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The effect of strong intermolecular and chemical interactions on the compatibility of polymers

A A Askadskii

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Abstract. The data on compatibility and on the properties of polymer blends are generalised. The emphasis is placed on the formation of strong intermolecular interactions (dipole – dipole interaction and hydrogen bonding) between the components of blends, as well as on the chemical reactions between them. A criterion for the prediction of compatibility of polymers is described in detail. Different cases of compatibility are considered and the dependences of the glass transition temperatures on the composition of blends are analysed. The published data on the effect of strong intermolecular interactions between the blend components on the glass transition temperature are considered. The preparation of interpolymers is described whose macromolecules are composed of incompatible polymers, which leads to the so-called 'forced compatibility.' The bibliography includes 80 references.

I. Introduction

In the studies of polymer blends much attention is currently given to the effect of strong intermolecular and chemical interactions between the polymer blend components on their compatibility.

Investigation of compatibility of polymers is of importance from both scientific and practical points of view.[1–3] In one of the concepts, it is proposed to analyse compatibility of polymers using the solubility parameter (the density of cohesive energy). The equation used to assess the parameter of the polymer – polymer interaction (χ) includes the solubility parameters of each polymer

$$\chi = \frac{V}{RT}(\delta_1 - \delta_2)^2, \qquad (1)$$

where V is the molar volume of the rubber-like phase per repeating unit of the polymer; δ_1 and δ_2 are the solubility parameters of the polymers 1 and 2, respectively; R is the universal gas constant and T is the absolute temperature.

A A Askadskii A N Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 93 98. E-mail: andrey@ineos.ac.ru

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According to this concept, polymers are compatible if the interaction parameter is positive and its value is close to zero. Limitations of this approach have been analysed.[4] One of the limitations is associated with the necessity to calculate and measure the solubility parameter to a high accuracy. This is impossible for polymers since this parameter is assessed indirectly using determination of intrinsic viscosity of polymer solutions in various solvents followed by construction of the dependence of the intrinsic viscosity on the solubility parameter of the solvent in which the measurements have been carried out; construction of the dependence of the degree of swelling on the solubility parameter of the solvent in which swelling occurs, *etc*. The critical value of the parameter χ, *viz*., the upper limit of solubility, is determined from the following relationship[5]

$$\chi_c = \frac{1}{2(N_1^{-1/2} + N_2^{-1/2})^2},$$

where N_1 and N_2 are the degrees of polymerisation of the components 1 and 2, respectively. Calculations or experimental measurements of the solubility parameters should be carried out with an accuracy of 0.1 $(\mathrm{J\ cm^{-3}})^{1/2}$.

A concept of compatibility of polymers using the solubility parameter has been developed in detail.[4] In this study, individual contributions of the components into the solubility parameter were considered and the compatibility parameter (introduced previously[6]), which is the difference between the cohesive energy densities of the components, was used.

Let us consider other approaches to the prediction of the compatibility of polymers and the properties of blends obtained.

According to the reported data,[7–11] the solubility of polymers occurs if the following inequality holds

$$\mu < 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right). \qquad (2)$$

Here $\mu = \delta_p^2/\delta_s^2$, where δ_p is the solubility parameter of the polymer, δ_s is the solubility parameter of the solvent; the Φ value is found from the relationship

$$\Phi = \frac{4\left(V_s V_p\right)^{1/3}}{\left(V_s^{1/3} + V_p^{1/3}\right)^2}, \qquad (3)$$

where V_p and V_s are the molar volumes of the polymer and the solvent, respectively, and the a value is calculated using the formula

$$a = \frac{\gamma_{sp}}{\gamma_s}, \quad (4)$$

where γ_{sp} is the interface tension and γ_s is the surface tension of the solvent. The right part of the criterion (2) is represented in the form $2\rho\beta$, where $\rho = 1.374/2$ and $\beta = \Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right)$.

The interface tension is defined as follows:

$$\gamma_{sp} = \gamma_s + \gamma_p - 2\Phi\left(\gamma_s\gamma_p\right)^{1/2}, \quad (5)$$

where γ_p is the surface energy of the polymer.

An attempt to analyse the compatibility of polymers using the criterion for the polymer solubility in organic solvents, *viz*., relationship (2), has been undertaken.[11] Let us consider this criterion in detail.

II. Criteria for the compatibility of polymers

If a small amount of a polymer 1 is introduced into a polymer 2, the polymer 1 and the polymer 2 are considered as the 'polymer' and the 'solvent', respectively. The following cases are possible when using criterion (2).

