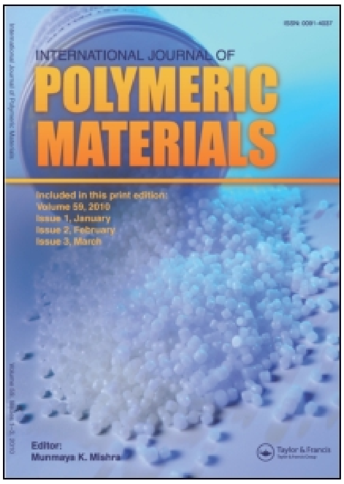
This article was downloaded by:
On: *19 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Physical Chemistry of Disorder in Polymer Chains Arrangement

Yury A. Shlyapnikov[a]
[a] Institute of Chemical Physics, Moscow, Russia (USSR)

To cite this Article Shlyapnikov, Yury A.(1992) 'Physical Chemistry of Disorder in Polymer Chains Arrangement', International Journal of Polymeric Materials, 18: 3, 179 — 187

To link to this Article: DOI: 10.1080/00914039208029319

URL: http://dx.doi.org/10.1080/00914039208029319

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1992, Vol. 18, pp. 179–187
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Malaysia

Physical Chemistry of Disorder in Polymer Chains Arrangement

YURY A. SHLYAPNIKOV
Institute of Chemical Physics, 117334, Moscow, Russia (USSR)

(Received April 6, 1992)

An individual homopolymer is considered as two-component system, one component being the polymer as such, and other—the multitude of elements of disorder—UODs—dissolved in the polymer. These elements are formed by various entanglements of long polymer chains and stable even in the polymer melt, in many cases behave like molecules of a certain quasi compound.

Some physico-chemical phenomena based on this model are discussed.

INTRODUCTION

Among other characteristics of the polymer affecting its physical and chemical properties there is the degree of the polymer chains entanglement, that is considered as a stable disorder. During many years we studied this disorder and its effect on various properties of various polymers. In this study we summarize the results of our work.

ANALYSIS AND DISCUSSION

Individual crystalline homopolymers, such as polyethylene, contain two phases in certain intervals of temperature and pressure. Applying formally the Gibbs phase rule:

$$F + P \geqslant C + 2 \tag{1}$$

where F is the number of freedom degrees, P—that of coexisting phases, and C—the number of components present in the mixture. For semicrystalline polymers, we have $F = 2$ (temperature and pressure) and $P = 2$ (crystalline and amorphous phases). Therefore, $C \geqslant 2$: an individual compound behaves like the mixture of at least two different compounds. To solve this controversy consider the reason preventing complete crystallization of polymers below certain melting temperature.

Polymers consist of long chain-like molecules, the arrangement of segments of these molecules in some sites of the polymer melt is close to that in ideal crystal, that is the short range order is obeyed there, when in other sites it markedly differ from it. Some of sites of short range order violation are those of polymer chains' entanglements, these entanglements of long polymer chains are stable enough and they are the very structures preventing complete crystallization of the melt. We assumed these entanglements and the polymer chain ends, the units of disorder (UODs), to be that lacking second component or the set of such components.[1,2]

The experiments show that sorption of numerous additives by polymers obey Langmuir law, i.e. References 3–5:

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

where $[A]_p$ is the additive concentration in the polymer, $[A]_m$—that in surrounding medium, a and b—coefficients. The ratio a/b is the limit the additive concentration in the polymer approaches with increasing concentration in the surrounding medium. Transforming Equation (2) into inverse coordinates $1[A]_p$ vs $1/[A]_m$ we get:

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

i.e., the Langmuir-type dependence Equation (2) in inverse coordinates transforms into straight line intersecting the ordinate axis in the point $x = 0$, $y = a/b$.

