

# Some Properties of Polyethylene–Heptadecane Mixtures

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**ABSTRACT:** A mixture of high-density polyethylene and its low-molecular-weight analogue heptadecane was studied. The mixture behaved as a compound, that is, differently from polyethylene. Heptadecane reduced the crystallinity of polyethylene, and it intricately changed the concentration of centers sorbing phenyl- $\beta$ -naphthylamine, the antioxidant, and simultaneously changed the equilibrium constant of

sorption. Heptadecane also prolonged the duration of the antioxidant action in polyethylene. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2597–2603, 2003

**Key words:** polyethylene (PE); additive; antioxidant; sorption; oxidation

## INTRODUCTION

A polymeric substance fundamentally differs in its properties from its low-molecular-weight analogues. The great length of a polymer chain makes its translational mobility negligibly small and preserves various violations of the short-range order in the polymer chain arrangement, that is, the topological disorder during the lifetime of the polymer sample.<sup>1,2</sup> Low-molecular-weight compounds that dissolve in a polymer first occupy the free-volume elements formed around these order violations,<sup>3</sup> although a certain portion of the dissolved compound is outside these elements in a mobile form. For a better understanding of the specific features of a polymeric substance, it is interesting to investigate mixtures of the polymer with its low-molecular-weight analogues. For this reason, we studied mixtures of the simplest polymer, linear polyethylene [PE;  $(-\text{CH}_2-\text{CH}_2-)_n$ ], with the linear hydrocarbon heptadecane [HD;  $\text{CH}_3-(\text{CH}_2)_{15}-\text{CH}_3$ ]. Being a low-molecular-weight model of PE, HD molecules are too short for the formation of stable knots or other interlacements. Our main interests were the variation of the sorption properties of the polymer toward the third compound, the antioxidant phenyl- $\beta$ -naphthylamine (PNA), and the variation of the reactivity of PNA toward peroxide radicals ( $\text{RO}_2^\cdot$ ).

To study the sorption properties, we registered the sorption isotherms for PNA from alcohol solutions with films of PE and its mixtures with HD.

The antioxidant effectivity of PNA in PE and its mixtures was used as a quantitative criterion of the reactivity.<sup>4,5</sup>

## EXPERIMENTAL

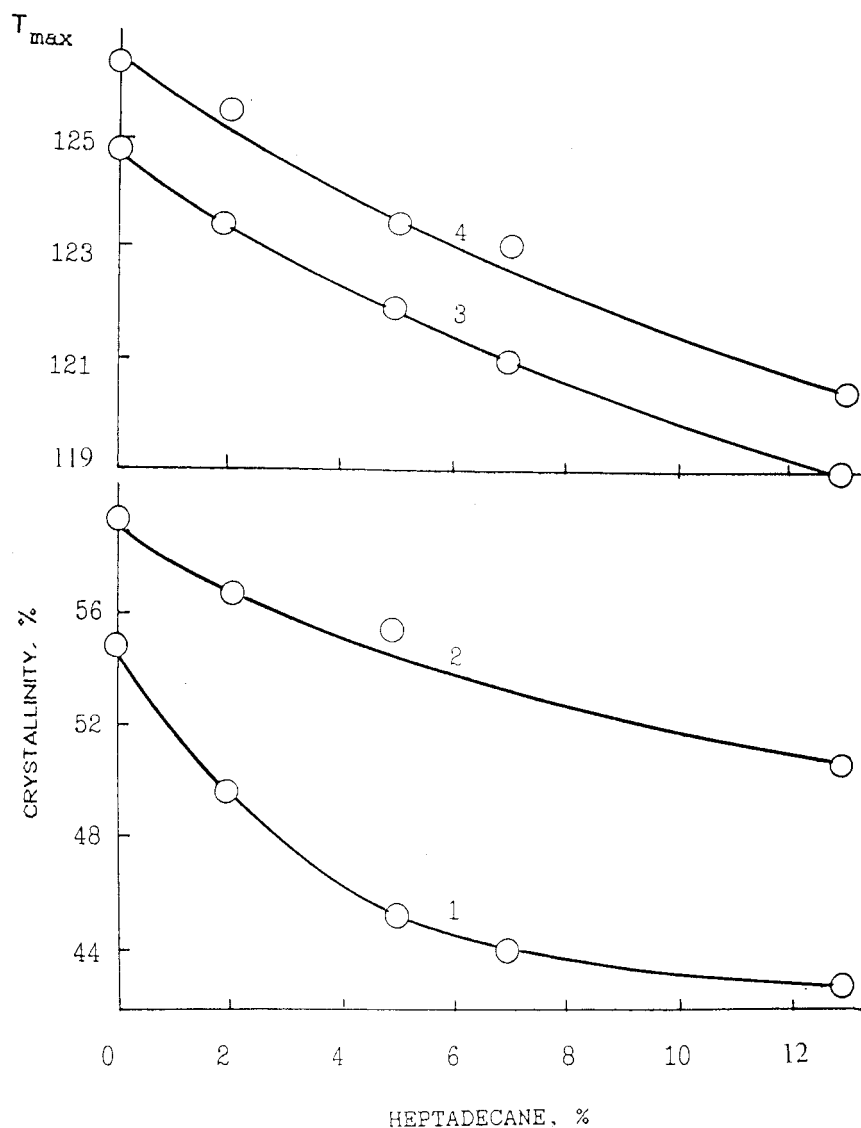
High-density PE in a powder form, consisting of 30- $\mu\text{m}$  particles (molecular mass = 300,000), was washed with alcohol for the removal of low-molecular-weight admixtures, and it was mixed with HD (mp = 22°C) at room temperature, with small quantities of ethanol added, which later was evaporated. The films (50  $\mu\text{m}$ ) of PE and its mixtures were pressed in a nitrogen atmosphere between two layers of aluminum foil at 180°C. The samples were investigated with differential scanning calorimetry; for the determination of the sorption isotherm, the films were saturated with PNA, an antioxidant, from an alcohol solution at 40°C for 200 h. Dissolved PNA was extracted by alcohol (there were two subsequent extractions at 40°C for 120 h each) and analyzed with spectrophotometry.<sup>5</sup>

