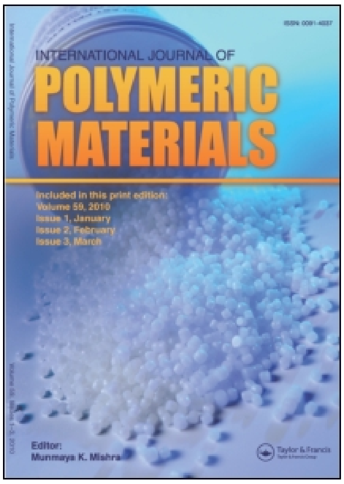

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Additives Solubility in Polymers*

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The dissolution of additives in polymer is considered from point of view of non-uniform polymer structure and existence of sorption centers arising around polymer chain entanglements. The review contains the quantitative data on solubility of different stabilizers in polymers and on effect of polymer structure and oxidation on additive solubility.

Keywords: Polymer additives; dissolution; sorption centers; temperature dependence; crystallinity; copolymers; polymer blends

1. INTRODUCTION

Polymer based materials, as usual, contain besides the polymer, different low-molecular weight compounds such as stabilizers, plastisizers, dyes, dissolved gases, accidental and technological impurities. During exploitation, these materials can come in contact with water, organic liquid, solid substances and also with food-stuffs that could result in the transfer of additives and impurities dissolved in polymer to the surroundings, polluting them and decreasing the life time of the polymer. On the other hand, low-molecular weight compounds from the surroundings can pass into the polymer. The transport of additives between polymers and surroundings is controlled by processes based on sorption (dissolution) and diffusion.

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The retardation of polymer oxidation involves the reactions between macroradicals forming during oxidation and stabilizer molecules. For this reason stabilizer should be good soluble in the polymer. If the stabilizer concentration is higher than its solubility it can easy leak from the polymer and form a separate phase inside the polymer resulting in fast change of its properties. The solubility depends on the type of stabilizer and polymer used, *i.e.*, their chemical and physical structure.

This review includes a unique cover on different aspects of additives solubility in polymers in light of the polymer degradation and stabilization.

2. NON-HOMOGENITY OF POLYMER SUBSTANCE

The polymeric substance is non-regular. This irregularity may display at different levels: molecular, topological and morphological (structural). The first level is due to the chain like structure of the polymer molecule and the existence of non-equivalency (anisotropy) along and across the polymer chain.

Topological irregularity is due to existence of ends of polymer chains and various polymer chain entanglements surrounded by relatively ordered substance in which the short range order is obeyed.

The third level, morphological irregularity, is based on the existence of relatively large (10^{-6}cm and greater) zones markedly differing in character of arrangement of segments of macromolecules forming these zones and in their physical properties. In crystalline polymers this irregularity gives rise to formation of crystalline and amorphous regions. Crystallites, zones in which the long range order in arrangement of monomer units exists, are divided by zones of non-ordered amorphous substance, where there is only a short range order. Crystallites form more complicated structures: fibrils which are the chains formed from a great number of crystallites divided by amorphous layers, and spherulites – three-dimension structures, having a spherical shape. The sizes of fibrils reach $10^{-5} - 10^{-4}$cm and those of spherulites are 10^{-2}cm and higher.

Low molecular weight compounds dissolved in a polymer are mainly present in the amorphous regions of the polymer substance. In the crystalline part they either do not dissolve or dissolve in extremely low quantities.

Bogaevskaya *et al.* [1] were the first who made direct experiments on the distribution of diazo-dyes in crystalline polymers. Using optical microscopy they showed that dyes concentrate in the less-ordered zones on the boundaries of spherulites and in zones inside the spherulites between the fibrils. The intensity of color decreased from the periphery to the center of the spherulites. Later the method of radiothermoluminescence (RTL) was used for the study the amorphous zones of polymers. It was shown [2] that the source of the light emission in polypropylene is the amorphous substance which does not turn the polarization plane, mainly disposing between spherulites and their external contours. The addition of phenyl benzoate to the polymer gives rise to quenching RTL at 240 – 270 K showing that the additive molecules are present in the same regions of amorphous substance.

Ultra-violet and fluorescent spectroscopy has been also used to carry out the distribution of stabilizer molecules in polypropylene [3 – 5]. It was shown [3] that during crystallization of the polymer there is a flow of additive from the growing crystallites to non-crystalline zones in the spherulites between the fibrils, and among the spherulites. The concrete distribution of additive depends on different factors (cooling rate, part of crystalline fraction). The authors of this study assumed that in the melt of the polymer additives are uniformly distributed.

The question about the detailed structure of topological irregularities of flexible-chain polymers is still not clear and discussed [6 – 10]. The data on the rheology of the polymer melts and their concentrated solutions demonstrate that they behave like polymer network with chemical bonds, *i.e.*, between the chains a specific topological knots with limited life time are formed. Their life time rapidly increase with molecular weight of the polymer and becomes minutes for polymers with $M > 10^6$ even when they above the glass transition temperature. The reptation model [6 – 8] has been proposed for the explanation of this effect, but the long-time memory in the polymer melt which can reach many hours cannot be explained according to this model [11].

De Gennes [11] assumed that during crystallization, chains that are knotted, and that are reeled in from both ends, might make very tight knots. These knots are expected to be very stable and to persist for long times after the sample is heated above the melting temperature.

Shlyapnikov [12 – 13] proposed "two-component model" for the explanation of nonhomogeneity of polymer oxidation. According to this model the polymer is considered as ideally ordered substance in which the elements of disorder are districted. These elements are the stable topological formations: knots, folds, ends and different entanglements of the polymer chains. The content of these elements may be expressed in units of concentrations. The great length of the polymer chains makes these topological structures very stable. These interlacements of macromolecules possess the definite sizes which in the simplest cases are about (1 – 3) 10^{-7} cm and violate the order in the arrangement of neighbouring monomeric units. The poor arrangement of polymeric substance in the zones of short range order violation results in the decrease of the polymer density in these zones, *i.e.*, these zones are carriers of free volume polymer contains.

3. REGULARITIES OF ADDITIVE DISSOLUTION

3.1. Sorption Isotherms

The additional information on polymer structure, the mechanism of additives dissolution and distribution may be obtained, studying the sorption isotherms, *i.e.*, the dependence of equilibrium concentration of the compound in the polymer on its concentration or vapor pressure around the polymer.

The simplest type of sorption isotherm corresponds to the case of ideal solution and is described by Henry's law: the concentration of compound A in the polymer ($[A]_p$) is directly proportional to its concentration (pressure) in the surroundings ($[A]_m$)

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

where γ is the coefficient of solubility.

Equation (1) means that dissolution of A does not results in the change of the properties of the polymer medium. In practice isotherms like (1) are observed only in the range of low concentrations of dissolved compound.

In many cases the sorption of additives is described by a law analogous to the Langmuir Eq. (2) or by its combination with Henry's law (3):

$$[A]_p = \frac{a[A]_m}{1 + b[A]_m} \tag{2}$$

$$[A]_p = \gamma[A]_m + \frac{a[A]_m}{1 + b[A]_m} \tag{3}$$

where a and b are constants; a/b ratio corresponds to the limit of A concentration in polymer.

The dependence (2) infers an existence of certain limited concentration of sorption centers in the polymer and, therefore, the process of dissolving a compound in the polymer may be considered as process of filling these centers. Equation (3) supposes that the Langmuir type sorption takes places at the same time with the sorption accordance with Henry's law.

The nature of sorption centers may be different. The polymer polar groups interacting with an additive (for example, due to formation of hydrogen bonds), as well as the regions with a lesser density of a polymer substance (the elements of free volume) in the polymer may be regarded as such centers. The latter have either a relaxed, or a topological nature [14–21]. Some authors [14–18] consider the sorption centers as microvoids and unrelaxed volume in the polymer below the glass transition temperature which disappear at high temperature. In contrast the centers arising around knots and other chain entanglements are more stable and can exist also in the polymer melt [20–21].

Consider that in the polymer a certain concentrations of the same centers Z is present which can interact with compound A. Let us suppose that the sorption of additive proceeds in two steps. First the additive forms a true solution, the concentration of A in this solution is related to its concentration around the polymer by Henry's law, that is $[A] = \gamma[A]_m$. Then this truly dissolved additive is reversibly sorbed by centers Z:

$$A + B \overset{K_a}{\rightleftharpoons} AZ \tag{4}$$

The equilibrium constant of sorption is

$$K_a = \frac{[AZ_a]}{[A]([Z_a] - [AZ_a])} \tag{5}$$

where $[Z_a]$ denotes the total concentration of the centers, both occupied or not occupied by A; $[AZ_a]$ is the concentration of compound A present in the sorption centers Z.

The total concentration of A in the polymer is the sum of $[A]$ and $[AZ_a]$, *i.e.* $[A]_p = [A] + [AZ_a]$. Assuming that $[A] \ll [AZ_a]$, we get:

$$[A]_p = \frac{K_a[Z_a]}{1 + K_a[A]} = \frac{\gamma[A]_m K_a[Z_a]}{1 + \gamma K_a[A]_m} \tag{6}$$

The formula (6) is equivalent to Langmuir type isotherm (4) assuming $a = \gamma K_a[Z_a]$ and $b = \gamma K_a$.

It is difficult to imagine that in the polymer there are various centers specific for each compound. The more probable that the different compounds can be sorbed by the same centers and there is the certain set of centers sorbing each definite compound.

The vapors pressure of antioxidants is a very low therefore a special device should be used to investigate the sorption isotherms of antioxidants from their vapors. The sorption of 2,6-di-*tert*-butyl-4-methylphenol by polypropylene at the temperature interval 110–200°C was studied measuring the antioxidant concentration in gas phase by UV spectrophotometry [21–22]. Figure 1a shows that the sorption isotherms of this antioxidant in polypropylene are non-linear at all the temperatures studied. Experimental data for each temperature may be transformed into straight lines in the coordinates $1/[A]_p$ *vs* $1/[A]_m$ (Fig. 1b).

