Physical chemistry of topological disorder in polymeric substances: size distribution of additive sorption centres

Yury A. Shlyapnikov
Institute of Chemical Physics, 117334, Moscow, Russia
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The simple formula for the size distribution of additive sorption centres in polymers previously found experimentally is derived theoretically based on a two-component model of polymer structure.

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The various entanglements of polymer chains may be divided into two groups: reversible ones formed and destroyed by thermal motion of neighbouring segments of macromolecules; and stable topological structures formed on polymer formation or precipitation from solution, which cannot be disentangled without shifting one or several ends of the polymer chains forming this entanglement.

Some time ago the author proposed a model of polymeric substances considering a polymer as a two-component system, the main component being the polymer as such, and the other being the multitude of various topological structures, like knots and interlacements of the polymer chains, which form the units of disorder (UODs) ζ_i. Being formed by long polymer chains, these UODs are very stable even in the polymer melt, where they are relatively mobile and in some cases may be considered as particles[1-3]. Their content in the polymer may be expressed in the units of concentration:

$$[\zeta]=\sum[\zeta_i]=(\text{number of UODs})/VN_A$$

where V is the sample volume and $N_A=6.02\times10^{23}$ mol^{-1} is the Avogadro constant. The model enables us, at least formally, to get agreement with the experimentally established existence of two coexisting phases in so-called crystalline polymers, the ratio of which changes reversibly with temperature (see for example ref. 4) and, apparently, with pressure.

The Gibbs phase rule:

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

where F is the number of degrees of freedom, which in our case is 2 (temperature and pressure), and P is the number of coexisting phases, which is also 2 (crystalline and amorphous ones), requires that the number of components in such a polymer C must be either two or greater. According to the two-component model, the lacking second component present in the polymer is formed by the multitude of various UODs.

Being sites of stable violation of short-range order, UODs contain a certain amount of excess volume compared to well ordered regions of the polymer. It is natural to suppose that low-molar-mass additives (A) dissolved in a 'solid' polymer are present mainly in the zones Z_i formed around UODs; that is, the sorption of A may be considered as complex formation:

$$A+Z_i \overset{K_{ai}}{\rightleftharpoons} AZ_i \tag{2}$$

Numerous experiments have shown that the sorption of many compounds with molar masses above 100 g mol^{-1} by various polymers obeys a law analogous to the Langmuir adsorption isotherm[5-8], which may be derived from equation (2) by supposing that all $K_{ai}=K_a=$ constant:

$$[A]_p=\frac{K_a\gamma_a[Z_a][A]_m}{1+K_a\gamma_a[A]_m} \tag{3}$$

where $[A]_p$ and $[A]_m$ are the additive concentrations in the polymer and in the surrounding medium, and $[Z_a]$ is the sum of concentrations of various Z_i taking part in the sorption of A. Rearranging formula (3) we get:

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

Formula (4) may be used for evaluation of $[Z_a]$, the concentration of centres participating in sorption of the given compound A, from the experimental dependence of $[A]_p$ on $[A]_m$.

In many cases the experimentally found values of $[Z_a]$ were independent of temperature above T_g and even above the polymer melting temperature[7,8]. Such stability can be explained only by the topological nature of the sorption centres formed by long-chain macromolecules. All other types of structures decompose in the polymer melt.

The Langmuir-type sorption isotherms (3) correspond to the case when the additive dissolved in the polymer does not change its structure. In some cases, especially at high additive concentrations and temperature, sorption is accompanied by swelling, and the sorption law (3) becomes violated[9]. We will not discuss this case here.

Dividing the process of sorption into two stages, namely dissolution of A in the ordered part of the polymer with formation of true solution, and formation

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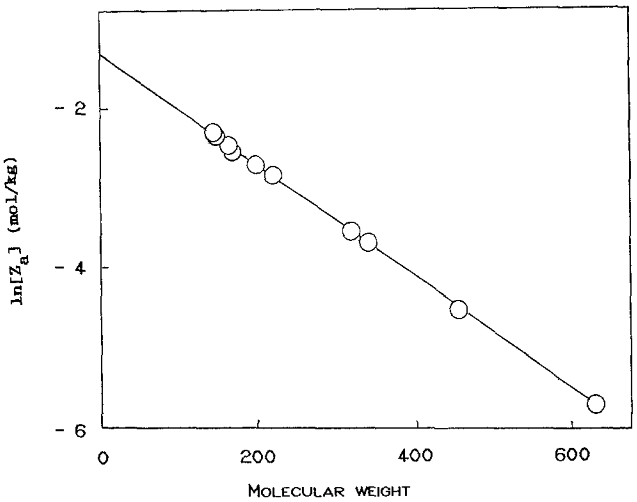

Figure 1 Experimental dependence of logarithm of sorption centres concentration $\ln[Z_a]$ on molar mass of sorbate M_a for sorption by high-density polyethylene from n-hexane (data from ref. 10)

of complexes of truly dissolved A with centres Z_i (concentration of truly dissolved A, $[A]\ll\sum[AZ_i]$), we denote the coefficient of proportionality $[A]/[A]_m=\gamma_a$.