1. Polymers 1 and 2 are incompatible. A small amount of a polymer 1 is introduced into a polymer 2 and, *v.v*., a small amount of a polymer 2 is introduced into a polymer 1. Then the compatibility criterion has the form

$$\mu_1 = \frac{\delta_{p1}^2}{\delta_{p2}^2} > 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a_1}\right) = 2\rho\beta_1, \quad (6)$$

$$\mu_2 = \frac{\delta_{p2}^2}{\delta_{p1}^2} > 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a_2}\right) = 2\rho\beta_2, \quad (7)$$

where δ_{p1} and δ_{p2} are the solubility parameters of the polymers 1 and 2, respectively;

$$\Phi = \frac{4\left(V_{p1}V_{p2}\right)^{1/3}}{\left(V_{p1}^{1/3} + V_{p2}^{1/3}\right)^2}, \quad (8)$$

where V_{p1} and V_{p2} are the molar volumes of repeating units of the polymers 1 and 2, respectively;

$$a_1 = \frac{\gamma_{p1,p2}}{\gamma_{p2}}, \quad (9)$$

$$a_2 = \frac{\gamma_{p1,p2}}{\gamma_{p1}}, \quad (10)$$

$$\gamma_{p1,p2} = \gamma_{p1} + \gamma_{p2} - 2\Phi\left(\gamma_{p1}\gamma_{p2}\right)^2, \quad (11)$$

where $\gamma_{p1,p2}$ is the tension at the polymer 1 – polymer 2 interface and γ_{p1} and γ_{p2} are the surface energies of the polymers 1 and 2, respectively.

Since the values of the left sides of the criteria (6) and (7) are larger than those of their right sides, polymers 1 and 2 are completely incompatible.

2. If a small amounts of a polymer 1 is introduced into a polymer 2, criterion (2) indicates that the 'solubility' of the first polymer in the second polymer occurs, *i.e*.,

$$\mu_1 = \frac{\delta_{p1}^2}{\delta_{p2}^2} < 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a_1}\right) = 2\rho\beta_1. \quad (12)$$

However, as indicated by calculations using the criterion (2), no 'solubility' of the second polymer in the first polymer should occur on introduction of the polymer 2 into the polymer 1, *i.e*., inequality (7) holds.

Usually, compatibility of two polymers is judged by the glass transition temperature of a blend. A blend of completely compatible polymers is characterised by one glass transition temperature, which is intermediate between those of the initial components. Blends of completely incompatible polymers are characterised by two glass transition temperatures corresponding to those of the initial components. In the case of partial compatibility, where both components are present in each microphase in different amounts, two glass transition temperatures are also observed; however, they are shifted 'towards each other' as compared to the glass transition temperatures of the initial components.

The dependence of the glass transition temperature on composition for the case where a polymer 1 is soluble in a polymer 2, whereas the polymer 2 is insoluble in the polymer 1, is shown in Fig. 1. As can be seen, initially the introduction of the polymer 2 into the polymer 1 affects slightly the glass transition temperature of the blend (curve *1*). Such a shape of the curve will be rationalised below taking a particular system as an example. It should be noted that in this case one glass transition temperature is observed for each blend, which suggests that the components are compatible. This behaviour of the blend can be associated with the microphase separation, which is characteristic of even homogeneous systems.[12]

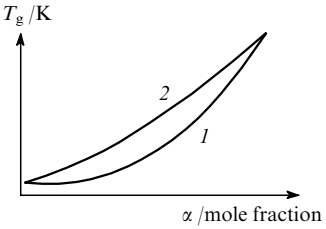


Figure 1. Dependences of the glass transition temperature on the composition for a system that meets criteria (7) and (12) (*1*) and for a blend of two completely compatible polymers (*2*).

3. Complete compatibility of the polymers occurs, *i.e*., the polymer 1 is soluble in the polymer 2, which is soluble in the polymer 1. In this case, the blend prepared is completely homogeneous, no microphase separation occurs and the 'property – composition' dependences are analogous to those of random copolymers. The criteria for compatibility take the form:

$$\mu_1 = \frac{\delta_{p1}^2}{\delta_{p2}^2} < 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a_1}\right) = 2\rho\beta_1, \quad (13)$$

$$\mu_2 = \frac{\delta_{p2}^2}{\delta_{p1}^2} < 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a_2}\right) = 2\rho\beta_2. \quad (14)$$

Such a blend is characterised by one glass transition temperature. A typical dependence of T_g on the blend composition is shown in Fig. 1 (curve *2*).