Transforming formula (6) we find:

$$1/[A]_p = b/a + 1/(a[A]_m) \tag{7}$$

If $1/[A]_m \to 0$, $1/[A]_p \to b/a$.

As seen from Figure 1b, the lines corresponding to different temperatures intersect the ordinate axis in the same point, *i.e.*, the ratio $a/b = [Z]$ is constant over the range investigated, both below and above the polymer melting temperature (170°C).

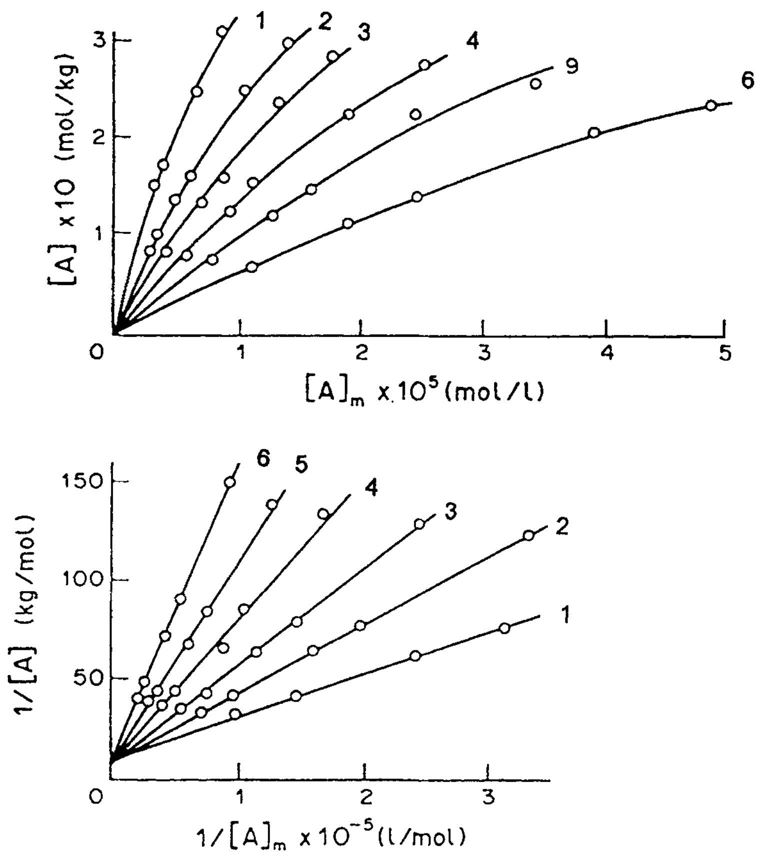


FIGURE 1 The sorption isotherms of 2,6-di-*tert*-butyl-4-methylphenol by polypropylene. Temperatures: 110°C (1), 120°C (2), 130°C (3), 140°C (4), 180°C (5) and 200°C (6).

Independence of the concentration of sorption centers on temperature was also observed studying the sorption of phenylbenzoate by polyethylene [*Z*] remained the same in temperature range from solid polymer to the polymer melt [22–23]. In case of sorption of diphenyl amine and phenylbenzoate by polypropylene the concentration of sorption centers changes near the melting point of the polymer but outside it remains constant [21, 24].

When sorption is carried out from the solution and solvent does not affect the polymer structure, the Langmuir type sorption can also take place but the concentration of sorption centers is usually less than that from gas phase (the reason of it we will discuss later).

In a polymer containing polar groups the mechanism of sorption may be more complicated and includes the interaction of polar groups of polymer (X) with groups of dissolved additive [21, 25, 26]:

$$A + X \rightleftharpoons AX \tag{8}$$

It was shown [25] that sorption of diphenyl methane, diphenyl amine and 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol) by polar polyamide-12 and nonpolar polyethylene obeys to Eq. (2) but the concentration of sorption centers $[Z]$ available for biphenol and diphenyl amine in polyamide was higher by factor of 14 and 16 than that in polyethylene; the concentration centers, participating in sorption of nonpolar diphenyl methane was only slightly different.

3.2. Mutual Sorption of Additives

Polymers are usually contain different additives present together. The existence in the polymer centers capable to sorb both additives (*i.e.*, A and B) should result in decrease in the concentration of one compound in the presence of another one due to the competition for sorption centers. Formally it may be presented as

$$\begin{aligned} A + Z_i &\rightleftharpoons AZ_i \\ B + Z_i &\rightleftharpoons BZ_i \end{aligned} \tag{9}$$

or

$$B + AZ_i \rightleftharpoons A + BZ_i$$

The concentration of A in the polymer as function concentration of B in the polymer is

$$[A]_p = \frac{\gamma[A]_m K_a [Z_a]}{1 + \gamma K_a [A]_m}\left(\sum([Z_i] - [BZ_i])\right) \tag{10}$$

If $\Sigma\ [BZ_i] \approx [B]_p$, the linear dependence between concentrations of both compounds should take place: the dissolution of B results in equivalent decrease of A concentration in the polymer. But it is not possible to have the complete replacement of one additive by another one. Substitution is observed only in limited range of both additives concentration which shows that there are some centers which do not take part in the substitution process (Fig. 2) [20, 22].

The role of the second compound *B* in scheme (9) can play low-molecular solvent occupying centers *Z*. As the result the concentration of *Z* in case of sorption from solution may be lower compared with that from gas phase. It was shown [21, 28] that [*Z*] are equal to 0.06 and 0.59 mol/kg in a case of sorption of diphenylamine by polypropylene from ethanol solution and from gas phase accordingly.

3.3. The Size Distribution of Additive Sorption Centers

The density of the polymeric substance in the sorption centers is lower than that for the surroundings polymer so that the centers may be considered as units of stable free volume present in the polymer. It is obviously seems that the free volume present in the center *Z* corresponds to the maximum volume of a molecule sorbed by this center. Most of the usual organic compounds possess approximately the same density. Thus for elementary unit of the free volume, there exists a certain maximum molecular weight of the compound sorbed by the center. In each polymer there must be a certain size distribution of the sorption centers, according to which the Langmuir sorption capacity of the polymer (*i.e.* [*Z*]) must decrease with increasing molecular of the additive.

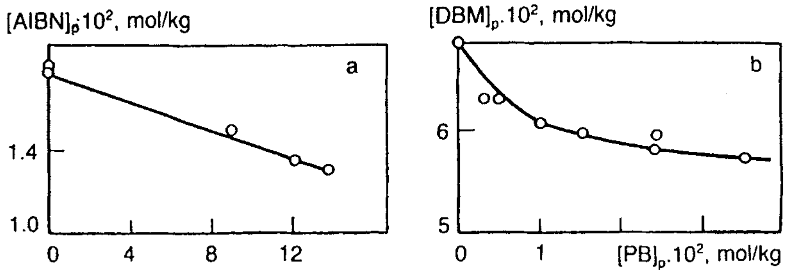


FIGURE 2 Replacement of azo-bis-isobutironitrile (a) and dibenzoylmethane (b) by phenyl benzoate in polypropylene; $[AIBN]_o = 0.6$ mol/l, benzene solution; $[DBM]_o = 0.2$ mol/l, ethanol solution 40°C.

On the other hand, the energy of interaction of the additive molecule with the polymer depends not only on the area of its contact with the polymer, which may be a function of the molecular weight but also on many factors including the chemical nature of the additive and polymer, so one cannot expect an simple correlation between the sorption constants K_a or $K_a\gamma$ and the molecular weight of the additive.

The sorption of various antioxidants by polyethylene from hexane and isopropanol solution was found to obey the Langmuir sorption law. The concentration of centers participating in sorption decreases with molecular weight (Fig. 3) and the dependencies for all systems studied are given by straight lines in coordinates Molecular weight – log$[Z]$ [29]. Thus this dependence may be written in the form

$$[Z] = \varphi \exp(-\nu M) \tag{11}$$

where for the system HDPE – *n*-hexane $\varphi = 0.26\,\mathrm{mol/kg}$ and $\nu = 7.0\,10^{-3}$.

The value of the product $K_a\gamma$ increases with the additive molecular weight. As seen from Figure 4, the experimental points fall between two straight lines separated by 0.3 logarithmic units.

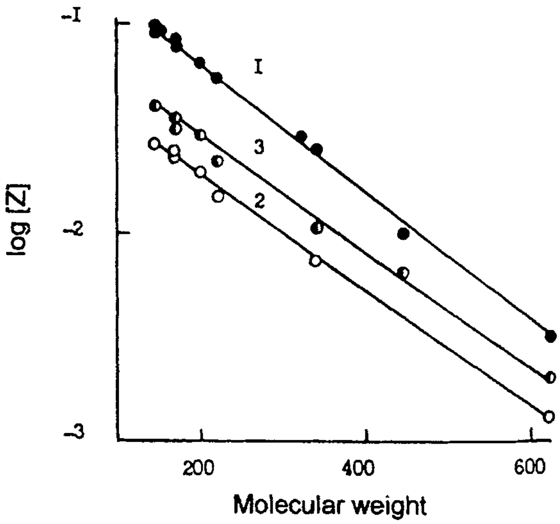


FIGURE 3 The concentration of sorption centers as a function of additive molecular weight. System: (1) HDPE – hexane; (2) HDPE – isopropanol; (3) LDPE – isopropanol, 50°C.