Our experiments have shown[4,5] that at sorption of many additives, of the polar aromatic compounds, in polyolefins the ratio a/b remains constant in wide temperature range, both below and above polymer melting temperature (Figure 1). This constancy may be explained supposing that the sorption (dissolution) of the additive A includes the real dissolution of A obeying the Henry law ($[A] = \gamma_a[A]_m$) and subsequent equilibrium formation of complexes:

$$A + Z_i \overset{K_{ai}}{\rightleftharpoons} AZ_i \tag{4}$$

The formula connecting the additive concentrations outside and inside polymers (the sorption isotherm) following from Equation (4) is:

$$[A]_p = \gamma_a[A]_m + \sum_i \frac{K_{ai}\gamma_a[Z_i][A]_m}{1 + K_{ai}\gamma_a[A]_m} \tag{5}$$

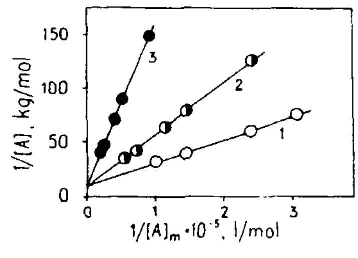


FIGURE 1 The sorption isotherms of phenyl benzoate by polypropylene from gas phase in the coordinates of Equation 3. Temperatures 110° (1), 130° (2), and 200°C (3).

It has been shown in References 4 and 5, that in many cases the sum in Equation (5) may be substituted with Langmuir-type expression, i.e. that:

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

or, neglecting the concentration of really dissolved additive $[A]$ compared to that in the sorption centers $\Sigma\ [AZ_i]$,

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

where $[Z_a] = \Sigma\ [Z_i]$ is the concentration of all types of centers sorbing A, and K_a is the certain average meaning of equilibrium constants K_{ai}.

Comparing Equation (5) with Equation (2) we find that the sorption limit a/b for a given low-molecular compound A is equal to the sorption center concentration $[Z_a]$.

According to Equations (4) and (6), we can expect that any factor decreasing the concentrations of sorption centers participating in the sorption of A will decrease its concentration in the polymer. Thus if we immerse the polymer sample into low-molecular solvent containing constant concentration of one additive A ($[A]_p$ = const.) and variable one of another, B, we can see that the concentration of A in this sample, $[A]_p$ decreases with increasing A concentration (Figure 2), the decrease being approximately equal to second additive concentration in the sample ($[A]_{po} - [A]_p \cong [B]_p$). This dependence may be explained by substitution of A with B in the sorption centers:

$$AZ_i + B \rightleftharpoons A + BZ_i \tag{7}$$

The role of second additive can play the solvent. For this reason the solubility of additives in polymers, i.e. the concentration of A in polymer being in equilibrium with the same A in crystals, varies depending on solvent surrounding both polymer and crystals.[6]

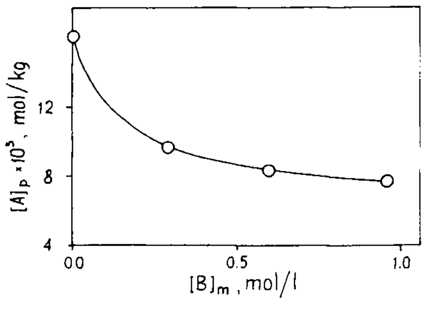


FIGURE 2 Concentration of azo-bis-isobutyronitrile in isotactic polypropylene $[A]_p$ as a function of concentration of phenyl benzoate $[B]_m$ in benzene solution, surrounding the polymer. 40°C, $[A]_m$ = 0.6 mol/kg.

At crystallization of polymer melt UODs are being ejected from the growing polymer crystals and accumulate in amorphous regions. As a result the sorption center concentration $[Z] = \Sigma\,[Z_i]$ and the solubilities of additives in the polymer in some cases are independent of polymer crystallinity in wide ranges of the latter.[7]

Repeated melting and crystallization of the same sample of isotactic polypropylene leads to the marked decrease of additives solubility in it, which may be explained by disentangling the polymer chain entanglements (knots) by leading facet of the growing crystal. In these experiments the centers sorbing larger molecules occurred to be more stable, apparently because they are based on more complex knots.[4]