The samples containing various concentrations of the antioxidant were oxidized in a vacuum device (described in ref. 5) at 200°C and at an oxygen pressure of 300 mmHg; water and other volatile products were absorbed with solid KOH. The concentrations of PNA in the samples and solutions were determined with ultraviolet spectrophotometry.<sup>5</sup> In one series of experiments, the oxidation of PE and its mixtures with 13% HD in the presence of a heavy phenolic antioxidant (the ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl-propionic acid) and pentaerythrol (Irganox 1010) was studied.

## RESULTS AND DISCUSSION

Studying the samples of PE and its mixtures, we twice heated the films from room temperature to 200°C, the heating rate being 16°C/min. As shown in Figure 1, both the degree of crystallinity, calculated from the heat of melting, and the melting temperature (i.e., the temperature corresponding to the maximum on the endothermic peak) decreased with increasing

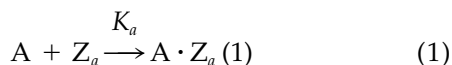
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**Figure 1** (1,2) Crystallinity and (3,4) melting temperature of PE as functions of the HD concentration: (1,3) before melting and (2,4) after melting.

amounts of HD. The second registration always showed greater values for both the crystallinity and melting temperature; this difference may be explained by either annealing of the stressed regions of the PE formed during the sample pressing or by the better mixing of the components during the first heating.

The sorption of low-molecular-weight compounds by polymers is often considered a two-step process:<sup>5-8</sup> first, compound A, penetrating from a surrounding medium into amorphous zones of the polymer, forms the true solution in it, and second, truly dissolved A is reversibly sorbed by certain centers  $Z_i$ :



where  $K_a$  is an equilibrium constant. After the equilibrium is established, a dependence between truly dis-