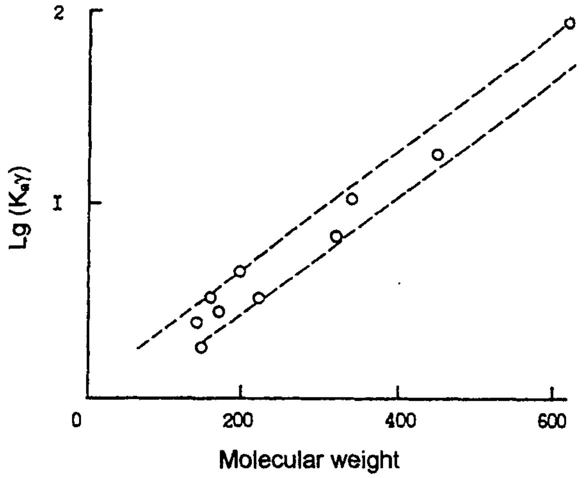


FIGURE 4 Log ($K\gamma$) as a function of additive molecular weight. System: HDPE – hexane, 50°C.

The dependence of [Z] on molecular weight found shows the distribution of the sorption centers according to the free volume they contain.

3.4. Changes of Polymer Structure Caused by Dissolved Additives

In some cases at high concentration of additive the sorption isotherms change their shape and a strong increase in sorption is observed (Fig. 5). It is interesting that the additive concentration in the polymer corresponding to the bend is practically independent of temperature. Such features of sorption isotherms, often observed in practice can be explained by means of polymer swelling resulting to changes in the polymer properties and mechanism of sorption [20–22].

In the work [30] the sorption of vapors of 2,6-di-*tert*-butyl-4-methylphenol by HDPE containing different concentration of heptadecane has been studied. It was shown that sorption isotherms at 100–200°C are presented by Eq. (6). The concentration of sorption centers has no dependence on temperature, but depends on the concentration of heptadecane in a polymer: it passes over the minimum at heptane concentration of about 1% (Fig. 6). The decrease of

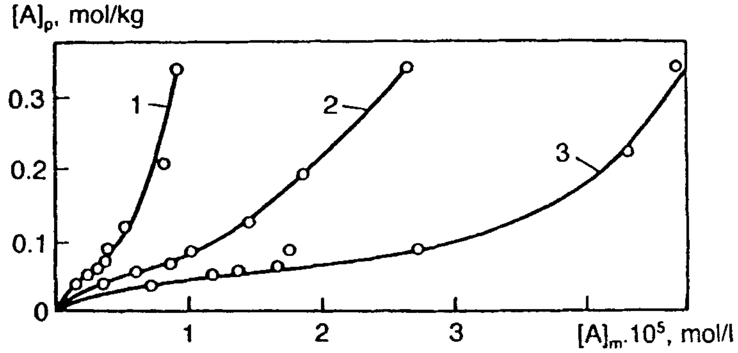


FIGURE 5 Sorption isotherms of phenyl-β-naphthyl amine by polypropylene from gas phase at 160°C (1), 190°C (2) and 210°C (3).

concentration of a sorption centers caused by heptadecane may be explained by the competition between heptadecane and phenol for sorption centers. To this, in particular, testifies an approximate coincidence of the $[Z]$ decrease with the amount of heptadecane introduced into the polymer in the range of 0.5% (0.02 mol/kg) concentrations. The right section of the curve $[Z]$ *vs* the heptadecane concentration may be explained by the rearrangement of Z centers by heptane.

In accordance with (6), the value $K_a\gamma = b$ characterizes the strength of bonding of an additive A with the sorption centers. As can be seen from the Figure 6, with an increase of the heptadecane concentration an a polymer, the value $K_a\gamma$ changes antibately to $[Z]$, *i.e.*, the low molecular hydrocarbon influences not only the concentration of the sorption centers, but also the properties of these centers. The opposite directions of the changes of $[Z]$ and $K_a\gamma$ result in a complex change of a vapor pressure of the antioxidant over the polymer ($[A]_m$) on heptadecane concentration. The enthalpy of solution changes by the similar way with heptadecane concentration.

The effect of low and high concentrations of octamethycyclotetrasiloxane (OMTS) on sorption of phenyl-β-naphthyl amine in melted LDPE was studied [31]. Figure 7 shows the amine concentration in gas phase above polyethylene as a function of the OMTS concentration in it at a constant amine concentration (0.08 mol/kg) in the polymer. As can been seen from the Figure 7, low OMTS

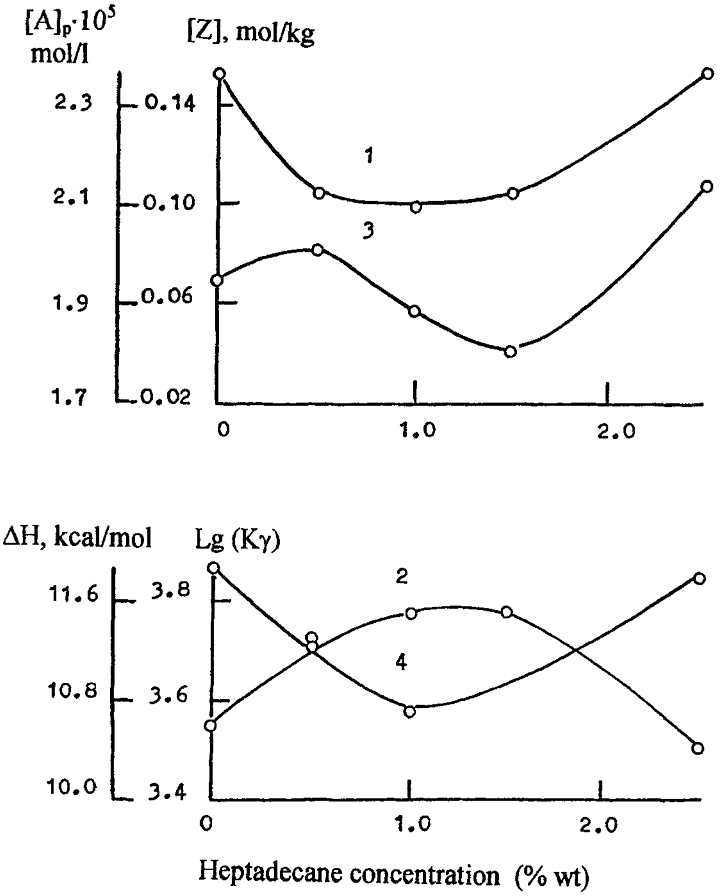


FIGURE 6 Dependence of [Z] (1), $K\gamma$ (2), $[A]_m$ (3) and ΔH (4) on the content of heptadecane in polyethylene; the values $K\gamma$ and $[A]_m$ were obtained at 200°C.

concentrations in the polymer increase the amine concentration in the gas phase, *i.e.*, that OMTS substitutes amine in the sorption centers according to expression (10). Above a certain OMTS concentration, which is about 0.003 mol/kg at 180°C and decreases with increasing temperatures, the amine concentration above the polymer sharply decreases, which can be attributed to the sorption centers rearrangement.

An analogous dependence has been observed in studying the dependence of the concentration of phenyl benzoate above poly-

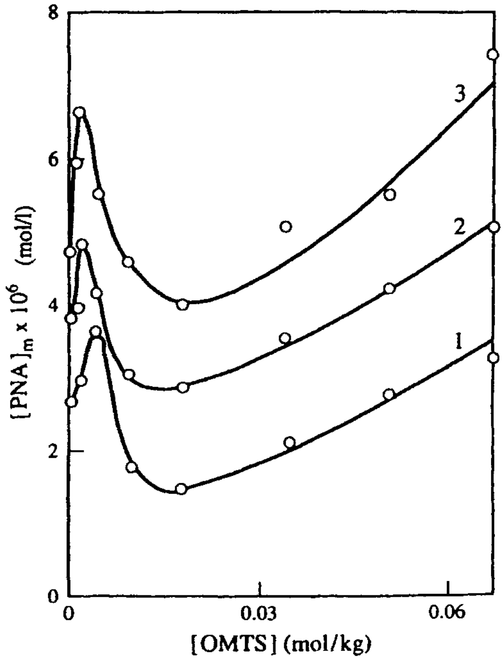


FIGURE 7 Concentration of phenyl-β-naphthyl amine in gas phase above polyethylene as a function of concentration of octamethylcyclotetrasiloxane $[\mathrm{PNA}]_p = 8 \times 10^{-2}$ mol/kg; 180°C (1), 190°C (2) and 200°C (3).

propylene melt on the concentration of natural antioxidant gossipol [56].

In other experiments [20, 27], high amount of phenyl benzoate (0.6 mol/kg) was added to the polypropylene melt and then was extracted from the rapidly cooled sample. The concentration of centers sorbing the same additive from benzene solution increased from 0.17 to 0.9 mol/kg, *i.e.*, 5.9 times. The increase in the concentration centers sorbing another additive, benzoil peroxide, was less pronounced (1.3-fold, from 0.033 to 0.044 mol/kg), and the concentration centers sorbing diphenyl methane decreased 2-fold (from 0.5 to 0.25 mol/kg).

To explain the change of sorption capacity it is necessary to suppose that different types of sorption centers are in equilibrium in the polymer melt

$$Z_{1j} \rightleftharpoons Z_{2j} \rightleftharpoons Z_{3j} \rightleftharpoons \cdots \rightleftharpoons Z_{nj} \qquad (12)$$

Compound A which can be sorbed by only one type of centers Z_{1j} (or by any part of them) can shift equilibrium (12) in such way that the concentrations of the centers sorbing this compound will increase, but those of other centers will decrease (scheme 13):

$$AZ_{1j} \rightleftharpoons Z_{2j} \rightleftharpoons \cdots \rightleftharpoons Z_{nj} \qquad (13)$$

This increases the sorption capacity of the polymer for compounds sorbed by centers Z_{1j}, in particular for compound A such as used for the melt treatment, and decreases the sorption capacity for all additives sorbed by any center except Z_{1j}.

4. SOLUBILITY OF STABILIZERS IN POLYMERS

4.1. Method of Determination

Solubility of additives in polymers is an important characteristic of polymeric system. Excess quantity of additive above its solubility can result in changes of polymer properties and fast degradation of polymer.