This dependence is described by the following relationship [10]

$$T_g^0 = \left[\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times \quad (15)$$

$$\times \left[\alpha_1\frac{\left(\sum_i \Delta V_i\right)_1}{T_{g1}} + \alpha_2\frac{\left(\sum_i \Delta V_i\right)_2}{T_{g2}} + 2\alpha_1(1-\alpha_1) \times 0.03\right]^{-1},$$

where α_1 and α_2 are the mole fractions of the polymers 1 and 2, respectively; $\left(\sum_i \Delta V_i\right)_1$ and $\left(\sum_i \Delta V_i\right)_2$ are the van der Waals

volumes of repeating units of the polymers 1 and 2, respectively; and T_{g1} and T_{g2} are their glass transition temperatures (calculated or experimental), respectively.

Let us consider the behaviour of polymer blends taking a number of well studied polymer blends as examples. The first of them is a blend of polystyrene (PS) (polymer 1) with poly(vinyl methyl ether) (PVME) (polymer 2).

The characteristics of this blend of various compositions have been studied in detail.[13–19] It is clearly seen in the plot of the dependence of the glass transition temperature on composition (Fig. 2, curve *2*) that the T_g value changes only slightly and is virtually independent of the blend composition as the PS content increases from 0 to 0.4. This dependence is not described by Eqn (15), which can be applied to random copolymers and homogeneous polymer blends.

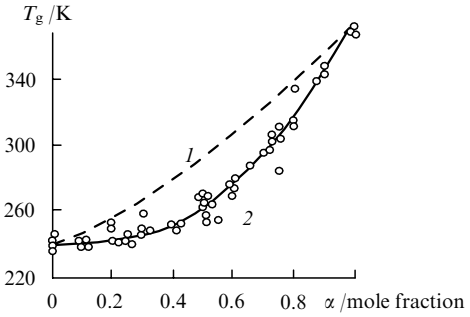


Figure 2. Dependence of the glass transition temperature of the PS–PVME blend on the PS content;
(*1*) calculations using Eqn (15); (*2*) calculations using Eqns (22) and (23).

Let us analyse in detail the compatibility of PS and PVME using criterion (2). First, we assume that PS is the solvent for PVME. The initial characteristics [solubility parameters (δ), surface energies (γ), molar volumes (V_m), cohesive energies $\left(\sum_i \Delta E_i^*\right)$, the van der Waals volumes $\left(\sum_i \Delta V_i\right)$, and glass transition temperatures (T_g)] required to calculate the values of the left and right sides of the criterion (2), are listed in Table 1. By substituting the corresponding values into criterion (14) we obtain in this case

$$\mu_2 = 0.684 < 1.218 = 2\rho\beta_2 .$$

The value of the left side of the criterion is smaller then that of the right side; hence PVME is readily soluble in PS.

Let us assume now that PVME is the solvent for PS. Using the compatibility criterion (6) and the data listed in Table 1, we get

$$\mu_1 = 1.462 > 1.175 = 2\rho\beta_1 .$$

The value of the left side of the criterion is larger than that of its right side; hence PS is insoluble in PVME. Hence introduction of PS into PVME can lead to microphase separation and the blend is expected to have one glass transition temperature. This is due to the fact that a portion of PVME will be compatible with PS. As a result, two microphases can be formed, one of which will contain only PVME, while the other will be a PVME–PS blend. The compatibility of the latter microphase with PVME will be improved as the PVME concentration in the second microphase is increased and at a certain PVME concentration, the second microphase will be completely compatible with PVME. Let us assess this critical PVME concentration. The relationship for calculating the solubility parameter of this polymer blend, which follows from the general relationship (see a monograph [10]), has the form

$$\delta^2 = \frac{\alpha\left(\sum_i \Delta E_i^*\right)_2 + 1(1-\alpha)\left(\sum_i \Delta E_i^*\right)_1}{N_A\left[\alpha\left(\sum_i \Delta V_i\right)_2 + (1-\alpha)\left(\sum_i \Delta V_i\right)_1\right]}, \qquad (16)$$

where α is the mole fraction of PVME in the blend; $\left(\sum_i \Delta E_i^*\right)_1$ and $\left(\sum_i \Delta E_i^*\right)_2$ are the molar cohesive energies of PS and PVME, respectively; N_A is the Avogadro constant; and $\left(\sum_i \Delta V_i\right)_1$ and $\left(\sum_i \Delta V_i\right)_2$ are the van der Waals volumes of repeating units of PS and PVME, respectively.

