

Physical Chemistry of Topological Disorder in Polymers: Reconstruction of Sorption Centers and Antioxidant Effectivity in Isotactic Polypropylene

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ABSTRACT: Formation and transformation of additive sorption centers in isotactic polypropylene was studied. According to a two-component model of a polymeric substance, these centers are formed around the elements or units of disorder (UODs) which are knots, folds, and other interlacings of long polymer chains. These elements are formed at the precipitation of the polymer and are stable even in the polymer melt because of the great lengths of the polymer chains. In some cases, the elements unable to sorb the given compound may be transformed into the sorption centers for it. When present in the sorption center, antioxidant molecules cannot move and react with macroradicals participating in the polymer oxidation, which results in the dependence of the so-called critical antioxidant concentration on that of the sorption centers. The theory of the formation and reconstruction of UOD-based sorption centers is discussed. Formation of a polymeric substance may be divided into two stages: polymerization or polycondensation of low-molecular compounds and self-assembling of macromolecules into polymeric material. Opposite to numerous investigations of the first step of this process and of the properties of the end products, the stage of transition of the macromolecules into the polymeric material and possibilities of regulating its properties in this stage are usually neglected. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1847–1854, 1998

Key words: additive; solubility; structure; topological disorder

THEORY: TOPOLOGICAL DISORDER AND SORPTION CENTERS

To explain some properties of polymers, a two-component model of polymeric compounds was proposed in ref. 1. According to the model, a polymeric compound is considered as the system of long ideally ordered polymer chains in which various topological structures—the units of disorder

(UODs): Folds, entanglements, and knots, are distributed. In the polymer melt, these UODs behave as quasiparticles possessing a certain mobility. For example, the simplest UODs shown in Figure 1 can slide along the molecules of which they are formed.^{1–3} In ref. 2, such sliding was called “reptation.” Below the melting temperature of crystalline polymer, UODs are expelled by growing crystals at the same time, preventing complete crystallization. Some consequences of this model were discussed in refs. 4 and 5.

Dissolution of the low molecular additive *A* in a polymer includes formation of the element of the free volume into which the additive molecule enters. It is obvious that if a certain element of

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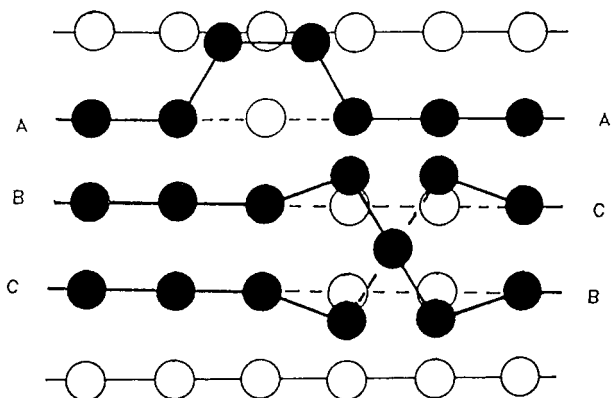
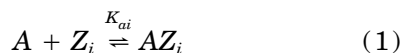


Figure 1 Scheme of the simple UODs: (A–A) folds; (B–B, C–C) interlacement.

the free volume is preexisting in the polymer the energy needed for dissolution is much lower. For this reason, we may assume that the sites into which the additive molecules penetrate, at least first, are the certain zones Z_i formed in the UODs or around the UODs. Thus, dissolution of the additive can be presented by the expression



For penetration into a sorption center, an additive A must possess a certain solubility in the ordered part of the polymer, which can be very small. But according to Henry's law, $[A]$, the concentration of A outside the sorption centers, is connected with that in the surrounding medium $[A]_m$ by the expression $[A] = \gamma_a[A]_m$, where γ_a is the coefficient depending on the nature of the medium.

If the additive concentration in the polymer is comparable with the sorption center concentration, the concentration of each type of complexes AZ_i may be presented by a Langmuir-type formula:

$$[AZ_i] = \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \quad (2)$$

If there are many various types of centers Z_i , by neglecting the out-center solubility, we may write

$$[A]_p = \sum_i [AZ_i] = \sum_i \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \quad (3)$$

By analyzing expression (3), we may see that at

$[A]_m = 0$, $[A]_p = 0$, and if $[A]_m \rightarrow \infty$, so that $[A]_p \rightarrow \Sigma[AZ_i] = [Z_a]$, the limit to which the additive concentration tends with increasing concentration of the same compound in the surrounding medium corresponds to the total concentration of centers sorbing this compound.