The polymer melt crystallization may be considered as the work of UOD solution compression by growing crystal. Denote the chemical potential of crystalline polymer, calculated per monomeric unit, μ_c, and that of amorphous polymer μ_a. The chemical potential of UODs dissolved in the polymer will be:

$$\mu_d = \mu_{do} + RT\frac{N_{\text{uod}}}{N_a} = \mu_{do} + RT\frac{[\text{UOD}]M_m}{1000} \qquad (8)$$

where M_m is the molecular weight of the monomeric unit, and $1000/M_m$ is the monomeric unit concentration in the bulk polymer in mol/kg. At the equilibrium $\Sigma_i\, \mu_i\, dN_i = 0$, or

$$\mu_c\, dN_c + \mu_a\, dN_a + \mu_d\, dN_a = 0 \qquad (9)$$

During the process of crystallization the increase in crystalline substance content is equal to decrease of that of amorphous phase, i.e. $dN_c = -dN_a$, and the concentration of UODs in amorphous phase is $[\text{UOD}]_o/(1 - \alpha)$, where $\alpha = N_c/(N_c + N_a)$ is the polymer crystallinity. In this case:

$$-\mu_c + \mu_a + \mu_{do} = \frac{RT[\text{UOD}]_o M_m}{1000(1 - \alpha)} \qquad (10)$$

Assuming that each type of foreign units present in the polymer chain decreases the chemical potential of crystalline phase in proportion to its content N_{fi}, i.e.

$$-\mu_c = -\mu_{co} - \Sigma\, \varkappa_i N_{fi} \qquad (11)$$

we get the resulting formula connecting the polymer crystallinity with UOD and foreign units (FU) concentrations:

$$1 - \alpha = \frac{RT[\text{UOD}]_o}{-\Delta G_{cr} - \Sigma\, \varkappa_i\, [\text{FU}]_i} \qquad (12)$$

where $-\Delta G_{cr}$ is $1000(\mu_a + \mu_{do} - \mu_c)/M_m$ – the change of Gibbs potential at crystallization of ideally ordered polymer calculated per one kilogram. Equation

(12) shows that the polymer crystallinity depends, besides other factors, on UOD concentration, i.e. on content of disorder present in the polymer.

The concentration of centers sorbing the additive A, $[Z_a]$, depends on molecular mass of the additive M_a as in Reference 8:

$$[Z_a] = [Z_o]\exp(-\varkappa M_a) \tag{13}$$

It is natural to suppose that some UODs can form several types of sorption centers Z_j. In the polymer melt the equilibrium must exist:

$$Z_1 \rightleftharpoons Z_2 \rightleftharpoons \ldots \rightleftharpoons Z_j \rightleftharpoons \ldots \rightleftharpoons Z_n \tag{14}$$

If the additive A is sorbed by only one type of center Z_1, added to the polymer melt it will move this equilibrium:

$$\begin{array}{l} Z_1 \rightleftharpoons Z_2 \rightleftharpoons \ldots \rightleftharpoons Z_j \rightleftharpoons \ldots \rightleftharpoons Z_n \\ \ \downarrow\!\uparrow \\ AZ_1 \end{array} \tag{15}$$

For each type of UOD the condition $\Sigma\,[Z_j] + \Sigma\,[AZ_j] = [\mathrm{UOD}_i] = \text{const.}$ is obeyed, thus the increase of Z_1 concentration will result in decrease of concentrations of all other types of centers $Z_j (j \neq 1)$.