The solubility of additive in a polymer corresponds to the concentration of this additive in the polymer being in the equilibrium with an additive (or with its saturated vapor). Formally, the solubility of additive in polymer corresponds to the point on the sorption isotherm ($[A]_p = S_A$) at the concentration of A in the surrounding equal to the concentration of A in its saturated vapor (or in its saturated solution, if additive dissolved in the solution) ($[A]_{ms}$).

In case of the Langmuir type sorption, the solubility (S_A) will be given as

$$[A]_p = S_A = \frac{\gamma[A]_{ms}K_a[Z_a]}{1 + K_a\gamma[A]_{ms}} \qquad (14)$$

As the sorption parameters: $[Z_a]$, γK_a can be obtained from independent experiments, *i.e.*, by using Eq. (2), the additive solubility in a polymer may be calculated if the concentration of A in its saturated vapor is known. In practice it is difficult to do because the vapors pressure of antioxidants with molecular weight more than 300 are very small. But in case of sorption from solution the solubility of additive in the polymer can be easy calculated by using the values of additive solubility in the solvent.

Billingham *et al.* [32] considered the solubility of additives in polymers based on regular solution theory: the solubility is defined by the condition that the (negative) free-energy of mixing of the liquid additive with the polymer is equal to the (positive) free energy required to convert the crystalline additive into a liquid at the same temperature. In this case the solubility of additive in the polymer is

$$-\ln S_A = (\Delta H_f/RT)(1 - T/T_f) + (1 - V_1/V_2) + \kappa \qquad (15)$$

where ΔH_f is the heat of additive melting, T_f its melting temperature, V_1 and V_2 the molar volumes of the additive and of the solvent, and κ the interaction parameter. According to Eq. (15) crystal with higher heat of fusion is expected to be less soluble in polymer than that with lower heat fussion. The additive solubility in the polymer can be predicted from data on its solubility in the gomological set of solvents by an extrapolation of the solubility data in the coordinates $\ln S_A$ *vs* $1/V_2$ to the point to the $1/V_2 = 0$ but this approach does not take into account the features of the polymer structure.

The direct method of measuring additive solubility includes the study the kinetics of additive dissolution in polymer when additive presents in equilibrium with its saturated vapors or with an additive immersed on the surface of polymer film [31-34]. For this purpose polymer film with an additive is kept in closed vacuum tube or in inert medium for different period of time. Usually, the solubility value corresponds to some ***plateau*** on the curve "the concentration of additive in the polymer *vs* time". At high temperatures the dissolution can be accompanied by change in the polymer structure and the solubility will change with time [33-34].

Because an additive used can be present in different crystalline or in amorphous states the value of the solubility depends on physical form of an additive [35-38].

To study the solubility the "sandwich" method is also used [36-39]: polymer film is placed between films over-saturated with the additive. The solubility measured by this way may be higher than in case of free additive method. This is probably due to the fact that the additive concentration in over-saturated film does not correspond to the true equilibrium and the additive vapor pressure over the over-saturated film is higher than that above the pure additive.

There are some indirect methods of measuring additive solubility. One of them is based on an diffusion experiments and measure of the additive concentration profile inside the film [36–41]. This method makes possible the simultaneous determination of the additive diffusion coefficient.

Other method includes the determination of the temperature dependence of vapor pressure of the additive above the pure additive and the polymer containing a definite concentration of the additive [42]. Intersection points of both curves (presumably in the coordinates $\ln P_a$ *vs* $1/T$) corresponds to the temperature at which the additive concentration in the sample is equal to its solubility.

Study of the temperature dependence of the transparency of the polymer films with various additives concentrations [43]. If the additive concentration in the polymer exceeds its solubility at the given temperature, the excess additive is emerging forming crystals or drops which sharply decrease the sample transparency. This method is not precise.

4.2. Temperature Dependence of Solubility

For description of the temperature dependence of additive solubility in the polymer Van't Hoff Eq. (16) is used

$$S_s = S_{so} \exp(-\Delta H/RT), \tag{16}$$

which is correct in only narrow temperature ranges. Among the reasons for the violation of this dependence are the phase transitions in the polymer (*i.e.*, near its melting) and in the additive. Another reason is the existence of stable sorption centers whose concentration in the polymer does not depend on the temperature. Let us assume that for a not too wide a temperature range, the vapor pressure (and the concentration) of A over the pure compound and the value γK_a change with temperature according to the exponential law. Taking into account Eq. (2) the temperature dependence of solubility will be

$$S_A = \frac{[Z]\omega \exp(-\Delta H/RT)}{1 + \omega \exp(-\Delta H/RT)} \tag{17}$$

where ΔH is the sum of the change of enthalpy of evaporation (sublimation) and sorption by centers Z. It follows from Eq. (17) that the dependence of solubility of additive A in polymer differs from Van't Hoff Eq. (16) but if the second term in the numerator of (17) is essentially less than 1 (*i.e.* $[A]_{ms}$ and γK_a are sufficiently small), Eq. (17) converts to

$$S_a = [Z]\omega \exp(-\Delta H/RT) \tag{18}$$

In this case the heat of solution of A will be equal to the difference between the heat of evaporation of A and the heat of dissolution of A in the sorption centers Z.

Figure 8 shows the solubility of compound A as a function of temperature calculated using Eq. (17) for some values of ω [33]. The solubility of A is seen to increase, approaching a certain limit equal

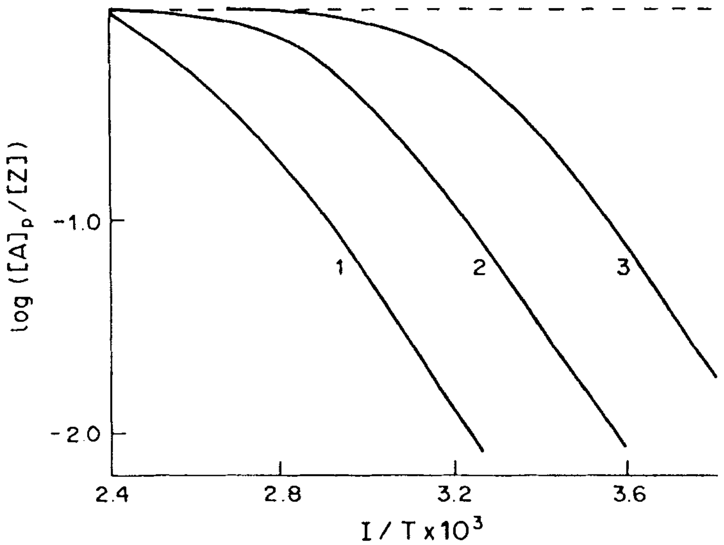


FIGURE 8 Dependence of solubility of compound A in polymer, calculated considering Eq. (17) at $\Delta H = 50\,\text{kJ/mol}$ and $\omega = 10^7$ (1), 10^8 (2) and 10^9 (3).

to [*Z*], which is independent of temperature, *i.e.*, the solubility of *A* will be also become virtually independent of temperature. The real dependence may be much more complicated because of changes in the sorption centers concentration in the phase transition points and a variation in the polymer properties caused by the dissolved additive [22, 33, 39, 44]. Figures 9 and 10 show the temperature dependence of some stabilizers in polypropylene, polyethylene and poly-4-methylpentene-1 [33]. Within the temperature range 30–200°C all dependencies in the coordinates "ln S_A *vs* inverse temperature" are complicated broken lines with both straight and curves sections. For example, three

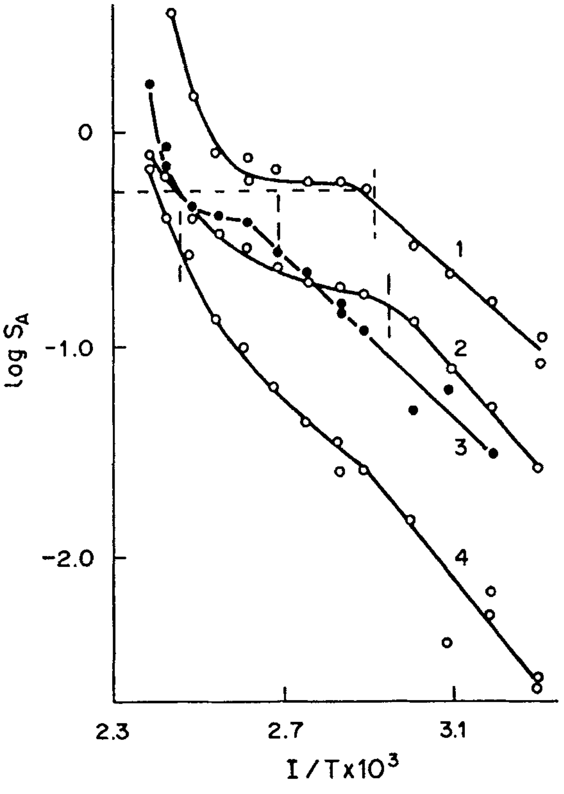


FIGURE 9 Solubility of 2,6-di-*tert*-butyl-4-methylphenol (1), of methyl ester of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (2), of 2,6-di-*tert*-butyl-4-phenylphenol (3) and of 2,2′-methylene -bis(4-methyl-6-*tert*-butylphenol) (4) in polypropylene as function of temperature.