Numerous experiments have shown that the experimental dependencies of $\Sigma[AZ_i]$ on $[A]_m$ are nondistinguishable from the Langmuir-type one.^{6,7} For some cases, this has been shown theoretically.⁷

Substituting $[Z_i]$ with $[Z_a]$ and accepting in accordance with the last assumption that all K_{ai} in (3) to be equal: $K_{ai} = K_a = \text{const}$, we get

$$[A]_p = \frac{\gamma_a K_a [Z_a] [A]_m}{1 + \gamma_a K_a [A]_m} \quad (4)$$

Transformation of the resulting expression (9) into the inverse form gives

$$\frac{1}{[A]_p} = \frac{1}{[Z_a]} + \frac{1}{\gamma_a K_a} \frac{1}{[A]_m} \quad (5)$$

Equation (5) may be used to check whether the experimental dependence corresponds to the Langmuir-type one, and for the evaluation of the sorption center concentration $[Z_a]$: If expression (5) is obeyed, the line $1/[A]_p$ versus $1/[A]_m$ intersects the ordinate axis in the point $y = 1/[Z_a]$. According to (4), the antioxidant solubility S_A is the equilibrium meaning of $[A]_p$ when $[A]_m = [A]_{\text{eq}}$ —the concentration of A around the polymer being in equilibrium with an excess of the pure additive: $S_A = \gamma_a K_a [Z_a] [A]_{\text{eq}} (1 + \gamma_a K_a [A]_{\text{eq}})^{-1}$.

FORMATION OF SORPTION CENTERS

UODs are formed in the polymer solution around the sites in which a segment of the polymer molecule crosses another segment of the same or another molecule. In the polymer solution, the number of sites in which a molecule passes close to another one is directly proportional to the polymer concentration. Adding the number of sites in which the molecule crosses itself, we get

$$\Sigma[\text{UOD}] = [Z_0] = a + b[\text{POLYMER}] \quad (6)$$

where $[Z_0] = \Sigma[Z_i]$.

As the site of decreased density, the UOD con-

tains a certain excess (free) volume formation which needs a certain energy ε_i . Assuming that this energy is directly proportional to the excess volume v_i ,

$$\varepsilon_i = qv_i \quad (7)$$

If the volume v_i is formed in the polymer solution, the energy of this volume formation decreases depending on the energy of the polymer-solvent interaction, and we may present q as the difference of two values:

$$q = q_0 - q_s \quad (8)$$

where q_s depends on the nature of the solvent and q_0 is independent of it. It must be especially noted that the dimension of q is the energy/volume, that is, the pressure.

Using the Boltzman law, we get a size distribution of UODs:

$$[Z_a] = [Z_0] \exp\{-(q_0 - q_s)v_a/kT\} \quad (9a)$$

where $[Z_a]$ is the concentration of UODs containing an excess volume v_a existing in the polymer solution.

If at the sedimentation of the polymer the volume v_a shrinks β times, the v_a in the bulk polymer will be β times smaller than those in the solution:

$$[Z_a] = [Z_0] \exp\{-\beta(q_0 - q_s)v_a/kT_s\} \quad (9b)$$

where T_s is the temperature of the polymer sedimentation.

If A is an organic compound consisting of carbon, oxygen, nitrogen, sulfur, and hydrogen and its molecular mass M_a is greater than 100, its density lies within the range 1.1 ± 0.1 . Assuming that the volume necessary to contain the A molecule in the sorption center is approximately equal to the molecular volume in the pure state, $v_a = M_a/1 N_A = M_a/6.62 \times 10^{23}$ ($N_A = 6.02 \times 10^{23}$ is the Avogadro number). Denoting

$$\beta(q_0 - q_s)/6.62 \times 10^{23} kT = \aleph \quad (9c)$$

we obtain⁸

$$[Z_a] = [Z_0] \exp(-\aleph M_a) \quad (10)$$

Such a dependence of $[Z_a]$ on the additive molecular mass M_a was found experimentally in ref. 9.

METHOD OF CRITICAL ANTIOXIDANT CONCENTRATION

To compare the phenyl- β -naphthylamine (PNA) antioxidant effectivities in PP-1 and PP-2, we used the method of critical antioxidant concentrations. The method was discussed in detail in ref. 10; here, we describe it in simplified form.