Experiments show that adding of phenyl benzoate to isotactic polypropylene melt (220°C) with consequent rapid cooling of the melt and extraction of this additive with ethanol results in marked increase of concentration of centers sorbing the same compound (Figure 3) and in decrease of that of centers sorbing another compound, diphenylmethane (Figure 4). Thus the same topological structure can form various sorption centers in the solid polymer.[4]

Elements of disorder play great role in kinetics of chemical reactions of low-

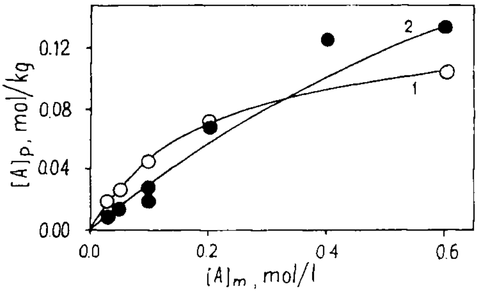


FIGURE 3 Sorption isotherms of phenyl benzoate from benzene solution at 40°C by usual isotactic polypropylene (1) and by the same polypropylene treated with phenylbenzoate, 0.6 mol/kg, in the melt state and then rapidly cooled.

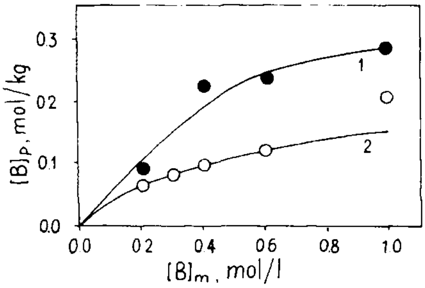


FIGURE 4 Sorption isotherms of diphenyl methane from benzene by isotactic polypropylene: usual (1) and treated with phenyl benzoate, 0.6 mol/kg, in the melt state (2) 40°C.

molecular compounds dissolved in polymer media. Three types of such reactions have been studied:

$$A \rightarrow \text{products} \tag{16}$$

$$A + B \rightarrow \text{products, and} \tag{17}$$

$$2A + \text{polymer} \rightarrow \text{products.} \tag{18}$$

Reaction $A \rightarrow$ products is either additive decomposition, or its isomerization. In the first case the reaction proceeds as:

$$A \rightleftharpoons (X^{\cdot} + {}^{\cdot}X) \rightarrow \text{products} \tag{19}$$

or, in the sorption center:

$$AZ \rightleftharpoons Z(X^{\cdot} + {}^{\cdot}X) \rightarrow \text{products} \tag{20}$$

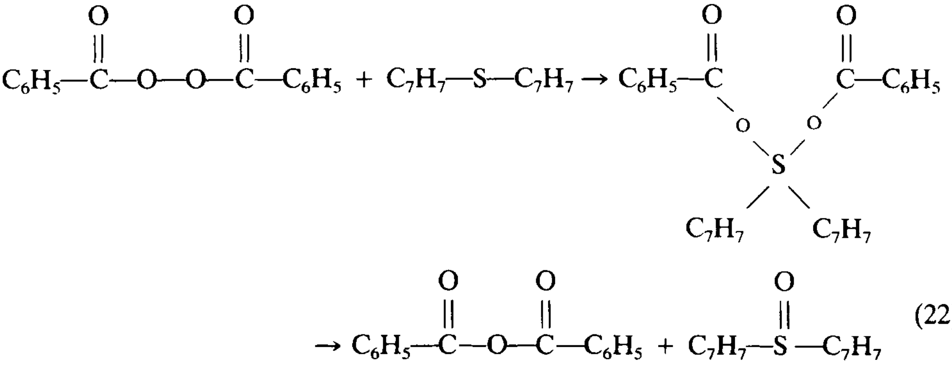
If a certain portion of energy ε is necessary to to decompose the complex AZ_i, a part of this energy $\varepsilon_i'(\varepsilon_i' < \varepsilon_i)$ is needed to liberate one of newly formed radicals. It is natural to suppose that the more stable is AZ_i, i.e. greater is ε_i, the greater will be ε_i', and the less will be free radical $X^{\cdot}$ yield compared to reactions inside the complex, namely $2X^{\cdot} \rightarrow A$ leading to decrease of apparent rate constant and $X^{\cdot} \rightarrow Y^{\cdot}$ with consequent $X^{\cdot} + Y^{\cdot} \rightarrow XY$ leading to decrease of free radical yield in the reaction. With increasing additive concentration in the polymer, $[A]_p$, the first will be occupied the centers Z_i in which the sorption energy ε_i is greater and, consequently, free radical yield is lower. Our experiments proved this suggestion: the apparent rate constant of benzoyl peroxide decomposition in polypropylene increases with increasing peroxide concentration, and another additive, phenyl benzoate, occupying some centers Z_i increased the rate of peroxide decomposition and the yield of free radicals formed in it.[9] In another reaction in polypropylene media, decomposition of azo-bis-isobutyronitrile, the rate constant was virtually independent of the additive concentration, but the free radical yield increased with increasing concentration.[10,11]