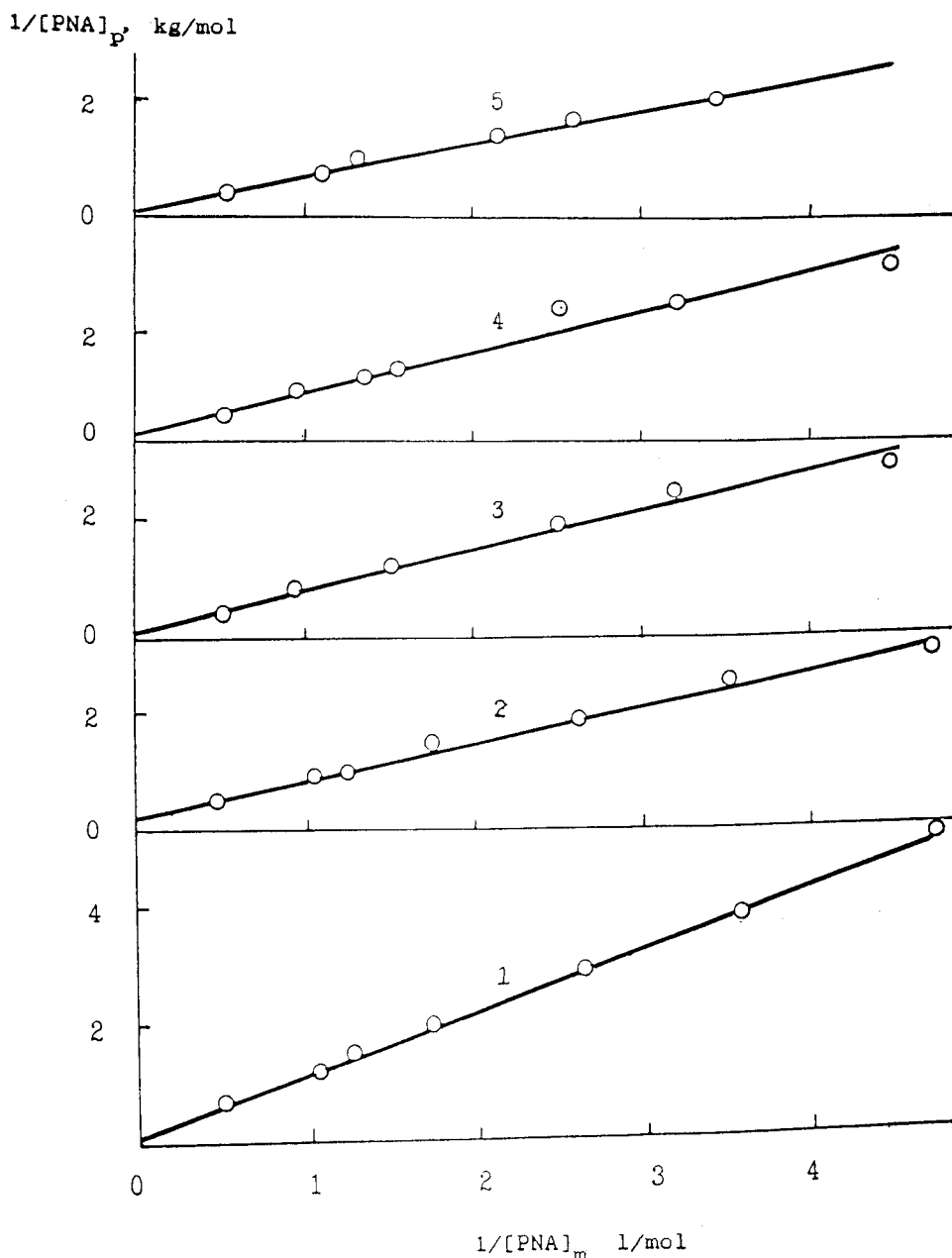
solved A in the surrounding medium ( $[A]_m$ ) and that in the polymer ( $[A]$ ) exists:

$$[A] = \gamma_a [A]_m \quad (2)$$

where  $\gamma_a$  is the coefficient of distribution ( $\gamma_a = [A]/[A]_m$ ). Neglecting the concentration of truly dissolved A with respect to the concentration of complex  $[A \cdot Z_a]$ , we obtain the formula connecting the concentration of A in the polymer with that in the surrounding medium:

$$[A]_p = (\gamma_a K_a [Z_a][A]_m) (1 + \gamma_a K_a [A]_m)^{-1} \quad (3a)$$

Analyzing the sorption isotherm, we may determine the sorption center concentration  $[Z_a]$ , the sorbing low-molecular-weight compounds denoted here as A, and the value of constant  $\gamma_a K_a$ , which characterizes the strength of complex  $A \cdot Z_a$ :



**Figure 2** Sorption isotherms of PNA by PE and its mixtures with HD from alcohol solutions in  $1/[PNA]_m$ - $1/[PNA]_p$  coordinates. The temperature was 40°C, and the concentrations of HD in the polymer were (1) 0, (2) 2, (3) 5, (4) 7, and (5) 13%.

$$[A]_p^{-1} = [Z_a]^{-1} + (\gamma_a K_a [Z_a])^{-1} ([A]_m)^{-1} \quad (3b)$$

The experimentally determined sorption isotherms for different samples possess analogous shapes and may be transformed into straight lines with  $1/[PNA]_p$ - $1/[PNA]_m$  coordinates,  $[PNA]_p$  and  $[PNA]_m$  being the concentrations of PNA in the polymer and in the alcohol solutions (Fig. 2).