Consider the branched chain reaction in which reaction centers X^* (concentration $[X^*] = x$) are formed with the rate W_0 , the probability of kinetical chain branching, that is, formation of additional active centers from the existing ones during the time unit, is f , and the chains terminate in the reaction with the antioxidant at the rate

$$W_t = k_t x[A] \quad (11a)$$

The equation of active center balance will be

$$\begin{aligned} \frac{dx}{dt} &= W_0 + fx - k_t x[A] \\ &= W_0 + (f - k_t[A])x \end{aligned} \quad (11b)$$

If $dx/dt = 0$, we have the so-called stationary reaction. In this case,

$$x_{st} = \frac{W_0}{k_t[A] - f} \quad (12)$$

x_{st} is always finite and positive; thus, the stationary solution of (14) is possible only if $k_t[A] > f$, or at $k_t = \text{const}$ if $[A] > [A]_{cr} = f/k_t$. If the antioxidant concentration lies below the critical value, the rate of chain branching is greater than that of chain termination and the active center concentration increases with self-acceleration. The rate of the chain reaction which is proportional to x also rapidly increases. Oppositely, if $[A] > [A]_{cr}$, $k_t[A] > f$ and the reaction rate remains limited and slow. The critical antioxidant concentration corresponds to the borderline between rapid non-stationary and slow stationary processes and may be easily determined experimentally, but the experimentally found value of $([A]_p)_{cr}$ is the sum of the critical concentration of the mobile antioxidant molecules $[A]_{cr}$ and of immobile ones $\Sigma[AZ_i]$.

The most convenient characteristics of the re-

action rate is the induction period: The time from the beginning of the reaction until the moment when the excess of the antioxidant above $([A]_p)_{cr}$ is consumed and a slow reaction turns into rapid one. On the curve "induction period versus initial antioxidant concentration," the critical concentration corresponds to the point beginning from which the induction period rapidly increases with the concentration.

In polymers, both macroradicals and complexes AZ_i are immobile. To react with the immobile macroradical $X^* = RO_2^*$, the antioxidant molecule must move in the sample, that is, only molecules A which are not bound into the complexes can retard the oxidation. It is natural to assume that in the samples of the same polymer the critical concentrations of the mobile antioxidant are the same.

When deriving eqs. (2)–(5), we substituted $\gamma_a[A]_m$ for $[A]$. Returning to $[A]$ and assuming that $K_a[A] \ll 1$ because the critical antioxidant concentrations are usually small fractions of their solubilities, we get from (4)

$$[A] = [A]_p K_a^{-1} [Z_a]^{-1} \quad (13)$$

and, correspondingly,

$$([A_p])_{cr} = [A]_{cr} K_a [Z_a] \quad (14)$$

EXPERIMENTAL

Isotactic polypropylene ProFax-650I with a molecular mass $M_w = 164,400$ and a wide molecular-mass distribution $M_w/M_n = 38$, produced by Himont Co. (USA) was washed with boiling heptane to remove the atactic fraction (PP-1), precipitated after washing from a 2% solution in boiling *p*-xylene (131°C) either by rapid cooling (mixing the polymer solution with cold alcohol) (PP-2) or by slow cooling with subsequent washing of the gel formed in the process of cooling (between 80°C and room temperature) (PP-3). In the first case, we froze the equilibrium existing at 131°C; in the second, the low temperature one. The additive was phenyl- β -naphthylamine (PNA), purified by vacuum sublimation, an antioxidant of relatively low effectivity, which property of the additive was made possible using the method of critical concentration for comparing the ratios of its mobile molecules in the polymer melts. The powders of PNA and polypropylene were mixed by adding a small

amount of the alcohol with subsequent drying at room temperature. The method of determination of the PNA concentration was described in ref. 11.

RESULTS AND DISCUSSION

As shown in Figure 2, the sorption isotherms of PNA in the samples of PP-1, PP-2, and PP-3 from heptane and the solutions markedly differ. All the isotherms may be described by eq. (4) with $[Z_a] = 5.7 \times 10^{-3}$ mol/kg and $\gamma_a K_a = 55$ L/mol for PP-1, $[Z_a] = 4.5 \times 10^{-2}$ mol/kg and $\gamma_a K_a = 12.2$ L/mol for PP-2, and $[Z_a] = 6.8 \times 10^{-3}$ mol/kg and $\gamma_a K_a = 62$ L/mol for PP-3.

At high additive concentrations and at temperatures above the polymer glass transition temperature T_g and especially above the polymer melting temperature, the simple law (4) is violated and the additive concentration in the polymer becomes greater than the $[Z_a]$ calculated at moderate A concentrations.⁹ To explain this phenomenon, consider the possibility of sorption-center transformation.