As known from chemical kinetics, the rate of chemical reaction between two compounds is direct proportion to the product of reactant concentrations if at least one reactant is composed from mobile particles. The reaction between two additives, A and B, dissolved in the polymer, can proceed either as transformation of the triple complexes ABZ^*, based on large centers Z^*, or through reactions of mobile molecules $A + B$; $A + BZ_i$ and $B + AZ_j$. The complexes AZ_i and BZ_j cannot interact because of their immobility. The rate of the first direction of reaction will rapidly approach the limit equal to $W_{ab^*} = k^* \lim[ABZ^*] = k^*[Z^*]$, where k^* is the rate constant of ABZ^* transformation to products, and the apparent rate constant of this reaction at high enough reactant concentrations will be:

$$k_{ab}^* = \frac{W_{ab^*}}{[A]_p[B]_p} = \frac{k^*[Z^*]}{[A]_p[B]_p} \qquad (21)$$

and will be decreasing with both reactant concentrations. The rates of other reactions will be dependent on the ratios $[A]/[A]_p$ and $[B]/[B]_p$ which vary with reactant concentrations $[A]_p$ and $[B]_p$. The dependence of mobile molecules concentration on the overall concentration of additive can be found by substituting $[A]$ for $\gamma[A]_m$ into Equation (6) and solving resulting equation. The dependence calculated for several meanings of K_a in coordinates $[A]/[A]_p$ vs $[A]_p/[Z_a]$ is the system of S-shaped ascending lines (Figure 5).[12]

The experimental dependencies of apparent rate constants, i.e. of the ratio $k = W/[A][B]$, of several bimolecular reactions in polymers may be presented by sum of this ascending line and descending line corresponding to Equation (19). As an example Figure 6 shows such dependence for interaction of benzoyl peroxide with dibenzyl sulphide in atactic polypropylene and in polyisobutylene:



(22)

The rate constant of this reaction in low-molecular solvent (in isooctane) is independent on reactant concentration, but in its high-molecular analog is expressed by the curved line with minimum, i.e. may be considered as the sum of descending and S-shaped ascending lines.[12,13] The rate of reaction of substituted o-quinones (Q) with polypropylene or polyethylene (RH):

$$2Q + 2RH \rightarrow QR_2 + QH_2 \qquad (23)$$

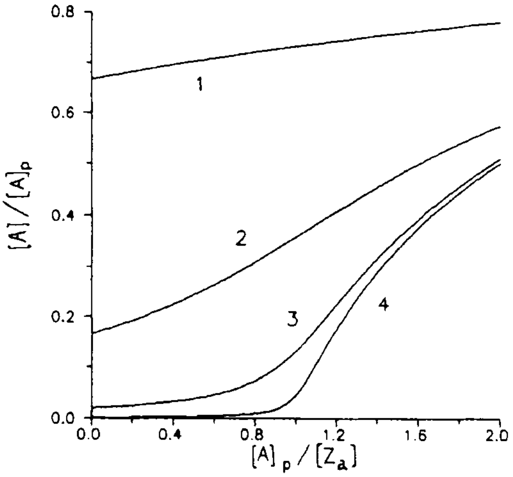


FIGURE 5 The ratio of mobile additive molecules to overall additive concentration $[A]/[A]_p$ as a function of the ratio of the additive concentration to that of sorption centers $[A]_p/[Z_a]$, calculated from Equation (6) assuming $[Z_a] = 0.01$ mol/kg, $K = 5$ (1), 50 (2), 500 (3), and 5000 kg/mol (4).