Substituting the characteristics of the polymers (see Table 1) into relationship (16), we get

$$\delta^2 = \frac{22988 - 14292\alpha}{66.13 - 29.57\alpha} 4.18 \text{ J cm}^{-3}. \qquad (17)$$

It was proposed [10] that the surface energy of a blend be assessed using the equation

$$\gamma = \left[\alpha C_1 + (1-\alpha)C_2\right]\left[\alpha\left(\sum_i \Delta E_i^*\right)_2 + (1-\alpha)\left(\sum_i \Delta E_i^*\right)_1\right]\left\{\left[\alpha\left(\sum_i \Delta V_i\right)_2 + (1-\alpha)\left(\sum_i \Delta V_i\right)_1\right]^{2/3}\left[\alpha m_2 + (1-\alpha)m_1\right]^{1/3}\right\}^{-1}, \qquad (18)$$

where C_1 and C_2 are the coefficients for PVME (nonpolar polymer) and PS, respectively, and m_1 and m_2 are the numbers of atoms in repeating units of PS and PVME, respectively.

After substituting the values of the parameters (see Table 1) into relationship (18) we obtain

$$\gamma = (0.0231\alpha + 0.1046)\frac{22988 - 14292\alpha}{(109.8 - 49.1\alpha)^{2/3}(16 - 6\alpha)^{1/3}}. \qquad (19)$$

To perform further analysis, it is necessary to estimate the molar volume of the blend

$$V = \alpha \cdot 53.68 + (1-\alpha)\cdot 97.08 . \qquad (20)$$

To calculate the values of the left and right sides of the criterion (2), let us use expressions (17), (19) and (20). In this case, we will consider a two-component blend in which one of the components is PVME, while the second component is a PVME–PS blend (microphase) with various mole fractions of PVME (α). The results of calculations are shown in Fig. 3 in the form of two dependences of both parts of the criterion (2) on α. The intersection point of the dependences corresponds to the PVME content in the microphase at which PVME becomes compatible with this microphase. The threshold concentration (α_{cr}) is equal to 0.62. At this PVME concentration, the van der Waals volume of the blend is

$$\left(\sum_i \Delta V_i\right)_{cr} = 60.7 \times 0.62 + 109.8 \times 0.38 = 79.36 \text{ Å}^3 .$$

Table 1. Values of δ (J cm^{-3})$^{1/2}$, γ (mJ m^{-2}), V_m (cm^3 mol^{-1}), $\sum_i \Delta E_i^*$ (J mol^{-1}), $\sum_i \Delta V_i$ (Å^3) and T_g (K) for PS, PVME and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).

Polymer	δ	γ	V_m	$\sum_i \Delta E_i^*$	$\sum_i \Delta V_i$	T_g
PS	18.6	41.6	97.1	22988	109.8	373
PVME	15.4	33.4	60.7	8696	60.7	245
PPO	18.2	44.4	103.8	23587	117.4	–

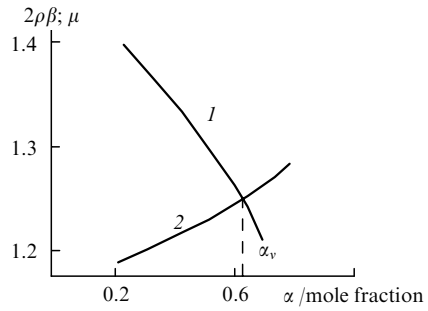


Figure 3. Dependence of μ and β on the PVME content in the microphase.

Now we can calculate the glass transition temperature of the blend with $\alpha_{cr} = 0.62$. To this end, let us use the following equation [10]

$$T_g = \left\{ \alpha_{cr} \left[\left(\sum_i \Delta V_i \right)_2 - \left(\sum_i \Delta V_i \right)_1 \right] + \left(\sum_i \Delta V_i \right)_1 \right\} \times$$
$$\times \left\{ \alpha_{cr} \left[\left(\sum_i \Delta V_i \right)_2 \Big/ T_{g2} - \left(\sum_i \Delta V_i \right)_1 \Big/ T_{g1} \right] + \right. \quad (21)$$
$$\left. + \left(\sum_i \Delta V_i \right)_1 \Big/ T_{g1} + 2\alpha_{cr}(1 - \alpha_{cr}) \times 0.03 \right\}^{-1} .$$