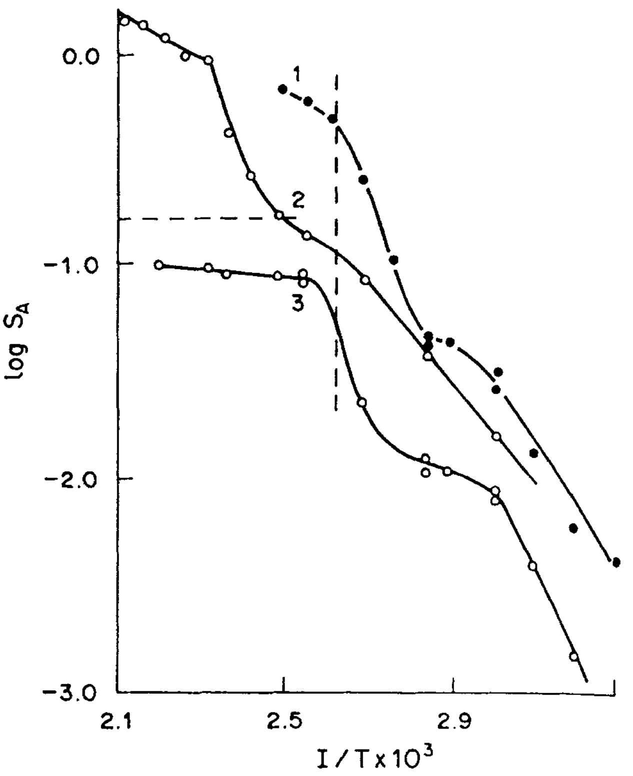


FIGURE 10 Solubility of phenyl-β-naphthyl amine in LDPE (1), PP (2) and poly-4-methylpentene-1 (3) as function of temperature.

sections differing in heat of solution can be distinguished in the curve for 2,6-di-*tert*-butyl-4-methylphenol in the PP (Fig. 9, curve 1). Within the range 30–70°C the solubility changes according with Eq. (3.16) with $\Delta H = 33\,\mathrm{kJ/mol}$; within the range 70–110°C it changes only slowly; above 130°C it rapidly increases again. The solubility of phenyl-β-naphthyl amine in PP and PE has been studied below and above the polymer melting temperature (Fig. 10, curves 2 and 3). As seen from this figure, the slops of the curves, *i.e.*, the heat of solution of additive changes near the polymer melting temperature.

The bends in the curves in some cases correspond to temperatures of phase transition of additive (the additive melting points are shown in the figures by arrows) but in some case this is not so. The additive concentration at which the solubility only slightly changes with temperature corresponds to the center of sorption concentration found from the sorption isotherms in independent experiments. Such $[Z]$ values for 2,6-di-*tert*-butyl-4-methylphenol and phenyl-β-naphthyl amine in PP are 0.5 and 0.17 mol/kg. At temperatures close to the polymer melting temperature a rapid increase in solubility is observed, caused by the change of polymer structure in the presence of additive.

Table I contains the values of equilibrium solubility of stabilizers in polyolefins and in rubber, of the heat of solution, and of the temperature ranges in which these values were determined. The solubility of stabilizers decreases with their molecular weight but simple dependence between these characteristics is absent. Solubility of phenolic-type stabilizers in polyolefins and in rubbers is greater that of aromatic amines with the same molecular weight. Sulphides are high soluble in polyolefins probably due to the presence of aliphatic group in their molecules [39]. There is the great difference in solubility of two sterically hindered amines in PE with close molecular weight (396 – 423 and 481); [40] nitroxides are less soluble than the corresponding amines [41].

As seen from Table I, the solubility of many stabilizers at room temperature are markedly lower than the concentrations at which the additives are usually added to polymers (0.1 – 0.5% by weight). Thus, an excess of a stabilizer added to a polymer often emerges (sweats or blooms) from it.

4.3. Effect of Crystallinity and Supermolecular Structure

Additive solubility in non-polar rubber is greater that in crystalline polyolefins (see Tab. I) because the crystalline region of polyolefins is non available for additives and crystals decrease the plasticizing action of dissolved compounds. There is no simple correlation between polymer crystallinity and additive solubility. The solubility of additives depend not only on volume of amorphous fraction but also on its structure. It was shown [48] that the solubility of diphenyl amine and phenyl-β-naphthyl amine in solid polyethylene with different crystallinity is practically constant and only slightly decreases at high crystallinity of the polymer. The authors attribute this to the irregularity of

TABLE I Solubility of stabilizers in polymers

Stabilizer	*M.W.*	*Polymer*	*Temp. Range °C*	S_A, % *at* 25°C	*lg* S_{Ao}	ΔH *kJ/mol*	*Ref.*
2,6-Di-*tert*-butyl-4-methylphenol	220	LDPE	30–72	1.9	7.83	43.0	22
		iPP	30–70	1.75	6.11	33.5	22
		Butadiene rubber	–	18*	–	–	45
		Chloroprene rubber	–	11.3*	–	–	45
2,4,6-Tri-*tert*-butyl phenol	262	LDPE	30–80	0.83	15.78	90.6	22
		iPP	30–50	0.55	7.28	43.2	22
2,6-Di-*tert*-butyl-4-phenylphenol	282	iPP	40–100	0.45	6.11	36.9	22
		PMP	30–50	0.39	13.82	81.3	22
3,5-Di-tert-butyl-4-hydrohyphenylpropionic methylate (Fenosan-1)	292	LDPE	30–90	0.37	8.38	50.3	22
		iPP	30–60	0.61	7.34	43.1	22
		PMP	30–60	0.05	15.78	97.6	22
		PVB plasticized (26%)	30–60	7.2	10.48	52.6	46
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol	340	LDPE	30–80	0.08	3.74	27.6	39
		LDPE	23–90	3.5	3.34	15.9	39
		iPP	30–80	0.063	7.17	47.8	22
		iPP	50–100	1.17	4.71	26.8	22
		PMP	30–90	0.012	7.75	55.3	22
		Butadiene rubber	22–80	2.0	5.38	29	45
		Chloroprene rubber	–	2.3*	–	–	45
4,4′-Tiobis(6-*tert*-butyl-m-cresol) (Santonox)	358	LDPE	23–90	9.10^{-4}	11.11	80.9	39

2,2′-Methylenebis(4-chloro-6-*tert*-butylphenol)	360	iPP	40–100	0.38	4.54	28.5	22
2,2′-Methylenebis(4-ethyl-6-*tert*-butylphenol)	368	LDPE	23–90	0.18	3.95	26.8	39
2,2′-Methylenebis(4-methyl-6-α-methylcyclohexylphenol) (Nonox WSP)	420	LDPE	23–90	0.14	4.91	32.8	39
		iPP	40–90	0.17	4.06	27.6	39
		Butadiene rubber	70–100	2.0	4.34	23.0	47
		Butadiene-Acrylonitrile (18%) rubber	70–100	2.2	5.11	27.2	47
		Butadiene-Acrylonitrile (40%) rubber	70–100	0.8	4.69	27.2	47
4,4′-Methylenebis(2,6-di-*tert*-butylphenol) (Ionox 220)	424	LDPE	23–90	0.028	5.20	38.5	39
Octadecylic ester of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (Irganox 1076)	530	LDPE	52–90	–	7.60	45.5	39
		LDPE	23–52	0.016	10.97	72.8	39
1,1,3-Tris (5-*tert*-butyl-4′-hydroxy-2′-methylphenyl) butane (Topanol CA)	544	LDPE	23–90	0.105	6.3	47.3	39
		LDPE	50–100	0.009	6.66	49.7	39
Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) ethoxycarbonylethyl sulphide (Irganox 1035)	643	LDPE	23–74	0.017	9.00	61.6	39
		LDPE	74–90	–	6.78	46.9	39
2,4,6-Tris(3,5-*tert*-butyl-4-hydroxybenzyl)mesithylene (Ionox 330)	775	LDPE	23–90	0.013	3.04	28.1	39
		iPP	50–100	0.004	8.59	62.9	32

TABLE I (Continued)

Stabilizer	*M.W.*	*Polymer*	*Temp. Range °C*	S_A, % *at 25°C*	*lg* S_{A_0}	ΔH *kJ/mol*	*Ref.*
Tetramethylene-3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)-propionate methane (Irganox 1010)	1178	LDPE	23–90	0.005	8.60	62.4	39
		LDPE	50–100	0.02	5.30	39.0	39
		iPP	50–100	0.15	4.45	31.8	32
Phenyl-β-naphthylamine	220	LDPE	30–60	0.06	3.62	27.7	22
		iPP	60–100	0.048	2.64	22.6	22
		PMP	30–60	0.009	4.26	36.1	22
		Butadiene rubber	28–80	1.4	5.91	33.0	42
		Butadiene-Acrylonitril (18%) rubber	–	12.1*	–	–	42
Ester of 2,2,6,6-tetramethyl-4-piperidinol and stearic acid (technical grade)	396 423	LDPE	–	2–2.2*	–	–	40
Bis(2,2,6,6-tetramethyl-4-piperidinyl)sebacate (Tinuvin 770)	481	LDPE	–	0.1*	–	–	40
Bis[2,2,6,6-tetramethyl-4-piperidinyl-1-oxyl]sebacate	511	iPP	25–90	0.008	11.07	75.0	41
		iPP	100–114	–	2.76	16.9	41
		HDPE	25–90	0.018	7.88	55.2	41
		LDPE	25–80	0.02	8.68	59.5	41
		L-LDPE	25–80	0.041	7.65	52.0	
Dilaurul thiodipropionate	514	LDPE	23–40	0.79	9.20	53.2	39
		LDPE	40–90	–	2.15	10.8	39
Distearyl thiodipropionate	682	LDPE	23–66	0.75	5.00	29.3	39
		LDPE	66–90	–	0.64	7.7	39

*Solubility at 22–23°C.

the amorphous regions of the polymer, the density of which decreases with increasing polymer crystallinity. Moisan [42] showed that the solubility of Irganox 1076 in polyethylene at 60°C only weakly changes with polymer crystallinity in the range from 43% to 57% (density range 0.92–0.94 g/cm^3) but at higher temperatures (70°C and 80°C) the solubility decreases with polymer crystallinity. It should be noted that crystallinity measured at room temperature can considerably change with temperature especially in the polymer premelting region.