In writing eq. (7), we supposed that the energy of the formation of the UOD is in direct proportion to the free volume it contains. The energy of formation of bubblelike cavities is a nonlinear function of its volume, and to correspond to this assumption, UODs must be zones of loose packing of polymer chain segments which rearrange at the penetration of the dissolved compound.

If $\varepsilon_i = qv_i$, the value of $\Delta\varepsilon_i/\Delta v_i = q$ does not depend on both v_i and Δv_i values. If the reconstruction of the sorption center is caused by the additive A dissolved in the polymer, that is, $S = A$, eq. (8) may be written as $q = q_0 - q_a$. On the other side, because the dimension of $\Delta\varepsilon_i/\Delta v_i$ is the pressure, meaning that if 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 , that is, to rearrange this center, the certain minimal (threshold) value of the osmotic pressure of the truly dissolved part of the additive in the polymer $P_A = q - q_a$ is needed, which does not depend on the size of v_i . In the polymer melt, when all the volume of the polymer sample is accessible for the mobile part of the additive, this osmotic pressure P_A is

$$P_A = RT[A] = RT\phi[A]_p \quad (15)$$

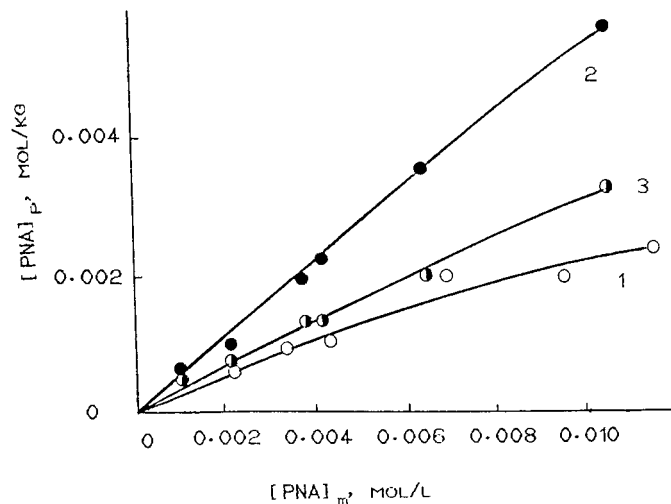


Figure 2 Sorption isotherms of PNA by (1) PP-1, (2) PP-2, and (3) PP-3. 40°C.

where $\phi = [A]/[A]_p$ is the variable coefficient which may be calculated from expression (4). At low $[A]_p$ values ($[A]_p \ll [Z_a]$),

$$P_A = RT[A] = RT[A]_p(K_a[Z_a])^{-1} \quad (16)$$

Transformation of the UOD into a new sorption center Z_{ai}^* may be written as



Assuming that because of the low translation mobility in the solid polymer these new centers after removal of A must exist as relatively stable structures, we studied the effect of high concentrations of PNA in the melt of various polymers on the solubility of the same additive in the solid polymer prepared from this melt.

As seen from Figure 3, if we prepare the polymer films by melting the polymer powder containing the same large concentration of PNA (0.6 mol/kg) at 220°C and after cooling the samples kept them in saturated vapors of the same additive at 40°C, the concentration of the additive decreases, tending to certain limits different for PP-1, PP-2, and PP-3, which were 0.32, 0.22, and 0.17 mol/kg, correspondingly. The concentrations of PNA in nontreated samples in the same conditions were 1.1×10^{-2} , 0.5×10^{-2} , and 0.45×10^{-2} mol/kg at 40°C, that is, many times less than those in the treated ones.

To investigate the process in detail, we studied the dependence of the limiting concentrations

(i.e., solubilities) of PNA in PP-1 after keeping the samples in saturated PNA vapors at 40°C in the initial concentration of the additive in the polymer melt. As seen from Figure 4, the solubility of PNA in the polymer increases when its concentration in the melt exceeds a certain limit (0.15–0.2 mol/kg). Such dependence shows that a certain limiting concentration of the additive is needed to form the new structures sorbing this additive. Similar results were obtained from