Substitution of the parameters for the components of the system (see Table 1) into relationship (21) gives $T_{g\,cr} = 284$ K. To find the dependence of T_g on composition of the blend formed by PVME and the critical blend, *i.e.*, by a blend composed of PS and PVME with $\alpha_{cr} = 0.62$, let us use Eqn (21). Finally, we get

$$T_g = \left\{ \alpha \left[\left(\sum_i \Delta V_i \right)_2 - \left(\sum_i \Delta V_i \right)_{cr} \right] + \left(\sum_i \Delta V_i \right)_{cr} \right\} \times$$
$$\times \left\{ \alpha_{cr} \left[\left(\sum_i \Delta V_i \right)_2 \Big/ T_{g2} - \left(\sum_i \Delta V_i \right)_{cr} \Big/ T_{g\,cr} \right] + \right. \quad (22)$$
$$\left. + \left(\sum_i \Delta V_i \right)_{cr} \Big/ T_{g\,cr} + 2\alpha_{cr}(1 - \alpha_{cr}) \times 0.03 \right\}^{-1} ,$$

where α is the mole fraction of PVME.

Relationship (22) is suitable only in the range $0.62 < \alpha < 1$. The dependence plotted using Eqn (22) is shown in Fig. 2 (curve *2*). It can be seen that this dependence fits well the experimental points.

To describe the dependence of T_g on the composition of the PVME–PS blend on the interval $0 < \alpha < 0.62$, first of all it is necessary to calculate the van der Waals volume of the blend with $T_g = 284$ K. The corresponding formula has the form

$$\sum_i \Delta V_i = 0.62 \left(\sum_i V_i \right)_2 + 0.38 \left[0.62 \left(\sum_i \Delta V_i \right)_2 + \right.$$
$$\left. + 0.38 \left(\sum_i \Delta V_i \right)_1 \right] .$$

Substituting the required values (see Table 1) into this equation, we get

$$\sum_i \Delta V_i = 67.8 \text{ Å}^3 .$$

The dependence of T_g on the composition of the blend, one of the components of which is PS and the second component is a microphase with $T_g = 248$ K, is as follows:

$$T_g = \left[\alpha'(109.8 - 67.8) + 67.8 \right] \times$$
$$\times \left[\alpha' \left(\frac{109.8}{373} - \frac{67.8}{284} \right) + \frac{67.8}{284} + 2\alpha'(1 - \alpha') \times 0.03 \right]^{-1} , \quad (23)$$

where α' is the effective mole fraction of PS (from 1 to 0.38). Actual mole fraction of PS in the blend is found from the following equation

$$(1 - \alpha) = 0.38 + \alpha' 0.62 ,$$

where α is the mole fraction of PVME and $(1 - \alpha)$ is the mole fraction of PS in the combined blend.

Substituting the right part of the equality

$$\alpha' = \frac{(1 - \alpha) - 0.38}{0.62}$$

into relationship (25), one can find the dependences of T_g on the blend composition at high PS content, *i.e.*, on the interval $0 < \alpha < 0.62$ (see Fig. 2).

Thus, the solubility criterion (2) can be used to describe the dependence of the glass transition temperature of a polymer blend in which one of the components is a good solvent for the second component, but the second component is a poor solvent for the first component.

Let us consider a simpler case where two polymers are completely compatible with each other taking a well studied [20–24] PS–PPO blend as an example. Let us assume that PS is the solvent for PPO. Using the solubility criterion (2) and the values of the physical characteristics of the blend components (see Table 1), we obtain: $\mu_2 = \delta_2^2/\delta_1^2 = 0.959$; $\Phi = 1.0$; $\gamma_{1,2} = 0.0456$; $a = 0.001096$ and $2\rho\beta_2 = 1.328$ (δ_1 and δ_2 are the solubility parameters of PS and PPO, respectively). Since $\mu_2 < 2\rho\beta_2$, then, according to criterion (2), PS is a good solvent for PPO.

Let us assume now that PS is the solvent for PPO, then $\mu_1 = \delta_1^2/\delta_2^2 = 1.043$, $\Phi = 1.0$, $\gamma_{1,2} = 0.0456$, $a = 0.00103$ and $2\rho\beta_1 = 1.33$. In this case, the value of the left side of the criterion (2) is smaller than its right side, *i.e.*, compatibility can also occur. Experiments confirm that this pair of polymers is completely compatible, therefore the dependence of the glass transition temperature on composition of the PS–PPO blend is the same as that for random copolymers [*i.e.*, it is described by relationship (21)]. The plot of this dependence is shown in Fig. 4. As can be seen, the calculated curve fits well the experimental points.