The values of  $[Z_a]$  and  $\gamma_a K_a$  depend on the content of HD in the polymer (Fig. 3): with an increasing content of HD,  $[Z_a]$  first decreases, passes over a minimum at 2% HD (or 0.083 mol/kg of HD), and then virtually linearly increases until 13% HD. In the same time,  $\gamma_a K_a$  passes over a maximum and decreases. In the model

used, the decrease in  $[Z_a]$  at low concentrations of HD may be explained by the substitution of one low-molecular-weight compound, PNA, by another, HD, in the centers:



It is obvious that the weaker the complex is, that is, the less  $\gamma_a K_a$  is, the more easily decomposed it is by the third compound, here HD. The decomposition of the weaker complexes must result in an increased ratio of the stronger ones. This is the reason that the average values of  $\gamma_a K_a$  for the remaining complexes increases.

According to refs. 1-3 and 8, the sorption centers are formed around topological structures, that is, various

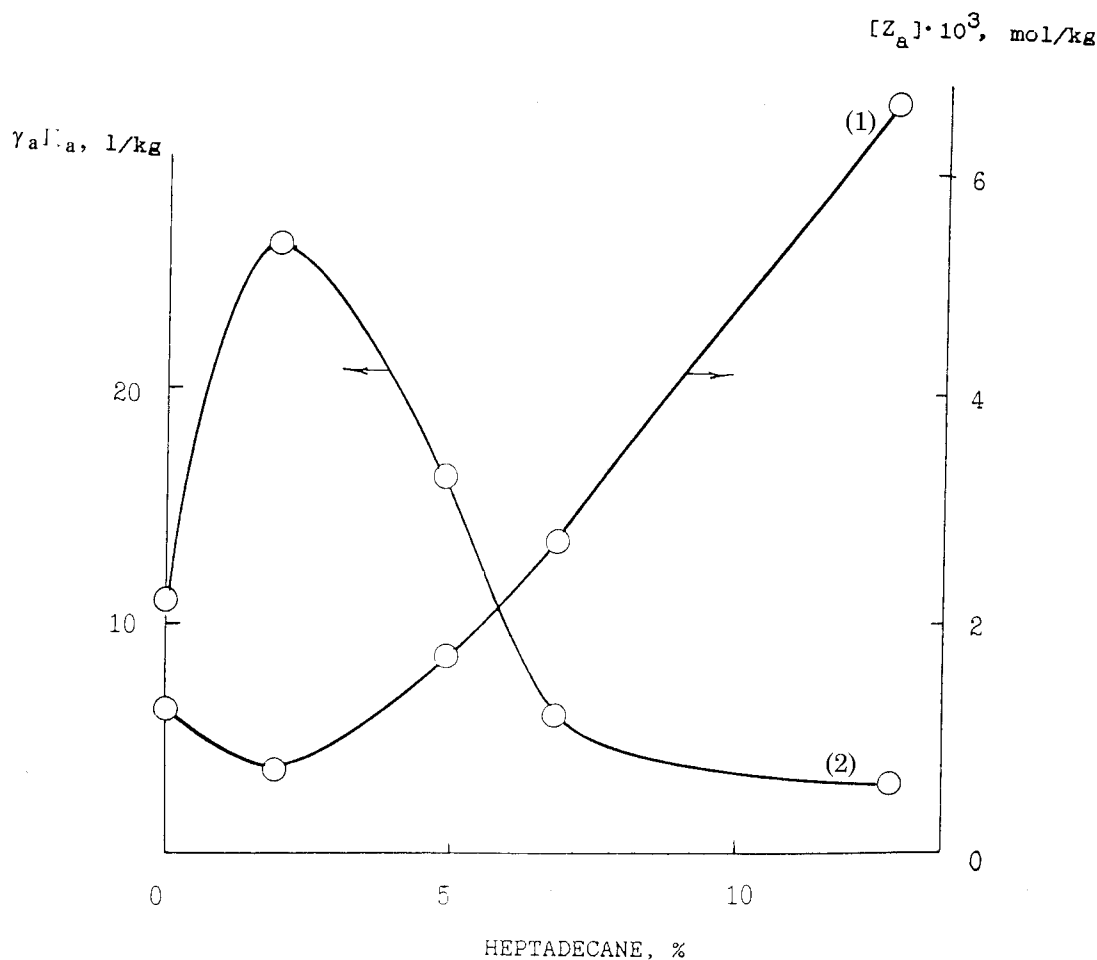


Figure 3 (1)  $[Z_a]$  and (2)  $\gamma_a K_a$  as functions of the content of HD in PE. The temperature was 40°C.