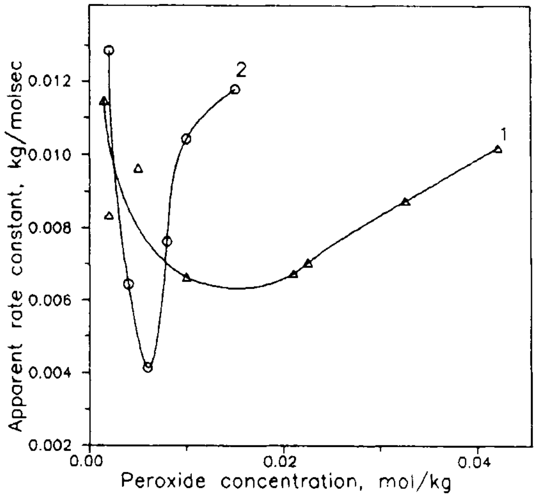


FIGURE 6 The apparent rate constant of interaction of benzoyl peroxide with dibenzyl sulphide as a function of the peroxide concentration in atactic polypropylene (1) and polyisobutylene (2). 50°, sulphide concentration 0.01 mol/kg (1) and 0.011 mol/kg (2).

proceeding in centers Z^* rapidly reaches the limit equal to $k_q[Z^*]$, where k_q is the rate constant of complexes QQZ^* transformation to end products, and is in the wide range virtually independent of the reactant concentration.[14]

Thus many various properties and processes regulations in polymers can be explained considering disorder existing in the polymer as the multitude of various units of disorder (UODs), which in many cases behave like molecules.

In general, such usually used polymer characteristics, as composition, shape, and size distribution of macromolecules must be supplemented with concentration, type and spatial distribution of the units of stable disorder present in it.

References

1. Yu. A. Shlyapnikov, *Doklady Akad. Nauk SSSR*, **202**, 1377 1972).
2. Yu. A. Shlyapnikov, *Europhysics Conference Abstract*, **51**, 311 (1981).
3. R. M. Barrer, J. A. Barrie and J. Slater, *J. Polym. Sci.*, **27**, 177–197 (1958).
4. Yu. A. Shlyapnikov and A. P. Mar'in, *Acta Chimica Hungarica*, **124(4)**, 531–539 (1987).
5. Yu. A. Shlyapnikov and A. P. Mar'in, *Eur. Polym. J.*, **23**, 623–627 (1987).
6. I. Sataitc, A. P. Mar'in, S. Juskeviciute and Yu. A. Shlyapnikov, *Vysokomolek. Soedin.*, **B27**, 215–219 (1985).
7. B. A. Gromov, N. E. Korduner, V. B. Miller and Yu. A. Shlyapnikov, *Doklady Akad. Nauk SSSR*, **190**, 1381–1382 (1970).
8. G. B. Gedraitite, A. P. Mar'in and Yu. A. Shlyapnikov, *Eur. Polym. J.*, **25**, 39–41 (1989).
9. A. P. Mar'in and Yu. A. Shlyapnikov, *Doklady Akad. Nauk SSSR*, **215**, 1160 (1974).
10. A. P. Mar'in and Yu. A. Shlyapnikov, *Vysokomolek. Soedin.*, **B17**, 635–637 (1975).
11. Yu. A. Shlyapnikov, T. V. Monakhova and I. S. Gaponova, *Vysokomolek. Soedin*, **A21**, 875–881 (1979).
12. N. N. Kolesnikova and Yu. A. Shlyapnikov, *Eur. Polym. J.*, **23**, 633 (1987).
13. N. N. Kolesnikova and Yu. A. Shlyapnikov, *Vysokomolek. Soedin.*, **B19**, 184–186 (1977).
14. E. S. Torsueva and Yu. A. Shlyapnikov, *Vysokomolek. Soedin.*, **B19**, 377–379 (1977).