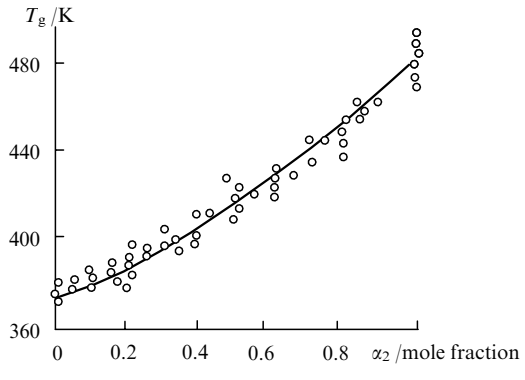


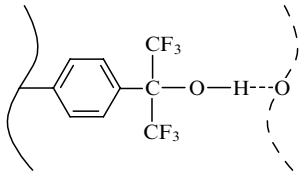
Figure 4. Dependence of the glass transition temperature of the PS–PPO blend on the content of the second component.

It should be noted that this approach used to predict compatibility of polymers has the advantage that no introduction of fitting parameters is required. In other words, to analyse compatibility of polymers using the approach considered, one needs to know only the chemical structure of the components, which makes it possible to calculate the necessary physical characteristics of the polymers.

III. The effect of strong intermolecular interaction on the compatibility of polymers

Mixing of two and more polymers can be accompanied by additional strong intermolecular interaction between their chains, *e.g.*, by hydrogen bonding or strong dipole-dipole interactions, which does not occur between the macromolecules of individual polymers.

In studies concerned with the analysis of the compatibility of polymers and properties of the blends prepared, primary emphasis is placed on these specific interactions. The scheme below illustrates an example of such an interaction:



This interesting phenomenon is observed, *e.g.*, in blends of poly[styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene] (STHFPS) with such polymers as a polycarbonate based on bisphenol A, poly(butyl methacrylate) and PPO.[25] Due to the presence of hydroxyl groups in this copolymer, hydrogen bonds between the copolymer and polycarbonate are formed, which determines substantial improvement of their compatibility. Two glass transition temperatures (which suggests incompatibility) are clearly seen in the thermograms obtained by the DSC method for PS – polycarbonate blends. The situation becomes quite different when the above copolymer is introduced into the blend instead of PS; in this case, one glass transition temperature (which suggests compatibility) is observed in the thermograms and the T_g value increases as the polycarbonate concentration increases.

This effect is also observed in a blend of STHFPS and crystalline poly(ethylene oxide) (PEO).[26] The degree of crystallinity of PEO in the blend changes in such a manner that the melting temperature of the blend decreases. The formation of hydrogen bonds between PEO and the copolymer was studied as a function of temperature. Hydrogen bonds dissociate as temperature increases; however, they reform on cooling. Even in the case of crystalline polymer such as PEO, hydrogen bonding between chains of polymers mixed leads to the improvement of their compatibility, the suppression of crystallisation and to the formation of a homogeneous system.

The behaviour of blends of STHFPS with such polymers as poly(vinyl acetate), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate), poly(n-butyl methacrylate) (PBMA), PVME, PPO, polycarbonate based on bisphenol A, poly(styrene-*co*-acrylonitrile), as well as with amorphous and crystalline esters and polyamides has been studied.[27] The effect of intermolecular interaction between macromolecules of the blend components on their compatibility was confirmed by measurements of the glass transition temperatures and by FT-IR spectroscopy.

Compatibility of STHFPS with a number of aliphatic polyamides such as nylon-6,12 and *N*,*N*′-dimethyl-nylon-6,12 was studied in detail.[28] Observation of one glass transition temperature for a blend was considered as the compatibility criterion. Polymers with glass transition temperatures that differ appreciably from T_g of PS and the copolymer were used. For instance, nylon-6,12 has a T_g of 46 °C, whereas its melting temperature lies in the interval 206 – 215 °C. To estimate the effect of crystallinity on the compatibility, nylon-6,12, *N*,*N*′-dimethyl-nylon-6,12 and copolymers with variable content of the latter were used. It has been shown that (i) hydrogen bonds are formed between the blend components; (ii) they dissociate on heating and restore on cooling and (iii) the introduction of a small amount of hydroxyl groups into PS improves compatibility of such incompatible polymers as PS and polyamide. Hence, the copolymer considered can serve as a compatibiliser.

Compatibility of substituted phenol condensation resins with PMMA was studied[29] and it was shown that the formation of hydrogen bonds between the blend components plays an important role for the improvement of compatibility. Thermodynamic parameters (enthalpy and entropy) of hydrogen bond dissociation were determined. The strongest effect on the compatibility have such substituents as NO_2 and Cl. All blends of these phenol resins with PMMA had one glass transition temperature, which indicated that the components were compatible. Dependences of the glass transition temperature on composition of the blends considered corresponded to three different cases.