interlacements of the polymer chains ( $\zeta_i$ ). The zones formed around these interlacements contain free (or excess) volume ( $v_i$ ). The increase in  $[Z_a]$  at high HD concentrations may be explained by the rearrangement of  $\zeta_i$ , which are initially inaccessible to the molecules of PNA. This rearrangement is accompanied by an increase in the free volume (i.e., with local swelling):



where  $Z_a^*$  is a structure consisting of the interlacement of the polymer chains and one or several HD molecules capable of sorbing compound A. We suppose that the formation of the new sorption centers in the ordered part of the polymer needs much more energy than the widening of the existing zone with a violated short-range order. To explain the experimentally determined dependence of  $\gamma_a K_a$  on the HD concentration, we must assume that the rearranged centers  $Z_a^*$  form weaker complexes with PNA; that is, they are characterized by lower values of  $K_a$ . As a result, at low HD concentrations, the average  $K_a$  (and  $\gamma_a K_a$ ) values increase, but at high concentrations they decrease with

the HD concentration. Here we may discuss only average values of  $[Z_a]$  and  $\gamma_a K_a$ .

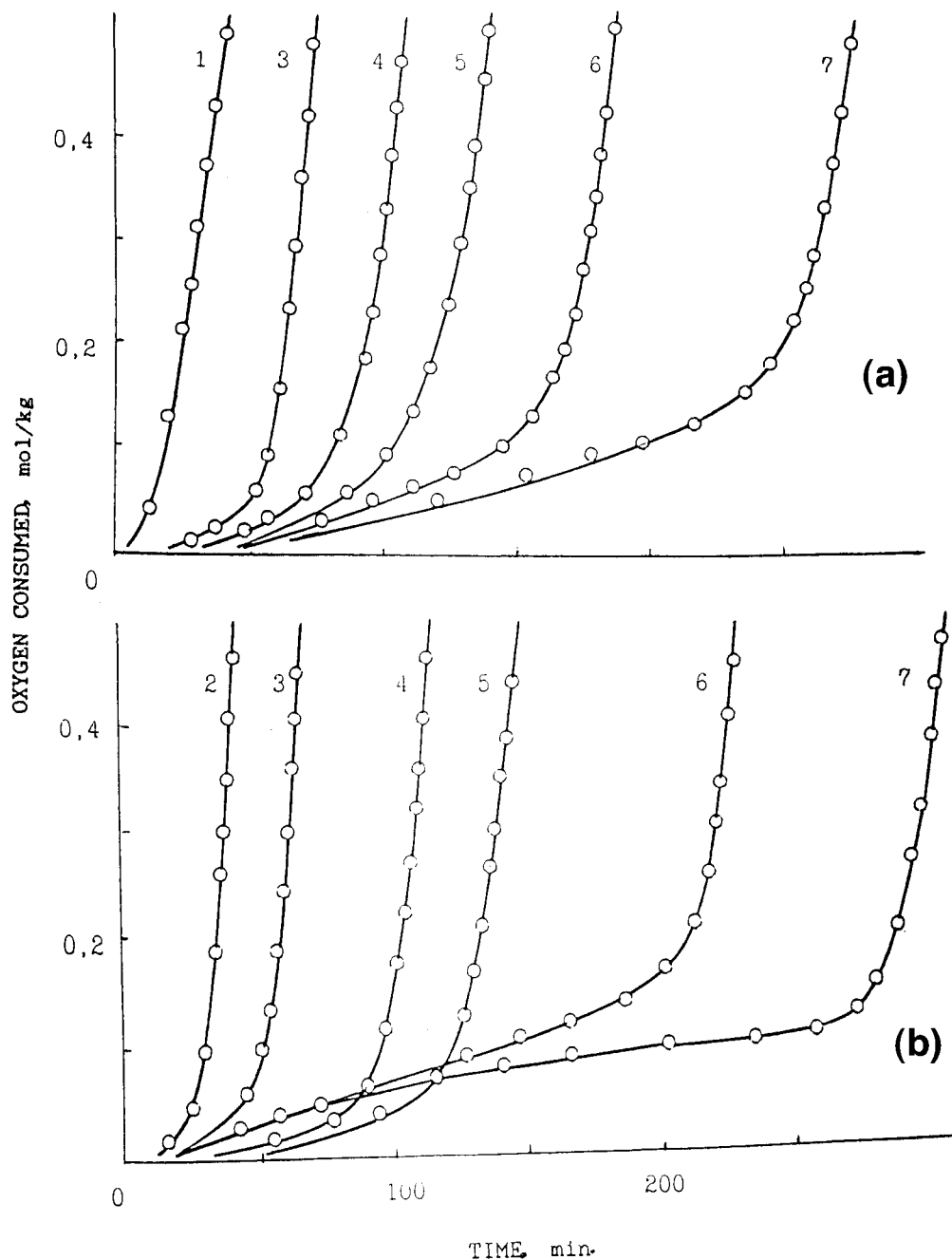
Consider the theory of the retardation of the oxidation of PE and its mixtures. The retardation of the oxidation reaction is based on the interaction of low-mobility macroradicals ( $\text{RO}_2^*$ ) with mobile molecules of an antioxidant (IH):