The role of the polymer supermolecular structure and polymer prehistory on antioxidant solubility has been studied. It has been shown that solubility of diphenyl amine, methyl ester of 3,5-di-*tert*-butyl-β-hydroxypropionic acid and 2,2′-methylene-bis(4-methyl-6-*tert*-butylphenol) in polyolefins prepared by rapidly cooling the polymer melt (structure with small spherulites) are higher than in the samples prepared by slow crystallization near the polymer melting temperature (the structure with large spherulites) [50–51]. As it is seen from Table II, the difference in solubility can reach by a factor of 2; the crystallinity measured by IR-method is practically the same [51].

The precipitation of polymer from different solvents has been used as a method to change the polymer structure and efficiency of antioxidant [52–54]. During the precipitation macromolecules have to overcome the interaction with molecules of the solvent which is more difficult in the case of "good" solvent and the polymer sample obtained after precipitation from a "good" solvent has to possess less perfect structure. It was shown that additives solubility in PP precipitated from decane ("good" solvent) were higher than that in chlorobenzene (Tab. III).

4.4. Copolymers and Polymer Blends

The solubility of phenyl-β-naphthyl amine in PP-PE blends and ethylene-propylene copolymers was studied in solid film and in the

TABLE II Solubility of diphenyl amine (mol/kg) in poly-4-methylpentene-1. Effect of film preparation [51]

Condition	*Solubility at* 60°*C*	*Solubility at* 110°*C*
Fast cooling of the melt	0.10	0.20
Slow cooling of the melt	0.064	0.11

TABLE III Solubility of additives (mol/kg) in polypropylene films at 60°C prepared by precipitation from different solvent [52]

Solvent	*Phenyl benzoate*	*Phenyl-β-naphthyl amine*
Chlorobenzene	0.13	0.01
Decane	0.17	0.02

melt [55]. It was shown that the solubility of the antioxidant at 60°C is practically independent on the composition of the polymer mixture (Fig. 11, curve 1) whilst the solubility in copolymers (Fig. 11, curve 2) has a minimum in the range of near 2% of propylene content and a wide maximum at 40% of propylene content. The vapor pressure (the concentration of the antioxidant over the melted polymer) at 180°C passes through a maximum which occurs at low (less than 7–10%) PP content (Fig. 12). It means that the physical structure of blends and copolymers in the melt changes with propylene content.

Table IV presents data on solubility of different stabilizers in LDPE, LDPE/LLDPE blend and in ethylene vinyl acetate copolymer [36]. The additives solubility in LDPE and in the blend is close while in

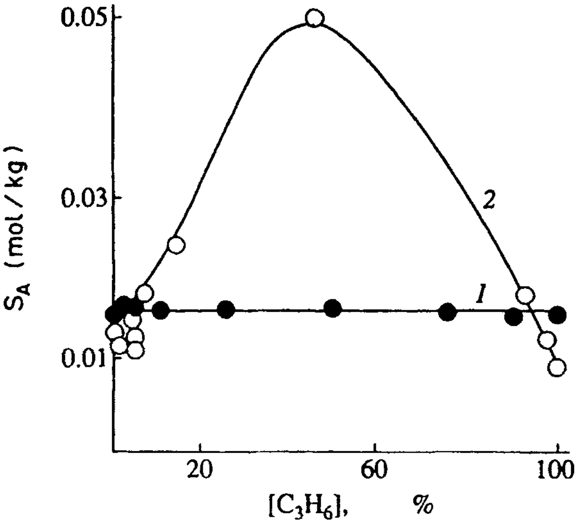


FIGURE 11 Solubility of phenyl-β-naphthyl amine at 60°C in PE/PP blends (1) and in ethylene-propylene copolymers (2) as a function of propylene content.

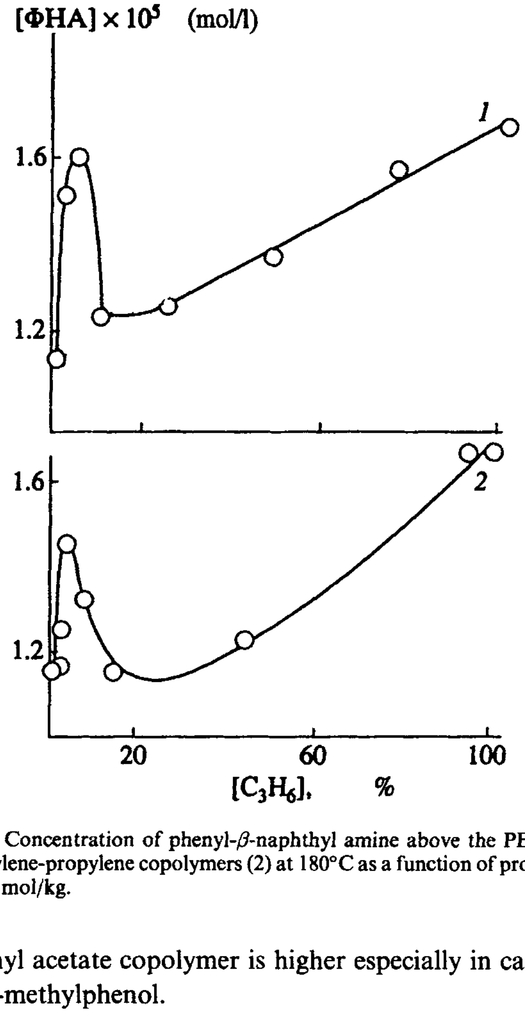


FIGURE 12 Concentration of phenyl-β-naphthyl amine above the PE/PP blends (1) and above ethylene-propylene copolymers (2) at 180°C as a function of propylene content $[PNA]_p = 0.08$ mol/kg.

ethylene vinyl acetate copolymer is higher especially in case of 2,6-di-*tert*-butyl-4-methylphenol.

4.5. Role of Polymer Polar Groups

As we told above the dissolution of polar additives in polymers containing polar groups can follow both mechanism of filling the sites and that of specific interaction of dissolved additive with the polar groups of the polymer. In going from nonpolar to polar polymers, *e.g.*, from polyolefins to aliphatic polyamides containing — CONH — groups, the polymer density increases owing the formulation of

TABLE IV Additive solubility (mg/cm^3) in ethylene polymers at 45°C [36]

Stabilizer	*Molecular weight*	*LDPE, α 45%*	*LDPE/LLDPE 60/40, α 52%*	*Ethylene vinyl acetate copolymer (3 mole % VA, α 36%)*
2,6-Di-*tert*-butyl para-cresol	220	36.1	31.1	101.5
1,1,3-Tris(2'-methyl-4'-hydroxy-5'-*tert*-butylphenyl)-butane	545	2.6	2.1	3.9
Tetramethylene-3-(3',5'-di-*tert*-butyl-4'-hydroxyphenyl)-propionate methane (Irganox 1010)	1178	0.9	0.7	1.4

hydrogen bonds between these groups. It was shown [33] that for polymers such as polyamide-12, polyamide-6,10, and polyamide 6,6 (or polyamide-6) the solubility of phenyl-β-naphthyl aimine increases in the order polyethylene-polyamide-12 and decreases with higher concentrations of these groups, whereas the solubility of the less polar additive phenyl benzoate and 2,6-di-*tert*-butyl-4-methyl phenol decrease over the whole range studied (Fig. 13).

4.6. Effect of Second Compound

As it was mentioned above in Chapter 3.2, the addition of second compound can decrease the sorption of the first due to the competition in sorption centers, and can also change the polymer structure. As the result, the additive solubility changes in the presence of second compound.

Figure 14 shows that octamethylcyclotetrasiloxane influences the solubility of the stabilizer in solid PE [31]. Effect of gossipol on solubility of phenyl benzoate in PP at 60°C is shown in Figure 15: the solubility of phenyl benzoate first increases and then decreases with concentration of gossipol in the polymer [56]. The same picture is observed if dilaurylthiodipropionate is present in the polymer along with gossipol. It is necessary to point out that addition of gossipol results in some reduction in polymer crystallinity. An increase in the solubility of phenyl benzoate with gossipol or sulphide content is probably due to decrease in crystallinity. The decrease in solubility

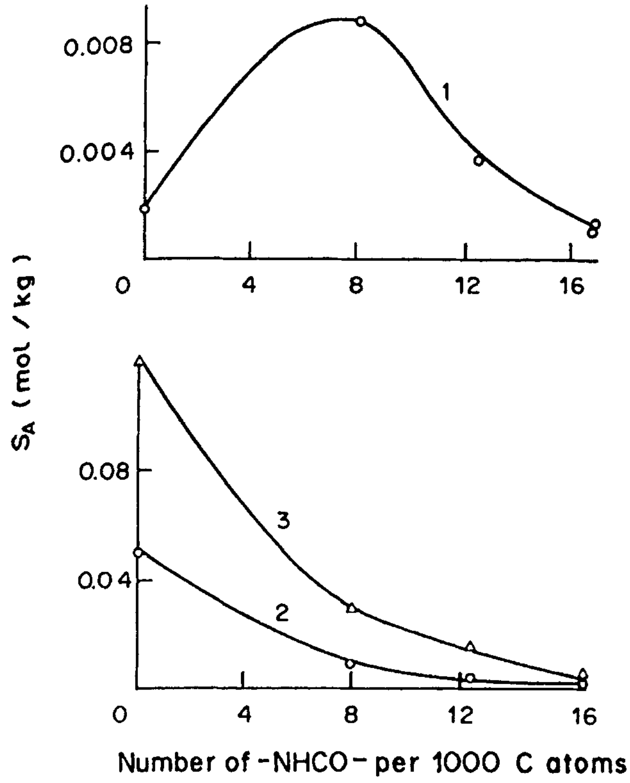


FIGURE 13 Solubility of phenyl-β-naphthyl amine (1), of 2,6-di-*tert*-butyl-4-methylphenol (2), and of phenyl benzoate (3) in polyethylene and in polyamides as function of amide group concentration 40°C.

of phenyl benzoate may be explained by the substitution of phenyl benzoate from sorption centers. This is in agreement with that fact that decrease in solubility of phenyl benzoate is approximately corresponds to amount of gossipol introduced in the polymer.