It has been shown in ref. 7 that taking into account the differences between equilibrium constants K_{ai} we get an equation differing from (3) in its form but experimentally indistinguishable from it. In all cases the limit to which the additive concentration in the polymer approaches with increasing $[A]_m$ if the polymer structure remains unchanged is the concentration of sorption centres $[Z_a]$.

Formation of excess (free) volume needs a certain energy, which depends on the properties of the solvent in which the polymer had been prepared or from which it was precipitated. We suppose that this energy is directly proportional to the excess volume that the entanglement contains:

$$\varepsilon_i=qv_i \tag{5}$$

It is natural to assume that the size distribution of ζ_i at the moment of their formation obeys the Boltzmann law: the ratio of the elements, the energy of formation of which exceeds ε_a, is given by the expression:

$$[\zeta_a]=(\textstyle\sum[\zeta_i])\exp(-\varepsilon_a/kT)$$

Assuming that the excess (free) volume that Z_i contains is either equal to or directly proportional to that present in ζ_i (coefficient of proportionality $\beta\approx1$), we get:

$$[Z_a]=[Z]_0\exp(-\beta qv_a/kT_f) \tag{6}$$

Here T_f is the temperature of polymer formation or precipitation.

In ref. 10 the size distribution of the additive sorption centres in high-density polyethylene has been investigated. The additives were organic compounds, mostly antioxidants, consisting of carbon, hydrogen and nitrogen or oxygen atoms. The densities of these compounds in the solid state or melt were 1.0–1.21 g cm^{-3}, i.e. $\bar{\rho}=1.1\pm0.1$ g cm^{-3}, and we may suppose that their molecular volumes in polymers approximately coincide with those in the pure state, i.e. are equal to $v_{ma}\simeq M_a/1.1N_A=M_a/6.62\times10^{23}$ cm^3, where M_a is the molar mass of the additive A. The medium in which the additives were dissolved was n-hexane, the low-molar-mass model of the polymer. As seen from *Figure 1*, the dependence found transforms into a descending straight line in coordinates $\ln[Z_a]$ vs. M_a, i.e.

$$[Z_a]=[Z]_0\exp(-\kappa M_a) \tag{7}$$

This coincides with (6) assuming $\kappa=\beta qv_a/kT_fM_a\simeq\beta q/\bar{\rho}N_AkT_f$. Transforming the latter expression we get

$$q\simeq\beta q=\kappa\bar{\rho}N_AkT_f \qquad \text{(energy/volume)} \tag{8}$$

Calculated from *Figure 1* for high-density polyethylene, $\kappa=1.6\times10^{-2}$ mol g^{-1} and $[Z]_0=0.26$ mol kg^{-1} (ref. 8). Substituting this into (8) and assuming $\rho=1.1$ g cm^{-3} and $T_f\simeq350$ K (the temperature of polyethylene synthesis being 70–80°C), we find that $q=5.1\times10^8$ erg cm^{-3} = 51 J cm^{-3}. This value is comparable with the heat of fusion of polyethylene crystals (293 J g^{-1})[11].

Thus the concentration and size distribution of entanglements, which characterize the level of disorder present in the polymer, may be evaluated by studying the sorption isotherms of various additives in the polymer.

REFERENCES

1 Shlyapnikov, Yu. A. *Dokl. Akad. Nauk SSSR* 1972, **202**, 1377
2 Shlyapnikov, Yu. A. *Europhys. Conf. Abstr.* 1981, **51**, 311
3 Shlyapnikov, Yu. A. *Khim. Fiz.* (*Russ. Chem. Phys.*) 1992, **11** (9), 1291
4 Braun, J. M. and Guillet, J. E. *J. Polym. Sci., Polym. Chem. Edn* 1975, **12**, 1119
5 Barrer, R. M. and Barrie, J. A. *J. Polym. Sci.* 1957, **23**, 331
6 Barrer, R. M., Barrie, J. A. and Slater, J. J. *J. Polym. Sci.* 1958, **27**, 177
7 Shlyapnikov, Yu. A. and Mar'in, A. P. *Eur. Polym. J.* 1987, **23**, 623
8 Bagdonaite, V. A. and Yushkevichute, S. S. *Vysokomol. Soedin.* (*B*) 1982, **24**, 55
9 Shlyapnikov, Yu. A. and Mar'in, A. P. *Acta Chim. Hung.* 1987, **124** (4), 531
10 Gedraitite, G. B., Mar'in, A. P. and Shlyapnikov, Yu. A. *Eur. Polym. J.* 1989, **25**, 39
11 Wunderlich, B. 'Macromolecular Physcis', Vol. 3, 'Crystal Melting', Academic Press, New York, 1980