# VALUES OF COHESIVE ENERGY FOR SOME POLYMERS

PHYSICAL CHEMISTRY

1965

SovietRxiv

## Abstract

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UDC 678.01:53+541.6

*PHYSICAL CHEMISTRY*

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# VALUES OF COHESIVE ENERGY FOR SOME POLYMERS

*(Presented by Academician V. A. Kargin, 12 IV 1965)*

P. Debye proposed a method for determining the mean radius of action of intermolecular forces in polymer solutions, $l$, based on measurements of the asymmetry of critical opalescence ([1]). Similar determinations of $l$ were carried out in a number of works ([2–7]). According to Debye's theory ([5]), the value $l^2$ depends on the mean-square radius of inertia of polymer coils in solution $\overline{R^2}$ (at the critical concentration and near the critical solution temperature $T_k$—the precipitation point), and also on the cohesive-energy densities polymer–polymer $\delta_{22}$, solvent –solvent $\delta_{11}$, and polymer–solvent $\delta_{12}$:

$$l^2 = \frac{l_{11}^2 \delta_{11}}{\delta_{11} + \delta_{22} - 2\delta_{12}} + \frac{2(\delta_{22} - \delta_{12})}{\delta_{11} + \delta_{22} - 2\delta_{12}} \overline{R^2}, \tag{1}$$

(here $l_{11}$ is the value of $l$ in the solvent). The value $\overline{R^2}$ can be determined, along with $l^2$, from the asymmetry of critical opalescence of solutions, if the molecular weight of the polymer fraction is sufficiently large ([4,5]). Since $\overline{R^2} \sim p$ ($p$ is the degree of polymerization), one should expect that $(l^2 - l_0^2) \sim p$, where

$$l_0^2 = \frac{\delta_{11}^2 \delta_{11}}{\delta_{11} + \delta_{22} - 2\delta_{12}}. \tag{2}$$

Figure 1 shows the dependence of $l^2$ on $p$ for fractions of poly-$\beta$-vinylnaphthalene (PVN) and polynaphthyl methacrylate (PNMA) in a number of solvents, and also for polybutyl methacrylate (PBMA) in isopropyl alcohol.

**Fig. 1.** Dependence of the square of the mean radius of action of intermolecular forces $l^2$ on the degree of polymerization $p$:
*Ia*–poly-$\beta$-vinylnaphthalene in phenylethyl alcohol; *Ib*–poly-$\beta$-vinylnaphthalene in benzyl alcohol; *Ic*–poly-$\beta$-vinylnaphthalene in a mixture of toluene–decalin (1:1.3); *IIa*–polynaphthyl methacrylate in benzyl alcohol; *IIb*–polynaphthyl methacrylate in phenylethyl alcohol; *IIc*–polynaphthyl methacrylate in tetralin; *IId*–polynaphthyl methacrylate in toluene; *III*–polybutyl methacrylate in isopropyl alcohol.

Fig. 1. Dependence of the square of the mean radius of action of intermolecular forces $l^2$ on the degree of polymerization $p$: Ia—poly-$\beta$-vinylnaphthalene in phenylethyl alcohol; Ib—poly-$\beta$-vinylnaphthalene in benzyl alcohol; Ic—poly-$\beta$-vinylnaphthalene in a mixture of toluene—decalin (1:1.3); IIa—polynaphthyl methacrylate in benzyl alcohol; IIb—polynaphthyl methacrylate in phenylethyl alcohol; IIc—polynaphthyl methacrylate in tetralin; IId—polynaphthyl methacrylate in toluene; III—polybutyl methacrylate in isopropyl alcohol

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Since the quantity $\delta_{11} = (Q - RT)/V_1$ is known in principle ($Q$ is the heat of evaporation of 1 mole of solvent at temperature $T_k$; $R$ is the universal gas constant; $V_1$ is the molar volume of the solvent), then, having determined $l^2$ and $\overline{R^2}$ for some polymer fraction and using the graph $l^2 = f(p)$ to determine $l_0^2$, one can calculate the cohesive-energy densities $\delta_{22}$ and $\delta_{12}$ from relations (1) and (2), transformed into the form

$$a = \frac{2\overline{R^2} - (l^2 - l_0^2)}{l^2 - l_0^2} = \frac{\delta_{11} - \delta_{12}}{\delta_{22} - \delta_{12}}, \tag{1a}$$

$$b = \frac{l_0^2}{l_{11}^2} = \frac{\delta_{11}}{\delta_{11} + \delta_{22} - 2\delta_{12}} \tag{2a}$$