where  $k_t$  is the rate constant.

With a decreasing ratio of mobile antioxidant molecules not bound to sorption centers, to get the same effect of retardation, we must introduce into the polymer a greater antioxidant concentration. However, the greater part of the antioxidant is consumed not in reaction (6) but in an undesired reaction with high-mobility molecules of oxygen dissolved in the polymer





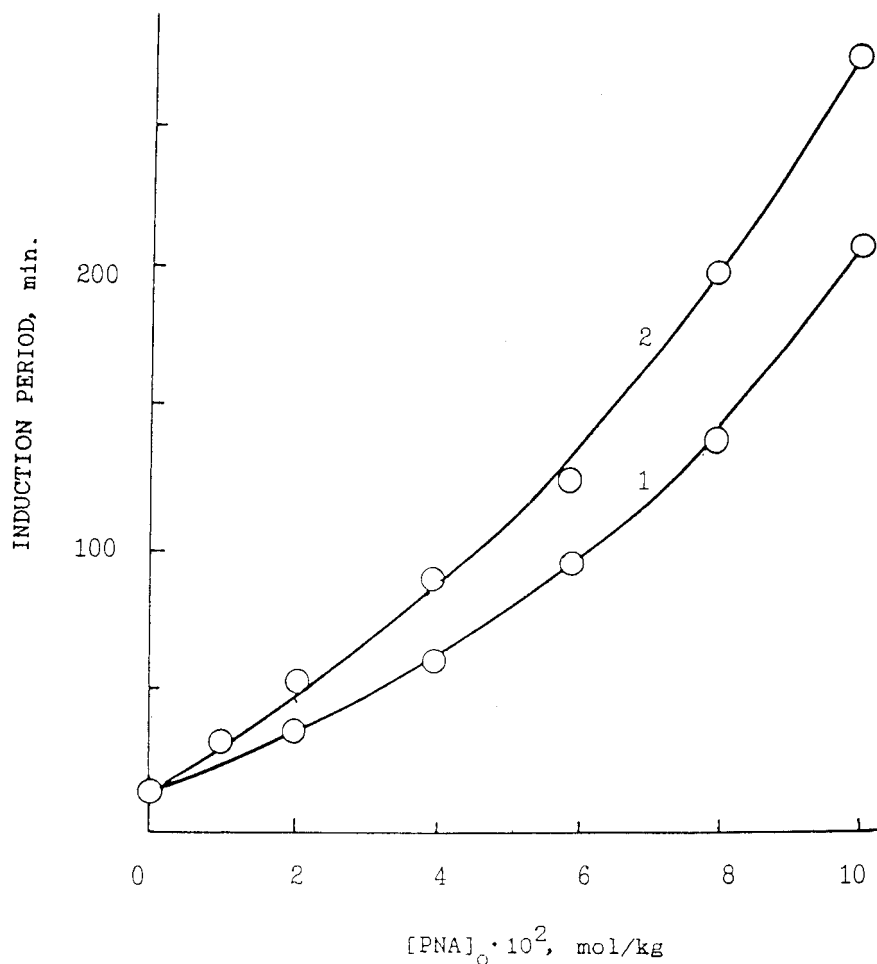
**Figure 4** Oxygen consumption over the course of the oxidation of (a) PE and (b) its mixtures with 13% HD with (1) 0, (2) 0.01, (3) 0.02, (4) 0.04, (5) 0.06, (6) 0.08, and (7) 0.10 mol/kg PNA. The temperature was 200°C, and the oxygen pressure was 300 mmHg.

with a subsequent interaction of free radicals  $I^{\cdot}$  and  $RO_2^{\cdot}$  with the surrounding substance, that is, with the monomeric units of the polymer. The mobile oxygen molecules react, although at different rates, with both mobile and immobile antioxidant molecules.

