherm of phenyl-β-naphthylamine by polyethylene from heptane solutions at 40°C: (○) nontreated polymer and (●) polyethylene after multiple kneading at 220°C.

cooled to room temperature). In Figure 3, the sorption isotherms of phenyl-β-naphthylamine from alcohol by nontreated and treated samples are presented. Calculated from data of Figure 3, the meanings of $[Z_a]$ decreased from 2.5×10^{-2} to 1.3×10^{-3} mol/kg, that is, 19 times.[10]

When slow crystallization changed the sorption centers concentration, the kneading of the polymer melt by repeating pressing and folding did not change it. In our experiments,[11] the polyethylene film was folded and pressed at 220°C until the calculated formal thickness of the initial film was 8×10^{-10} cm, that is, until the initial polymer structure was completely destroyed. As shown in Figure 4, the sorption isotherms of phenyl-β-naphthylamine for the initial and treated polyethylene films virtually coincided: the ξ_i's responsible for the sorption centers formation moved during polymer pressing without disentanglement.

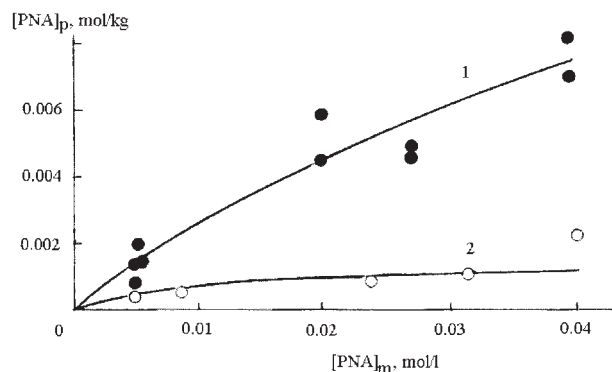Heating the polymer mixed with the large amount of additive above the melting temperature temporally

changed the sorption centers. As shown in Figure 5, after the isotactic polypropylene powder was heated to 220°C with various initial concentrations of phenyl-β-naphthylamine and with subsequent cooling to 40°C in the saturated vapors of the same additive, the concentration of phenyl-β-naphthylamine in the sample rapidly decreased to a limit depending on the initial additive concentration. Analogously, the concentration of phenyl benzoate was changed (Fig. 6). This limit rose approximately linearly after a certain initial additive concentration (Fig. 7) and also depended on the method of polymer precipitation.[12,13] These additive concentrations in the samples heated in the saturated additive vapors corresponded to the additive solubility, which, as we observed, depended

Figure 3 Sorption isotherms of phenyl-β-naphthylamine by isotactic polypropylene from alcohol solutions at 50°C: (1) usual polymer and (2) polymer after 12 cycles of melting and crystallization.[9]
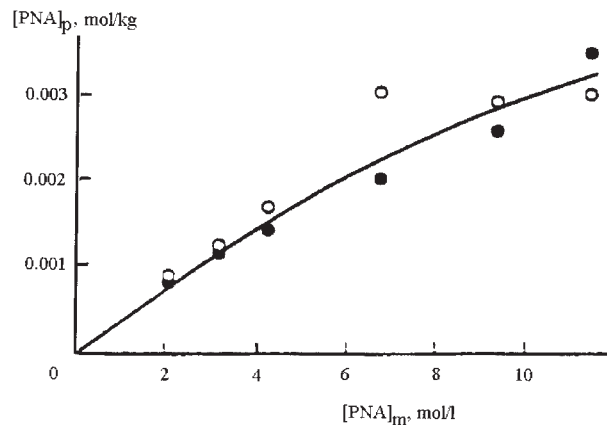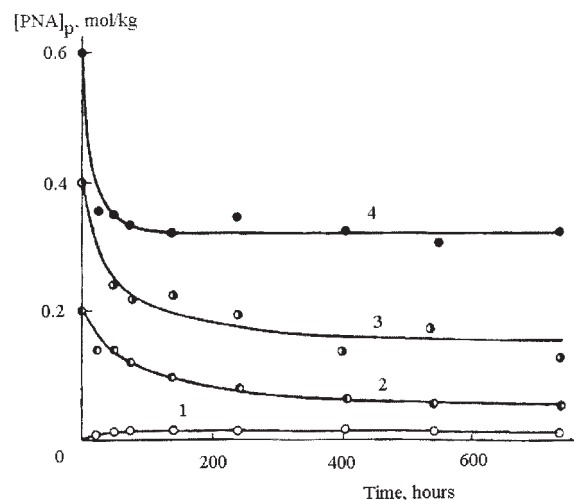

