

Electronic supplementary information

DEFINITION OF THE COMPOSITIONS OF MICROPHASES DURING FORMATION OF POLY(EPOXY URETHANE ISOCYANURATE) NETWORKS

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S1. Description of the solubility criterion

The solubility criterion includes solubility parameters δ . In the initial form, the concept of solubility parameter was suggested for nonpolar compounds. However, later it was substantially developed in the works of Hansen, Hoy, and other researchers. In particular, we managed to modify the concept of solubility parameters, which received the highest number of citations in the foreign literature, not to mention the domestic literature. The modified concept takes into account the effect of dispersion interactions and strong intermolecular interactions and hydrogen bonds on the cohesive energy. The solubility parameter δ is calculated by the following formula

$$\delta^2 = \frac{\sum_i \Delta E_i^*}{N_A \sum_i \Delta V_i} \quad (\text{S1})$$

where $\sum_i \Delta E_i^* = k(\sum_i \Delta E)_0$ is the cohesive energy of a solvent or a polymer repeating unit, reduced so many times, as the van der Waals volume of the molecule or the repeating unit is smaller than the molar volume; k is the coefficient of molecular packing of the liquid or the polymer; N_A is the Avogadro's number.

The solubility parameter is determined by relation $\delta^2 = \delta_D^2 + \delta_{DD}^2 + \delta_H^2$, where δ_D^2 is the solubility parameter defined by the energy of dispersion interaction, δ_{DD}^2 is the solubility parameter defined by the energy of dipole–dipole interaction, and δ_H^2 is the solubility parameter defined by the energy of hydrogen bonds.

As for the prediction of compatibility of the polymers and their solubility in organic solvents, in this case a single solubility parameter is not sufficient, which was noted in a series of publications. The physical meaning of the parameters, which are included in the solubility or compatibility criterion, consists in the fact that if the soluble particles feature a degree of curvature, then at the positive curvature (for example, insertion of a globule into a liquid) the Laplace forces are emerging that tend to press the globule to the dissolved compound. At the negative curvature, these forces cause the wedging effect, which tend to separate the globule from the dissolved compound. The higher the curvature degree (the lower the radius), the stronger the arising forces. If the wedging effect exceeds the attraction force, then there is a probability of separation of the globule and its transition to the solution. However, this is not enough. The work done by the surface tension of the solvent must exceed the energy of cleavage of intermolecular bonds at the junction of the globule to the compound. In general, the formation of a surface that arises during immersion of a solid body into a solvent, causes adhesional wetting work W_A , which is equal to $W_A = \gamma_{sp} - (\gamma_p + \gamma_s)$, where γ_p is the polymer surface energy, γ_s is the solvent surface tension, γ_{sp} is the interfacial tension.

The probability of prediction of criterion (1) or (2) is 85%. This was tested on 350 polymers of various structures. The physical parameters that are directly related to the criterion of thermodynamic compatibility are described above. They can be supplemented with the molar volumes of the components which are included into the value of Φ in the solubility criterion

$$\Phi = \frac{4(V_{p,1} \cdot V_{p,2})^{1/3}}{(V_{p,1}^{1/3} + V_{p,2}^{1/3})^2} \quad (\text{S2})$$

where $V_{p,1}$ and $V_{p,2}$ are the molar volumes of polymer **1** and **2**, respectively.

Furthermore, the solubility criterion includes also the following physical parameters: $\mu \leq 2\rho\beta$, where $\mu = \frac{\delta_p^2}{\delta_s^2}$, δ_p and δ_s are the solubility parameters of the polymer and solvent, respectively, $\rho = \frac{\varepsilon_{max}^p r_s}{\varepsilon_{max}^s r_p}$, ε_{max}^p is

the maximum relative deformation of polymer intermolecular bonds at the moment of their separation and transition into the solvent, ε_{max}^s is the maximum liquid strain, at which the continuity is disrupted, r_s is the characteristic bond size of the Frenkel's swarms of the solvent, and r_p is the small radius of the bond globule for the polymer.

These notions are described in detail in the previous publications [1–4].

S2. Description of the Cascade software

The Cascade software allows one to predict many physical properties of the polymers with linear and network structures based on their chemical structures. To calculate the physical properties of polymers based on chemical structures of repeating units, the method of atomic physical constants is used that takes into account the van der Waals volumes of atoms which comprise the repeating unit of a linear polymer or a repeating moiety of a network polymer as a fundamental characteristic. The polymer repeating unit is considered as a set of anharmonic oscillators formed by pairs of atoms included in this unit. A difference between the experimental and calculated data obtained by the developed scheme usually falls within 3–5%, although in some cases it composes less than 3% or more than 5%. The Cascade program is based on the computer-processed approach devised at INEOS RAS, which is predominantly atomistic. For each atom, an averaged energy of intermolecular interactions is introduced, and the effect of separate polar groups is taken into account by the introduction of a restricted set of increments similar for different types of dipole–dipole interactions and hydrogen bonds. At the same time, since each polar group has a distinct chemical structure and, consequently, distinct van der Waals volume, the contribution of each group into the intermolecular interaction will be different.

The presence of the minimum amount of constants and increments enable the calculation of a large number of polymer structures independent from the complexity of their chemical structures. These calculations are useful and necessary not only for solution of the main problem, connected with the prediction of the properties of polymers and copolymers before their synthesis. The computer program allows one to analyze the solubility of polymers and their compatibility with each other. It enables the analysis of the effect of different groups included in polymers, for example, by polymer analogous transformations on the properties of the resulting systems, on the composition of microphases during microphase separation, it also provides means for analysis of the effect of branching and structural defects in finely cross-linked polymers on their properties and to address many other issues.

The Cascade computer program allows one to calculate the dielectric loss tangent at different frequencies (from 10^2 to 10^6 Hz); the dependences of the polymer softening points on the content of a plasticizing agent or a solvent. The program contains special options for different properties of the polymer of any chemical structures depending on the molecular mass, microtacticity, crystallinity degree, and temperature. There is also a possibility to calculate the temperature dependences of density, molecular packing coefficient, specific and molar volumes.

The Cascade software allows one to calculate over 60 physical characteristics of linear and network polymer structures as well as low-molecular organic liquids which are used as solvents for polymers. Noteworthy, it is the only one current program that enables the calculation of physical properties of polymer networks. The physical properties which can be calculated for network polymers include glass-transition temperature, onset temperature of intensive thermal destruction, refractive index, dielectric permeability, equilibrium rubbery modulus, and many others. The program enables the prediction of compatibility of polymers with each other as well as their solubility in organic solvents. There is also a possibility to calculate the properties of copolymers, homogeneous mixtures of polymers, and so on.

References

1. A. A. Askadskii, Yu. I. Matveev, M. S. Matevosyan, *Vysokomol. Soedin., Ser. A*, **1990**, 32, 2157–2166.
2. Yu. I. Matveev, A. A. Askadskii, *Vysokomol. Soedin., Ser. A*, **1986**, 28, 1365–1372.
3. Yu. I. Matveev, A. A. Askadskii, *Vysokomol. Soedin., Ser. A*, **1989**, 31, 617–622.
4. Yu. I. Matveev, A. A. Askadskii, *Vysokomol. Soedin., Ser. A*, **1994**, 36, 436–443.