The experimental curves of oxygen consumption by PE and its mixture with 13% HD over the course of their oxidation at 200°C and at an oxygen pressure of 300 mmHg are shown in Figure 4(a,b). The curves possess analogous shapes, and the rates of oxygen consumption after the induction period virtually co-

incide, but the values of the induction period markedly differ. As seen in Figure 5, the induction periods of the oxidation of mixtures containing 13% HD are, at the same antioxidant concentrations, approximately 20% longer than the induction period of PE itself.

The marked difference in the induction periods of PE and its mixtures has been observed during oxidation in the presence of the ester of 3,5-di-*tert*-butyl-4-hydroxy-phenylpropionic acid and pentaerythrol (Irganox 1010): at 200°C and at an antioxidant concentration of 0.01 mol/kg, the induction period of PE



**Figure 5** Induction period of the oxidation of (1) PE and (2) its mixture with 13% HD as a function of the concentration of PNA. The temperature was 200°C, and the oxygen pressure was 300 mmHg.

oxidation was 720 min, and that of the mixture was 910 min, that is, 26% longer (Fig. 6).

If the concentration of the mobile part of the antioxidant is  $[IH] = [A]$  and its total concentration in the polymer is  $[A]_p$ , at  $[A] \ll [A]_p$ , the ratio of mobile antioxidant molecules according to eqs. (3) and (4) is<sup>9</sup>

$$[A]/[A]_p = (K_a [Z_a])^{-1} \quad (8)$$

As noted previously, in the reaction with the immobile macroradicals  $RO_2^*$ , only mobile antioxidant molecules participate. Taking this into account, we may determine the apparent (or effective) rate constant of chain termination  $[(k_t)_{\text{eff}}]$ :

$$W_t = k_t [A] = (k_t)_{\text{eff}} [A]_p \quad (9)$$

where  $w_t$  is the rate of reaction.

The expression connecting the real rate constant for mobile antioxidant molecules and  $(k_t)_{\text{eff}}$  calculated per total antioxidant concentration is

$$(k_t)_{\text{eff}} = k_t (K_a [Z_a])^{-1} \quad (10)$$

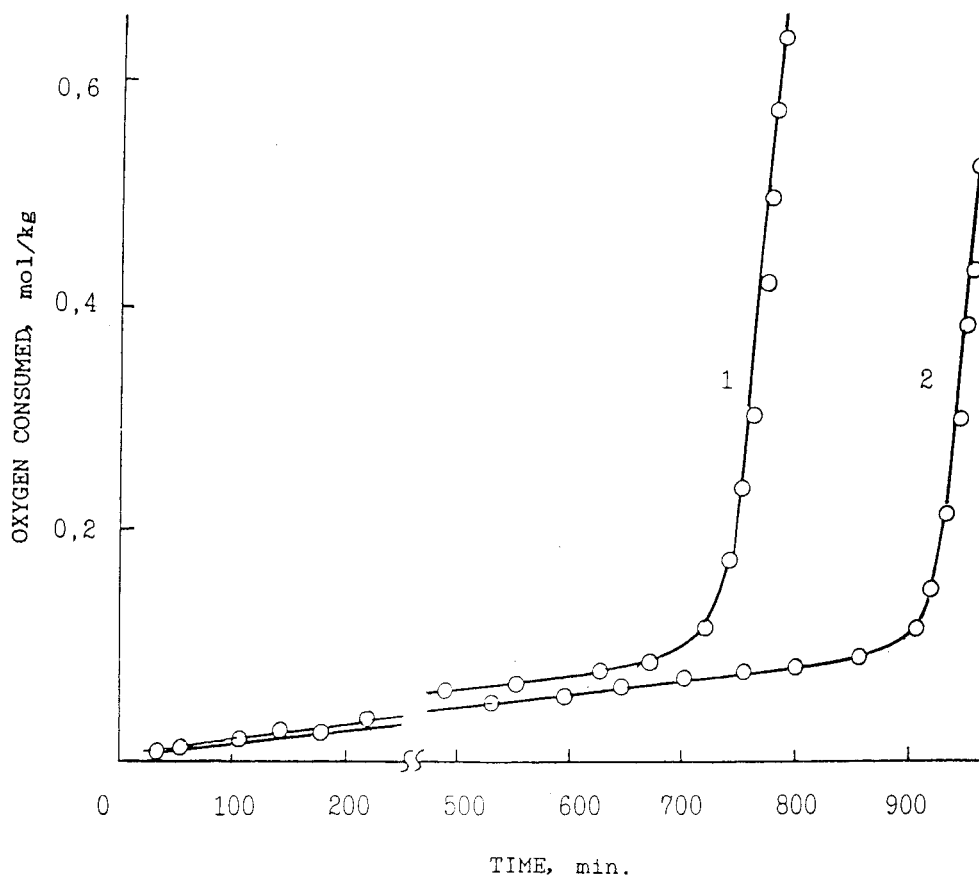
That is, the apparent rate constant must be inversely proportional to  $K_a [Z_a]$ .