Figure 5 Variation in the concentration of phenyl-β-naphthylamine in isotactic polypropylene samples during heating in saturated vapors of these compounds at 40°C. The initial additive concentrations were (1) 0, (2) 0.2, (3) 0.4, and (4) 0.6 mol/kg.
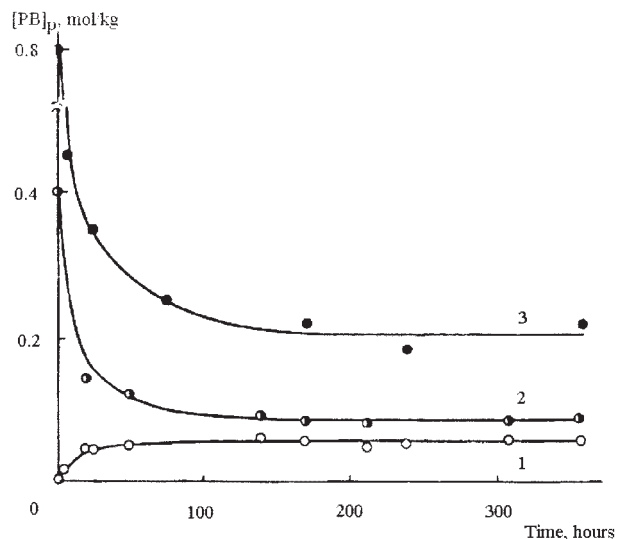
Figure 6 Variation in the phenyl benzoate concentration in isotactic polypropylene samples during heating in saturated vapors of these compounds at 40°C. The initial additive concentrations were (1) 0, (2) 0.4, and (3) 0.6 mol/kg.

on the sample prehistory. Similar dependencies were observed with another additive, phenyl benzoate. To explain this, we concluded that at high additive concentrations, the ξ_i's were transformed into unstable sorption centers (Z^*_{ai}):

$$\xi + A \rightarrow Z^*_{ai}A \tag{11}$$

The newly formed centers possessed a different stability: a part of them was already destroyed at low temperatures (40°C). To destroy other elements, the polymer had to be heated to at least 100°C (Fig. 8[13]).
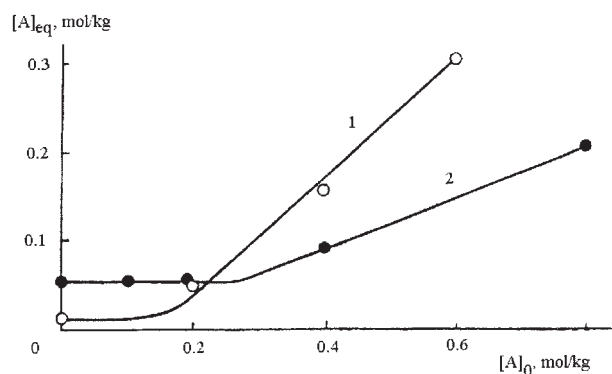

Figure 7 Limiting concentrations of (1) phenyl-β-naphthylamine and (2) phenyl benzoate in isotactic polypropylene as a function of the initial additive concentration in the polymer at 40°C.

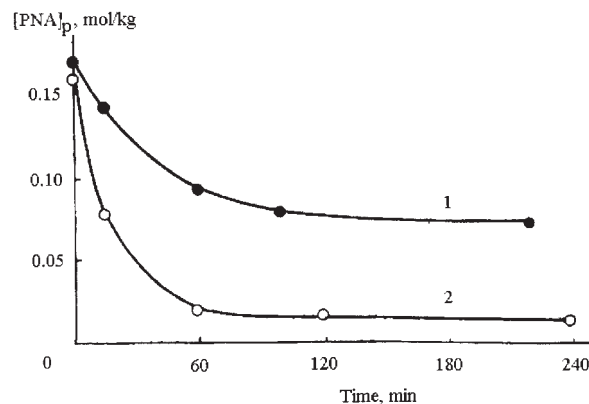**Figure 8** Variation in the solubility of phenyl-β-naphthylamine in isotactic polypropylene samples prepared from the melt containing 0.6 mol/kg of this additive during heating at (1) 80 and (2) 100°C in saturated additive vapors.

These dependencies demonstrated examples of short-term memory.

Thus, the total concentration and size distribution of the elements of topological disorder were formed at polymer precipitation and were decreased by another sedimentation, special treatment of the polymer, or repeated crystallization, but the properties of these elements was reversibly changed by treatment of the polymer with low molecular additives. The processes of relaxation of these elements differed in their rates.

In this article, we do not consider the oriented state of the polymers.

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