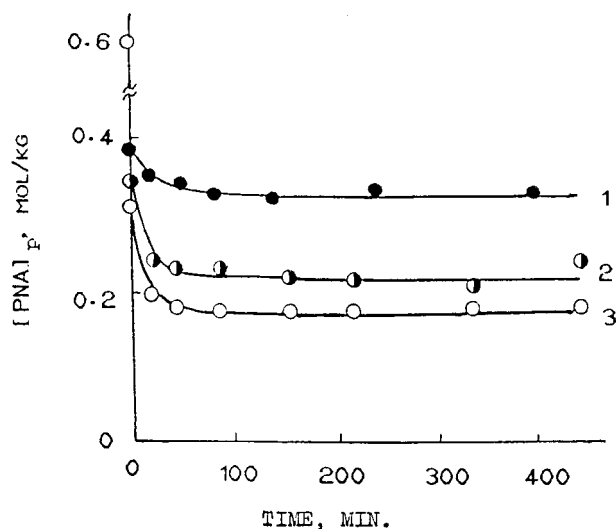


Figure 3 Variation of PNA concentration in polypropylene, prepared of melt containing high concentration of the same compound (0.6 mol/kg at 220°C) in atmosphere of saturated PNA vapors at 40°C: (1) PP-1; (2) PP-2; (3) PP-3.

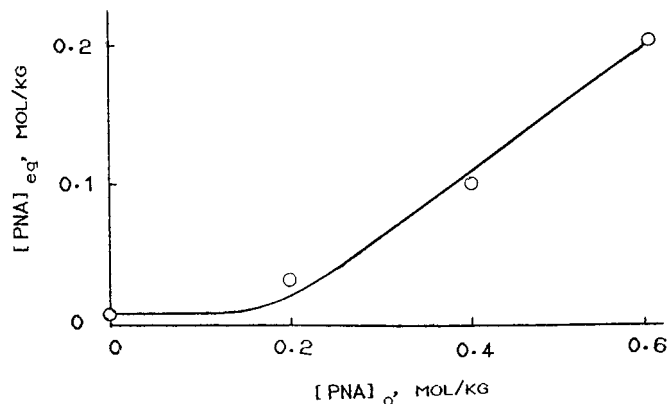


Figure 4 Dependence of PNA solubility in polypropylene on its concentration in the polymer melt: PP-1, 40°C.

studying the transformation of isotactic polypropylene caused by phenylbenzoate.¹²

By heating the samples of PP-1 prepared from the melt containing 0.6 mol/kg of PNA in a vacuum, we may destroy some newly formed centers. As seen from Figure 5, the solubility of PNA at 80°C decreases to 0.7 mol/kg, and when at 100°C, to 0.01 mol/kg, that is, to its solubility before treating. These experiments show that the new sorption centers formed were different in their stability, but above a certain temperature, they disappeared completely. It may be explained assuming that, opposite to the preexisting centers, the newly formed ones are microvoids, the sizes of which are large enough to contain one or several additive molecules. In the absence of the dissolved compound A, these microvoids collapse on heating.

The oxidation of PP-1, PP-2, and PP-3 was

studied at 180°C, that is, above their melting temperatures (about 160°C) and at an oxygen pressure of 300 mmHg in the presence of various concentrations of PNA. As seen from Figure 6, the curves of oxygen consumption show a so-called induction period: During a certain time, the rate of oxygen consumption is negligibly small, while after this period, the rate markedly increases.

Figure 7 shows that the curves' "induction period versus initial PNA concentration" according to the theory discussed possess noncoinciding sharp bends. Calculated from these bends, the critical concentrations for PP-1, PP-2, and PP-3 are, correspondingly, 0.02, 0.040, and 0.058 mol/kg. This shows that the difference in the level of disorder between the samples is preserved in even the polymer melt. It must be noted that the non-precipitated polymer PP-1 differs in the shape of the curve from PP-2 and PP-3, which difference

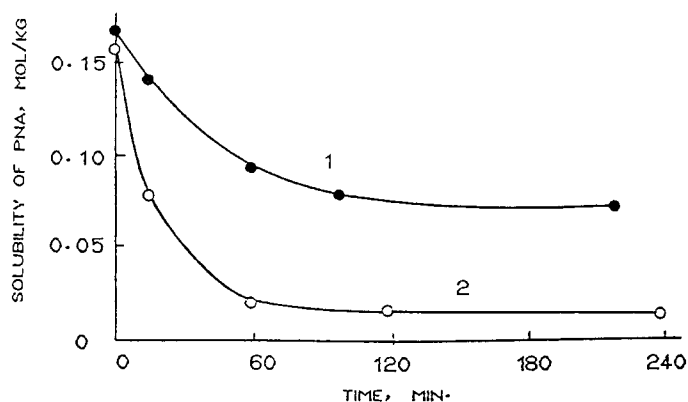


Figure 5 Changes of PNA solubility in the samples of PP-1, prepared from melt containing 0.6 mol/kg of this compound, after heating in a vacuum at (1) 80°C and (2) 100°C.