Plastisizers present in polymers change the polymer structure due to the increase in the mobility of polymer chains, and affect the additives solubility in the polymer. Poly(vinyl butyral) (PVB) containing plastisizers is used as stick material for the preparation of nonspleeted glasses and other optical systems. The film taken for these purposes has to possess a high transparency and it must be colourless. The solubility of antioxidants in nonplasticized PVB is low compared

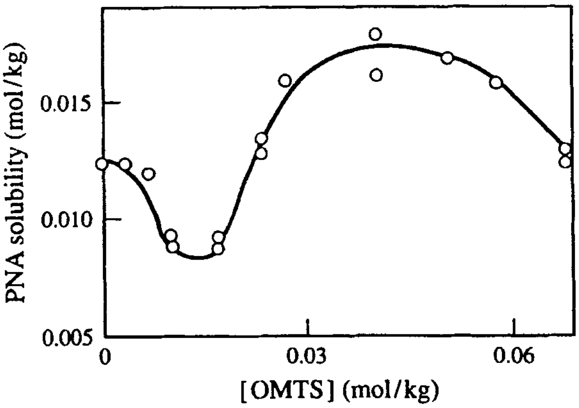


FIGURE 14 Solubility of phenyl-β-naphthyl amine in polyethylene at 60°C as a function of OMTS concentration.

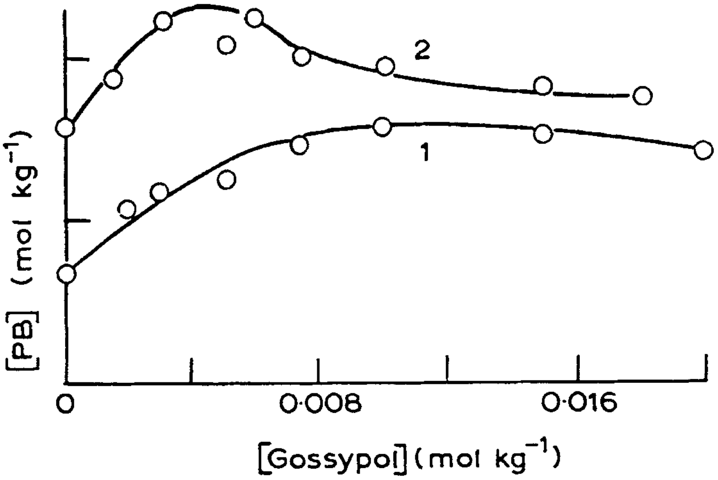


FIGURE 15 Dependence of solubility of phenyl benzoate in polypropylene on gossipol concentration in (1) the absence, and (2) the presence of 0.005 mol/kg of sulphide, 60°C.

with that in pure plasticizer *i.e.*, for ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl propionic acid and ethyleneglycol: 0.014 and 0.84 mol/kg (0.9% and 53% by weight) respectively [46].

If the solubility of antioxidant in plasticized PVB (S_{add}) is considered as a simple sum of the solubilities in the polymer (S_{PVB}) and in the plastisizer (S_{PLA}), *i.e.*,

$$S_{\mathrm{add}} = S_{\mathrm{PVB}} + x(S_{\mathrm{PLA}} - S_{\mathrm{PVB}}), \tag{19}$$

where x is the percentage of plasticizer in the polymer, one can expect a linear growth of antioxidant solubility in the polymer with the plasticizer concentration (Fig. 16, dotted line). The experiment shows a more complicated dependence: at low concentrations of the plasticizer (1–5% by weight) the solubility of the antioxidant in the polymer is higher than its follows from Eq. (19) but at higher concentration of plasticizer (10–40%) it is less than S_{add} (Fig. 16). [46]. The effect observed is due to the fact that at small concentrations, the plasticizer strongly affects the mobility of macromolecules and, as a result, increases the antioxidant solubility; at high concentrations there is solution of the polymer in the plasticizer with strong polymer-plasticizer interactions, which disturb the antioxidant dissolution.

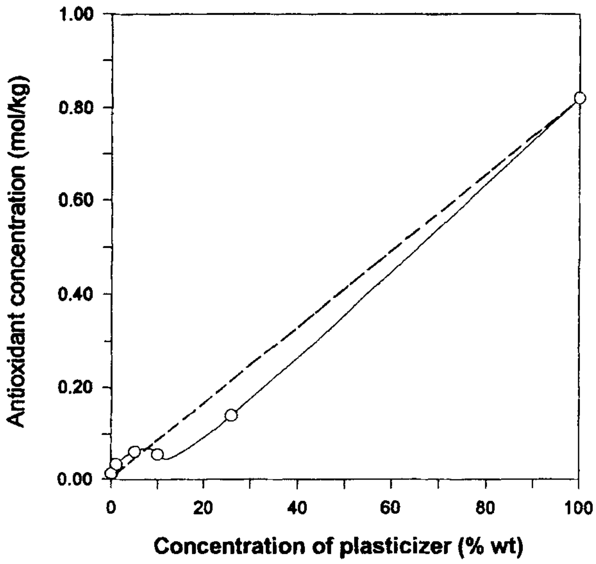


FIGURE 16 Solubility of methyl ester of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid as function of dihexyl adipate content in PVB at 60°C.

4.7. Role of Polymer Orientation

Orientation drawing of polyolefins results to considerable change in polymer structure and additive behavior: spherulites transform in fibrils, in amorphous zones the amount of regular conformers increases and irregular decreases [57], the solubility and diffusion coefficient of additive usually decrease with drawing but sometimes these relationships are more complicated [58–61]. Figure 17 shows the effect of elongation of PE on solubility of various antioxidants at 60°C. The crystallinity of the polymer determined by differential thermal analysis does not change with drawing while the crystallinity determined by IR-spectroscopy increases from 36% to 48% for ($\lambda = 0-5.5$), showing the changes in the conformation set of macromolecules [61]. Figure 18 shows the solubility of studied additives as function of the concentration of irregular gauche conformations in amorphous region of PE. The most significant difference in the additives solubility takes

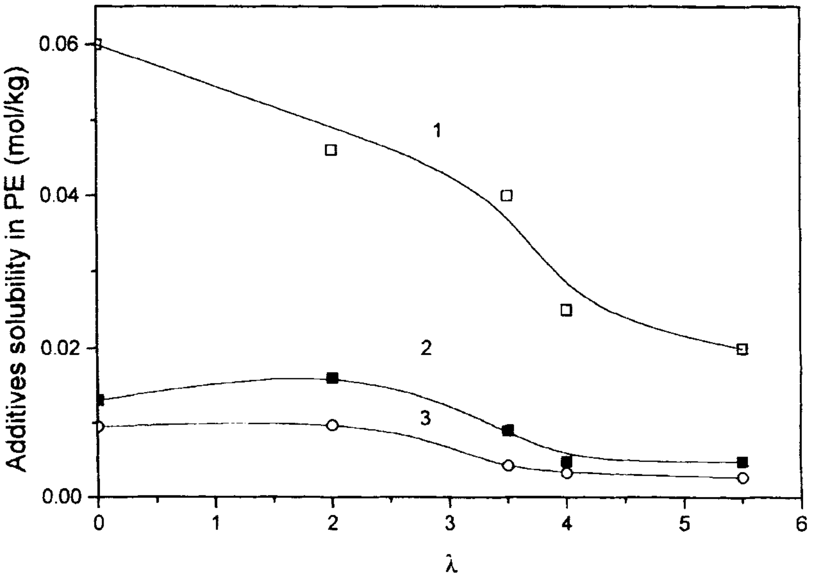


FIGURE 17 Dependence of solubility of methyl ester of 3,5-di-*tert*-butyl-4-hydroxyphenylpropionic acid (1), of 2,2′-methylene-bis-4-methyl-6-(1-methyl cyclohexyl-1)phenol(2), of ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl propionic acid and ethyleneglycol (3) in polyethylene on the degree of drawing (λ) at 60°C.

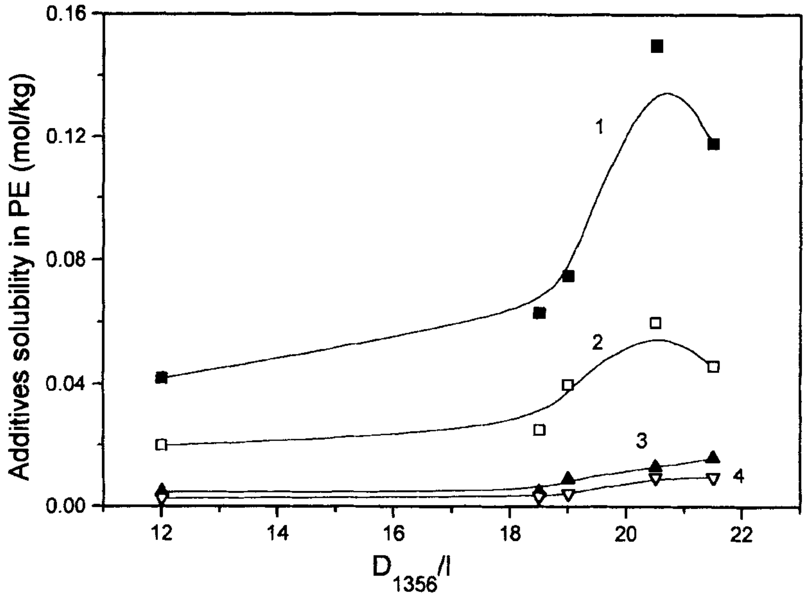


FIGURE 18 Solubility of phenyl benzoate (1), of methyl ether of 3,5-di-*tert*-butyl-4-hydroxyphenyl propionic acid (2), of 2,2′-methylene-bis-4-methyl-6-(1-methyl cyclohexyl-1) phenol (3), of ester of 3,5-di-*tert*-butyl-4-hydroxyphenyl propionic acid and ethyleneglycol (4) in polyethylene as function of absorption at 1356 cm^{-1}.

place in narrow range of changes in the content of irregular conformers.