1. The glass transition temperatures of blends are higher than the averaged glass transition temperature.
2. The glass transition temperatures of blends are lower than the averaged glass transition temperature.
3. The dependence of the glass transition temperature on the composition is *S*-shaped.

It was suggested that the behaviour of the blend corresponding to the first and the second case be describes using the following relationship:[29]

$$T_g = W_1 T_{g1} + W_2 T_{g2} + q W_1 W_2 , \qquad (24)$$

where T_{g1} and T_{g2} are the glass transition temperatures of the polymers 1 and 2, respectively; W_1 and W_2 are the weight fractions of the polymers 1 and 2, respectively; the parameter q characterises the strength of hydrogen bonding and can be interpreted as the contribution of hydrogen bonds, which can be considered as pseudocross-links.

It was found experimentally that the q values are negative and approximately equal in absolute values for NO_2 and Bu^t groups as substituents and positive for the Cl substituent. If F and Cl atoms are used as substituents, the q values are positive. (All the aforesaid is true in the case of *para*-substitution of the aromatic nucleus.) Hence, the dependences of the glass transition temperature on the composition of blends of phenol resins containing 4-*tert*-butyl or 4-nitro groups in the aromatic nucleus with PMMA correspond to the second case. For unsubstituted resins, these dependences correspond to the third case. Finally, for chlorine-substituted resins, the dependences correspond to the first case.

The *S*-like shape of the curve of the T_g dependence on the composition can be described by the following expression, which is more general than relationship (24)

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} + q W_1 W_2 , \qquad (25)$$

where k is a coefficient.

Relationship (25) was used to describe the dependence of the glass transition temperature on the concentration of components in blends of substituted phenol resins (see above) with poly(ethyl methacrylate) and PMMA (F and Bu^t were used as substituents in the resin) and in blends based on the unsubstituted phenol resin.[30] All three above-mentioned cases of changes in the glass transition temperature of the blends were established and all the parameters of Eqn (25) were found.

Hydrogen bonding of macromolecules in these polymer blends was studied by FT-IR spectroscopy,[31, 32] using the Patterson and Robard theory[33] and by construction of lower critical solution temperature (LCST) diagrams. Solubility and compatibility of poly(2-ethyl-2-oxazoline) was studied.

To assess the compatibility of poly(ethyloxazoline) with other polymers, two series of experiments were carried out. In the first series, films were studied based on blends of pairs of polymers, one of which was poly(ethyloxazoline), while in the second series the complexes were studied based on the same pairs of polymers. These complexes were prepared by mixing polymer solutions, separating the precipitate and drying it *in vacuo* to constant weight. It was established that the composition of the complex

differs from that of the initial blend, the former being determined by the ratio of polar groups responsible for the strong intermolecular interaction. The glass transition temperatures of blends of poly(ethyloxazoline) with polyacrylic acid are lower, whereas those of the complexes are higher than the additive values. The authors believe that this is due to the formation of a network of physical bonds in the complexes.

When studying the compatibility of PVME and styrene–methyl methacrylate copolymers, a critical composition of the copolymer was found [34] at which compatibility was observed. The PS content in such a copolymer must be ~ 60 mol. %. Phase diagrams were constructed on which the so-called 'compatibility windows' of these blends were determined.

In addition to the glass transition temperature, thermal stability of blends was also studied taking blends of poly(*p*-hydroxystyrene) with poly(vinylpyrrolidone) and poly(ethyloxazoline) as examples.[35] It was established that a small weight loss of poly(*p*-hydroxystyrene) (6%) on heating in the temperature interval 200–250 °C is due to the cross-linking reaction with the formation of ether bonds. It was mentioned that hydrogen bonds between the polymer chains affect the compatibility of the polymers.

Intermolecular complexes can be formed directly in the course of polymerisation.[36] For instance, they are formed upon photopolymerisation of acrylic acid in which PEO is dissolved. The glass transition temperatures of intermolecular complexes are higher not only than those of blends, but also than those of the initial components. These complexes are soluble in such solvents as dimethylformamide and dimethyl sulfoxide and swell to a certain degree in water and methanol; however, they do not swell in dioxane. A decrease in the number of groups capable of forming hydrogen bonds, *e.g.*, by copolymerising acrylic acid with methyl methacrylate, reduces the ability for complexation.