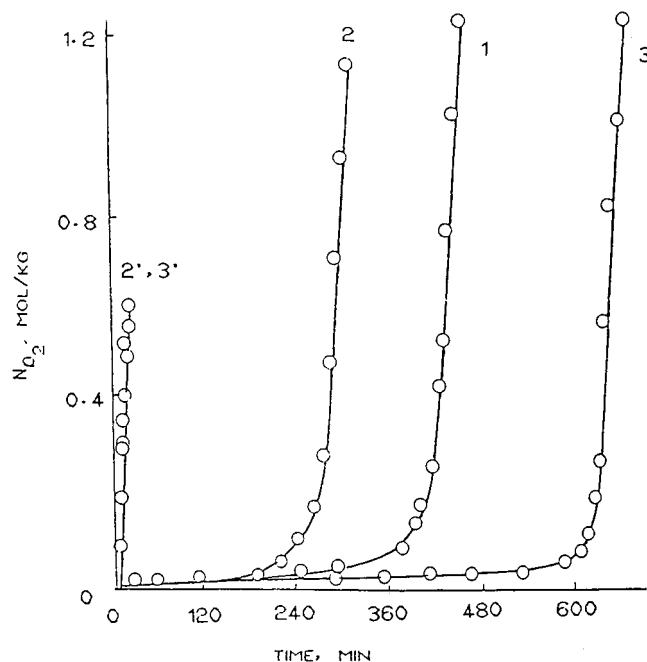


Figure 6 Oxygen consumption during oxidation of polypropylene samples, containing the antioxidant PNA, 0.06 mol/kg, at 180°C, oxygen, 300 mmHg: (1) PP-1; (2) PP-2; (3) PP-3; (2', 3') oxygen absorption by PP-2 and PP-3 in the absence of the antioxidant.

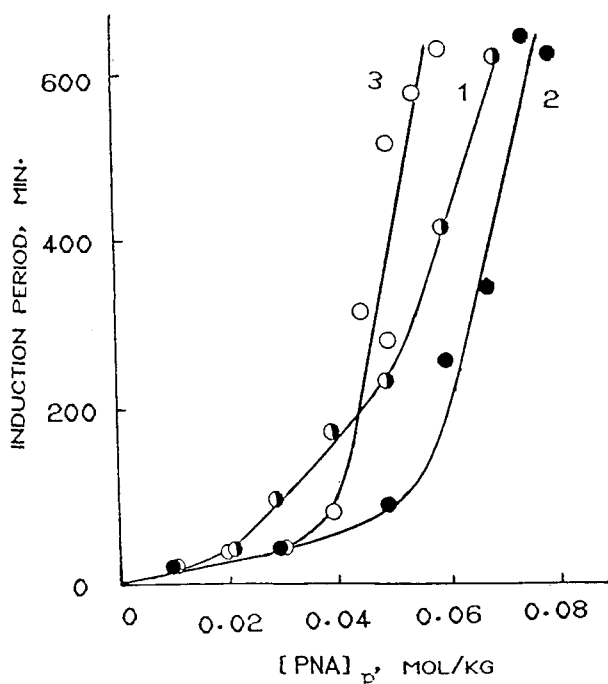


Figure 7 Induction period of oxidation of (1) PP-1, (2) PP-2, and (3) PP-3 as function of initial concentration of PNA: 180°C; oxygen, 300 mmHg.

may be attributed to lesser regularity of its structure. All the values of the critical concentration are greater than the corresponding $[Z_a]$, indicating that the polymer contained newly formed sorption centers Z_a^* along with the preexisting ones Z_a and makes a quantitative explanation of the difference in critical antioxidant concentration difficult.

As shown above, the properties of the bulk polymer depend not only upon the composition and the lengths of its molecules but also on the level of topological disorder in it. Variation of the level of the topological disorder may be achieved in several ways: by variation of the solvent from which the polymer is precipitated,¹³ by variation of its concentration before sedimentation,¹⁴ and, as shown here, by variation of the rate of precipitation. All these structures differ in the type and level of topological disorder, which does not change even above the polymer melting temperature (see also ref. 6). Each type of polymer structure contains the concentration of the sorption centers which is peculiar to the method of its preparation, but does not depend on the current temperature.

Subsequent transformation of the elements may produce additional sorption centers which ex-

ist only in the solid polymer. These centers are unstable and in isotactic polypropylene disappear on heating to 100°C.

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