Because the orientation drawing can result to deformation and disappearance of chain entanglements due to pull out of macromolecules from knots and other topological irregularities, one may expect that after further melting of oriented samples the additive solubility should tend to decrease compared with non-orientated one. The chain entanglements cannot recover quickly, otherwise a memory about change of the polymer structure should remain after polymer melting. Figure 19 shows the effect of orientation drawing on solubility of phenyl benzoate: curves 1 corresponds to the samples without additional treatment, curves 2 – to the samples which after drawing were heated in vacuum to 140°C followed by fast cooling. As can been seen from Figure 19, orientation of the polymer affects the solubility of the additive even if samples were heated above the polymer melting.

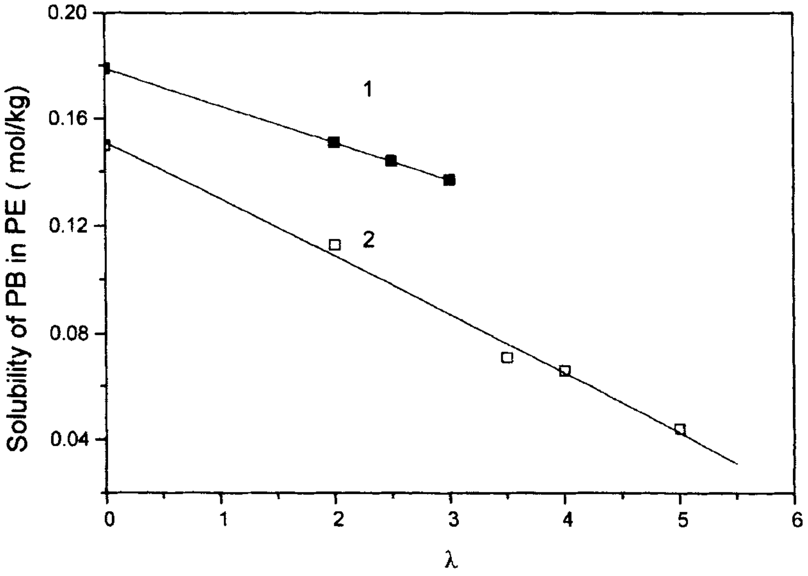


FIGURE 19 Solubility of phenyl benzoate in polyethylene at 60°C as function of degree of drawing; (1) samples after additional heating, (2) samples without additional heating.

According to Eq. (14) the solubility of additive in polymer depends on the additive concentration (pressure) over the individual compound and on of sorption parameters ($[Z]$, γ and K_a). Assuming that all changes introduced by orientation besides destruction and rearrangement of sorption centers, disappear at further polymer melting *i.e.*, γ remains the same in value, we obtain that at such polymer treatment only the concentration ($[Z]$) and (or) the properties of sorption centers (K_a) are changed.

4.8. Features of Dissolution of High Molecular Weight Additives

The increase in molecular weight of the antioxidant 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.

For additive dissolution, sorption centers should contain an excess volume large enough to locate the additive molecule. If this volume is less than that necessary for sorption, dissolution of A can occur only in case of rearrangement of this center resulting in change of the polymer structure. The process of center rearrangement may be presented by the scheme (20) followed by polymer swelling.

$$A + Z_i \longrightarrow AZ_i^* \rightleftharpoons A + Z_i^* \tag{20}$$

So, one can expect that the behavior of high molecular weight additives in a polymer will differ from that of additives with an average molecular weight.

The solubility of sterically hindered amines with molecular weights from 1364 to 2758 in PP were studied [34]. It was shown that the solubility of the stabilizers in PP at 100°C passes through a maximum with time and depends on molecular weight of the stabilizer: the higher the molecular weight of the stabilizer the higher its maximum concentration in PP (Fig. 20) [34]. To explain the features in the kinetics we may to assume that at high temperature molecules of larger size are

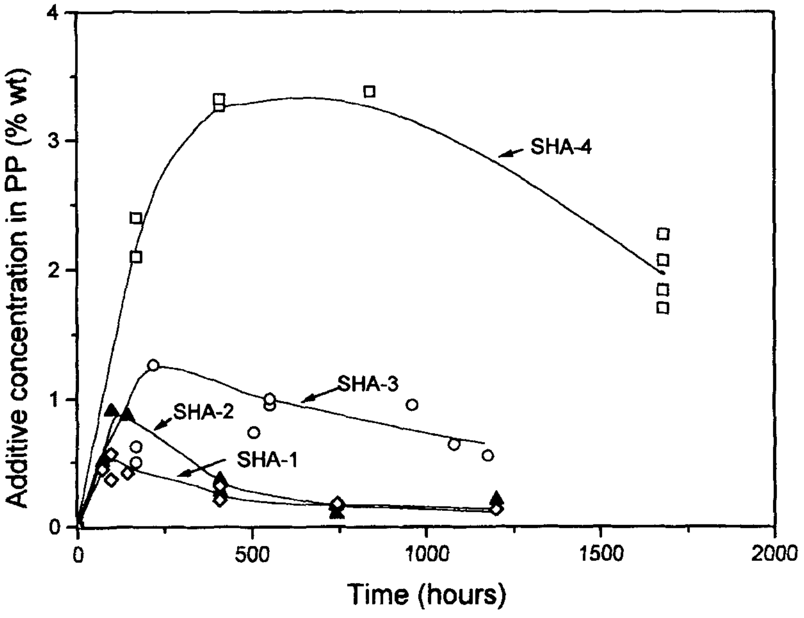


FIGURE 20 Kinetics of dissolution of stabilizers in polypropylene at 100°C: SHA-1 (m.w. 1364), SHA-2 (m.w. 1393), SHA-3 (m.w. 2286) and SHA-4 (m.w. 2758).

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 is probably due to annealing of the polymer in the presence of additives. The additive dissolution is accompanied by the change in the polymer crystallinity and in the concentration of irregular conformation in the amorphous zones of the polymer [34].

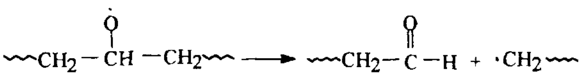
4.9. Effect of Polymer Oxidation

The oxidation reaction first involves the zones with lower polymer density packing containing polymer chain entanglements and can result in the diappearance of some of them. This process may be presented by the scheme:

$$Z_1 + nO_2 \rightarrow \varepsilon Z_2 \tag{21}$$

where Z_1 and Z_2 are the different types of sorption centers, and $\varepsilon < 1$.

Aliphatic chain scission proceeds in the oxidation reaction according to the scheme



$$\sim CH_2-\overset{\dot{O}}{\overset{|}{C}}H-CH_2\sim \longrightarrow \sim CH_2-\overset{O}{\overset{\|}{C}}-H + \cdot CH_2\sim \tag{22}$$

As seen from the scheme (22) polar aldehyde groups are formed in this process at the ends of broken chains. Thus, new formed center Z_1 may contain polar groups. In this case the solubility of polar additives may increase with oxidation. The solubility of diphenyl amine and phenyl benzoate were studied in polyethylene and in several aliphatic polyamides after oxidation [63]. The Figure 21 shows the solubility of these additives as a function of oxidation degree. At low oxidation degrees, up to 0.2-0.3 mol/kg of oxygen, the solubilities of both additives in all polymers studied decreases; at deeper stages the solubilities in polyamides still decrease, whilst in PE they increase. To explain the experimental data we should assume that oxidation results

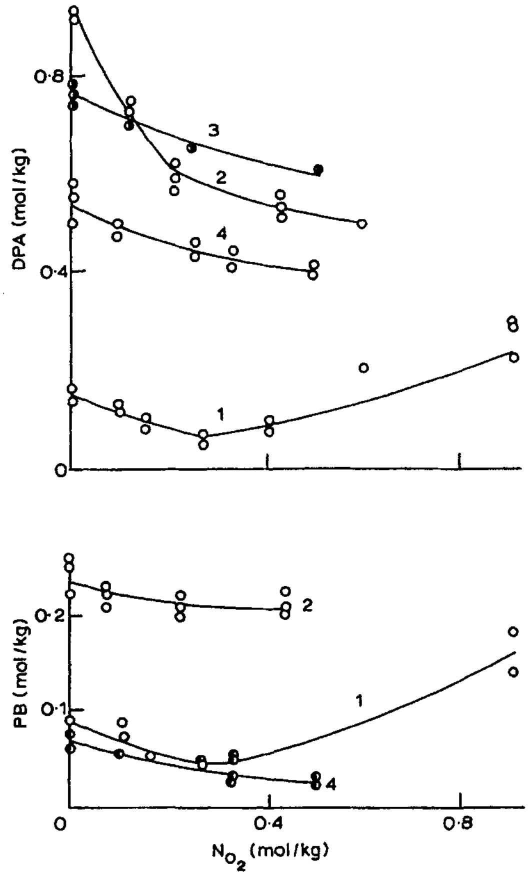


FIGURE 21 Solubility of diphenyl amine and phenyl benzoate as function of amount of oxygen absorbed in oxidation; polymers: (1) PE, (2) PA-12, (3) PA-6,10, and (4) PA-6,6; 60°C.

in the decomposition of one type of sorption centers and simultaneously the formation of other ones. In polyamides the concentration of polar amide groups are higher compared to those of new ones formed in oxidation. For this reason we only observe the decrease in additive solubility caused by polymer oxidation. In non-polar polyethylene, the effects of both processes are comparable, and we observed more pronounced and complicated variation of additive solubilities.

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