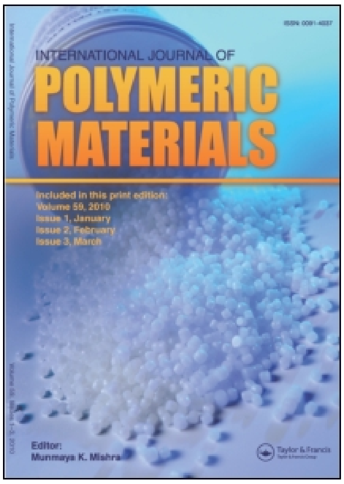

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Possibility of Regulating the Stable Disorder in Polymers

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Presence of topological characteristics, such as entanglement of polymer chains and chain ends are discussed in terms of their concentration and spatial distribution.

KEY WORDS Disorder, chain ends, entanglement, spatial distribution.

ANALYSIS AND DISCUSSION

In 1971 a model has been proposed by the author[1] considering the bulk linear polymer as solution of various topological structures, namely the ends and entanglements of polymer chains, in ideally ordered polymeric substance. These structures may be considered as the units of disorder (UODs) existing in the polymer. In the polymer melt these structures were supposed to behave like molecules of a certain quasi-compound ζ. The structures ζ distorting the order in surrounding polymer form the certain centers Z_i, containing the stable part of free volume present in the polymer. Consider some consequences of this model.

It is well known that many crystalline or semi-crystalline polymers contain two coexisting phases, crystalline and amorphous, in certain ranges of temperature and pressure, which is in contradiction with Gibbs phase rule:

$$F + P \leqslant C + 2$$

where F is the number of freedom degrees, which are temperature and pressure, that is $F = 2$, P-the number of coexisting phases, i.e. 2. Substituting these for F and P we get $C \geqslant 2$, i.e. an individual crystalline homopolymer must contain at least two components. If one component is the polymer as such, the lacking second component may be the multitude of UODs.

Dissolution of polar low-molecular-weight additive in the simplest non-polar polymer, polyolefin, may be described as formation of complexes of centers Z_i with additive A:

$$A + Z_i \overset{K_a}{\rightleftharpoons} AZ_i$$

This scheme leads to Langmuir-type dependence of additive concentration in the polymer $[A]_p$ on its concentration in surrounding medium $[A]_m$:

$$[A]_p = \frac{K\gamma[Z_a][A]_m}{1 + K\gamma[A]_m}$$

Here $[Z_a]$ is the complete concentration of the centers Z_i sorbing A, and γ is the coefficient connecting the additive concentration around polymer $[A]_m$ with that of mobile molecules A outside the centers: $[A] = \gamma[A]_m << [A]_p$. Such dependence had been observed by many authors (i.e. References 2, 3). In our works we have shown that the Langmuir sorption limit $[Z_a]$ above polyolefin glass-transition temperature, even in polymer melt, is independent of temperature, i.e. the centers Z are real material structures.[3]

Some properties of structures ζ and centers Z have been studied using the additive sorption as the method of investigation. Among them is size distribution of center concentration $[Z_a]$ on molecular mass of additive sorbed M_a^4:

$$[Z_a] = [Z_o]\exp(-\varkappa M_a)$$

The concentration of polymer chain entanglements ζ can be decreased by repeated melting and crystallization of crystalline polymers, leading to disentangling of these structures.[5] Disentangling of ζ results in decrease of concentration of centers based on these structures. On the other hand, the concentration of centers Z_a sorbing the additive A can be increased by adding A to the polymer melt in the high concentration enough to rearrange the polymer structure.[3]

Substitution of one additive A in the center by another B:

$$AZ + B \rightleftharpoons A + BZ$$

results in decrease of the additive solubility in the presence of another one.[3] Low-molecular also can substitute additives in the centers decreasing their solubilities.

The rate of decomposition of non-stable additive molecule depends on the site it is present in. If a radical pair is formed in A decomposition, the greater is the energy needed for the radical yield the lesser will be the average yield and decomposition rate, the stronger is the complex AZ_i the less is rate constant of additive decomposition in it. Complexes of additives with centers Z_i are immobile, and interaction of compounds A and B, present in a polymer mainly as complexes AZ_a and BZ_b, needs the yield of at least one of these molecules. As a result the regularities of chemical reactions in polymers markedly differ from those of analogous reactions in low-molecular liquids.[6–9] For example, the reaction of *o*-quinones with polypropylene:

$$2A + \text{polymer} \rightarrow \text{products}$$

proceeding in the large centers Z^* approaches the limit:

$$W = k_{\text{aaz}}[AAZ^*]$$

and becomes zero-order in quinone concentration[9] when the latter becomes high enough that the concentration of reacting complex $[AAZ^*]$ becomes virtually equal to $[Z^*]$. Sometimes the additives taking no part in chemical reaction studied affects its rate substituting reagents in some centers and thus changing their reactivities.

There are some other phenomena which can be explained taking into account the units of stable disorder formed around the polymer chain entanglements.

According to the model, the samples of the same polymer with the same composition, structure and size of molecules can differ in concentration and spatial distribution of UODs, i.e. in the level of disorder in the polymer chains arrangement. This difference will result in difference of the polymer properties in these samples, and varying UOD type and concentration we may get a variety of new materials from the same well known polymer. Now the methods of disorder variation are not used, at least consciously, in polymer technology.

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