The concentration of the antioxidant at which the rate of chain termination is equal to that of chain branching is called the critical antioxidant concentration. According to the theory of critical phenomena, under the same conditions, the critical concentration is inversely proportional to the rate constant of chain termination and, according to eq. (10), directly proportional to  $K_a [Z_a]$ .

In the course of oxidation, the concentration of the antioxidant decreases and at a certain moment reaches its critical value  $[A]_{\text{cr}}$ . In this moment, the process becomes self-accelerated, and after the critical time period  $\tau_{\text{cr}}$ , the induction period ends.

If above the critical concentration, the antioxidant is consumed mainly in a reaction with molecular oxygen, which is first-order in the antioxidant concentration

$$-d[A]/dt = k_{\text{eff}} [A] \quad (11)$$



**Figure 6** Oxygen consumption over the course of the oxidation of (1) PE and (2) its mixture with 13% HD with the antioxidant Irganox 1010. The temperature was 200°C, and the oxygen pressure was 300 mmHg.

the dependence of the induction period on the initial antioxidant concentration will be<sup>5</sup>

$$\tau = \tau_{cr} + (k_{eff})^{-1} \ln([A]_0/[A]_{cr}) \quad (12)$$

Moving from the individual PE to its mixtures with 13% HD, we see that the product  $\gamma_a K_a$  increases from 0.11 to 0.16 l/kg, and so the value of  $[A]_{cr}$  must increase with a reduction in the induction period. The other reason for the increase in the induction period is the simultaneous effect of HD on the rate of antioxidant oxidation, that is, on  $k_{eff}$  in eq. (12), which mainly proceeds in the sorption centers.

In our investigation, the sorption of PNA, the antioxidant, was studied at 40°C with an alcohol solution of PNA, and we obtained not  $K_a$  but its product  $\gamma_a K_a$ . At the same time, inhibited oxidation was studied at 200°C without any solvent. For this reason, we cannot expect any quantitative correlation between the data on sorption and inhibited oxidation, but one conclusion is quite definite: the molecules of the low-molecular-weight model behave as foreign inclusions in the polymeric matrix.

In ref. 10, the total concentration of topological structures in industrial PE ( $\Sigma[\zeta_i]$ ) was reported to be 0.26 mol/kg. The maximum value of  $[Z_n]$  found in this study was 0.069 mol/kg. In other words, even in the mixtures of PE with 13% HD, only approximately one-fourth of the topological structures participated in the formation of sorption centers for PNA.

## References

1. Shlyapnikov, Y. A. *Dokl Akad Nauk* 1972, 202, 1377.
2. Shlyapnikov, Y. A. *Russ Chem Rev* 1997, 68, 963.
3. Kolesnikova, N. N.; Shlyapnikov, Y. A. *Vysokomol Soedin* 1994, 36, 1322.
4. Shlyapnikov, Y. A. *Pure Appl Chem* 1980, 52, 337.
5. Shlyapnikov, Y. A.; Kiryushkin, S. G.; Mar'in, A. P. *Antioxidative Stabilization of Polymers*; London: Taylor & Francis, 1996.
6. Barrer, R. M.; Barrie, J. A. *J Polym Sci* 1957, 23, 311.
7. Assink, R. A. *J Polym Sci Polym Phys Ed* 1975, 13, 1665.
8. Mar'in, A. *Polymer Yearbook*; Harwood Academic: Reading, England, 2000; Vol. 17, p 3.
9. Shlyapnikov, Y. A. *Eur Polym J* 1998, 34, 1177.
10. Gedraitite, G. B.; Mar'in, A. P.; Shlyapnikov, Y. A. *Eur Polym J* 1989, 25, 39.