The value of $l_{11}$, according to measurements of critical opalescence in mixtures of low-molecular liquids, is 10-14 Å (8–11) and, without significant error, may be taken equal to 12 Å. Eliminating $\delta_{12}$ from (1a), (2a), one can obtain

$$\delta_{22} = \delta_{11}\left[1 - \frac{a-1}{(a+1)b}\right], \tag{3}$$

or, per 1 mole of monomer units of the polymer,

$$\delta_{22}V_2 = (Q - RT)\frac{V_2}{V_1}\left[1 - \frac{a-1}{(a+1)b}\right], \tag{3a}$$

where $V_2 = M_0\bar{v}$, $M_0$ is the molecular weight of the monomer unit, and $\bar{v}$ is the partial specific volume of the polymer in solution.

The result of calculating the molar cohesive energy $\delta_{22}V_2$ for PVN, PNMA, and PBMA is presented in Table 1. From consideration of the available data—

**Table 1**

| Solvent | $M_w \cdot 10^{-6}$ | $\varepsilon$ | $T_k$, °C | $l$, Å | $(\overline{R^2})^{1/2}$, Å | $a$ | $b$ | $\delta_{22}V_2$, kcal/mol |
|---|---|---|---|---|---|---|---|---|
| **Poly-β-vinylnaphthalene** | | | | | | | | |
| Phenylethyl alcohol | 1.12 | 13.1 | 59.9 | 21.0 | 221 | ∞ | 3.05 | 11400 |
| Benzyl alcohol | 1.12 | 13.1 | 63.5 | 46.0 | 139 | 21.3 | 2.78 | 12000 |
| Toluene–decalin 1 : 1.3 | 1.12 | 2.3 | 26.4 | 78.5 | 123 | 4.5 | 4.16 | 8800 |
| **Polynaphthyl methacrylate** | | | | | | | | |
| Phenylethyl alcohol | 2.6 | 13.1 | 52.0 | 52.2 | 88.7 | 4.2 | 8.6 | 20500 |
| Benzyl alcohol | 2.6 | 13.1 | 49.4 | 48.5 | 84.7 | 8.7 | 6.1 | 20000 |
| Tetralin | 2.6 | 2.7 | 25.0 | 64.7 | 62.9 | 1.8 | 9.7 | 16000 |
| Toluene | 2.6 | 2.4 | 36 | 79.9 | 67.5 | 0.87 | 10.6 | 13400 |
| **Polybutyl methacrylate** | | | | | | | | |
| Isopropyl alcohol | 1.3 | | 15.4 | 64.5 | 133 | 8.0 | 1.73 | 9700 |
| Isopropyl alcohol | 1.8 | | 16.0 | 64.7 | 145 | 9.7 | 1.73 | 9350 |
| Isopropyl alcohol | 3.0 | | 16.3 | 70.0 | 171 | 11.4 | 1.73 | 9100 |

–some preliminary conclusions may be drawn. The cohesive-energy values of a number of polymers, determined by the method of critical opalescence, have the same order of magnitude as $\delta_{22}V_2$ obtained for some polymers (polystyrene, polyethylene, polyisobutylene, natural rubber) by other methods (12, 13). For PNMA, the value of $\delta_{22}V_2$ obtained in alcohols proves to be substantially higher than in nonpolar solvents with a low dielectric constant $\varepsilon$, such as toluene or tetralin. Within the group of polar or nonpolar solvents, the values of $\delta_{22}V_2$ for a given polymer are sufficiently close.

The values of $\delta_{22}V_2$ for three fractions of PBMA (in one solvent) are very close, although one may note a tendency toward some decrease in $\delta_{22}V_2$ with increasing $M$, apparently associated with deviation of the points on the plot $l^2 = f(p)$ from a straight line (Fig. 1).

Sources of quantitative data on the cohesive-energy densities of polymers are few. The traditional method for determining $\delta_{22}$ is the investigation of polymer swelling (see, for example, (12)). Comparatively recently, it was proposed to use the relation between the cohesive energy and the internal pressure in a polymer (thermal pressure coefficient) (13). Attempts to calculate $\delta_{22}$ on the basis of

of additivity of cohesion energies for individual atomic groups (see, for example, ([14])). The indicated methods do not give entirely coincident results. Obtaining additional information is therefore highly desirable. In addition, in a number of technological processes the interaction of polymer molecules in solutions plays an essential role. In this connection, comparison of the average radii of action of intermolecular forces $l$, measured by the critical-opalescence method, and of the cohesion energies for a given polymer $\delta_{22}V_2$ in different solvents may have certain advantages.

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Received
18 III 1965

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*Note: Figure translations are in progress. See original paper for figures.*