The stability to thermal oxidation also depends on the formation of hydrogen bonds between the polymer chains (*e.g.*, for blends of PVME with modified PS).[37] The modified PS was a copolymer of styrene and *p*-(hexafluoro-2-hydroxy-2-propyl)styrene (2.5 mol. %), *i.e.*, it contained functional groups prone to form hydrogen bonds. However, due to the presence of hydroxyl groups in the copolymer, the stability of the system to thermal oxidation was enhanced (*i.e.*, these groups 'operated' as antioxidants). This resulted in lengthening of the induction period of the thermal oxidation of PVME and in a decrease in the rate of the process.

The above-mentioned formation of intermolecular complexes was also observed for poly(*N*,*N*′-dimethylacrylamide) and a phenol–formaldehyde (PF) resin.[38] The complexes were precipitated from solutions in acetone, ethyl acetate and dioxane. As before, the compositions of the complexes corresponded to the molar ratios of the components. The glass transition temperatures of the complexes were higher than those of the initial components. Complexes of poly-*N*,*N*′-dimethylacrylamide with *p*-methoxyphenol–formaldehyde resin were also formed; their glass transition temperatures were much higher than that of each component.[39,40]

Synthesis of interpenetrating polymer networks (IPN) based on compatible polymers, *viz.*, poly(1-hydroxy-2,6-methylphenylene) and PMMA, was reported.[41] Hexamethylenetetramine and 1,3-dioxolane were used as the cross-linking agents at different temperatures. The strength of hydrogen bonding in blends and IPN was shown to be determined by the change in the cross-linking temperature and by the decrease in the concentration of the groups capable of forming hydrogen bonds. The concentrations of these groups were varied by using methyl methacrylate–styrene copolymers. It was shown by FT-IR spectroscopy that the compatibility in these blends is retained unless the intermolecular interaction due to hydrogen bonds is lower than a certain critical value.

Hydrogen bonding affects the phase behaviour of polymer blends.[42] This study was performed with blends of poly(methyl methacrylate-*co*-styrene) with a PF resin in which hydroxyl groups were partially methylated. Compatibility diagrams were constructed and the so-called 'compatibility windows' were found, *i.e.*, regions of the diagram corresponding to complete compatibility or to the microphase separation.

The compatibility of homopolymer–copolymer blends was studied.[43] The first pair was a blend of poly(4-hydroxystyrene) with poly(n-butyl acrylate-*co*-*tert*-butyl acrylate). These blends are compatible when the butyl methacrylate content in the copolymer is $\geqslant 64\%$. The second pair was poly(*tert*-butyl acrylate) and poly(styrene-*co*-4-hydroxystyrene). The 'compatibility window' for this pair was observed at a concentration of 4-hydroxystyrene in the copolymer between 28 mol. % and 66 mol. %. The glass transition temperatures of compatible blends of poly(*tert*-butyl acrylate) and poly(styrene-*co*-4-hydroxystyrene) are much lower than the additive values and, which is the most interesting, they depend only slightly on the blend composition and are approximately equal to the glass transition temperatures of the copolymers. This can be explained only by the formation of hydrogen bonds between the blend components, which was experimentally confirmed by IR spectroscopy.

The concepts of the effect of strong intermolecular interactions on the compatibility of polymers were developed by Kim, Kwei and Pearce [44] who studied hydrogen bonding in IPN prepared from a compatible polymer blend of poly(1-hydroxy-2,6-methylphenylene) and PMMA. To decrease the number of carbonyl groups, poly(methyl methacrylate-*co*-styrene) at different monomer ratios was also used. Different cross-linking agents, *e.g.*, hexamethylenetetramine and 1,3-dioxolane, were used to prepare IPN. The strength of hydrogen bonding in IPN was varied by varying the conditions of the cross-linking reaction (in particular, temperature). Hydrogen bonding in the compatible blend of two above-mentioned polymers demonstrated reversible temperature dependence. In the case of semi-IPN and IPN prepared at temperatures higher than the T_g of the blend, the number of hydrogen bonds after cooling to room temperature differed from that in the initial blend. If poly(PMMA-*co*-styrene) was used instead of PMMA (*i.e.*, the number of carbonyl groups was appreciably decreased), semi-IPN did not form a single phase. However, semi-IPN and IPN synthesised at relatively low temperatures (below T_g of the blend) were homogeneous and contained a larger number of hydrogen bonds as compared with semi-IPN and IPN synthesised at high temperatures.[45]

Makhija *et al.*[46] studied poly[2,2′-(5,5′-bibenzoimidazole)diyl-*m*-phenylene] (PBI). Its blends with poly(4-vinylpyridine) of various monomer ratios were characterised by one glass transition temperature, which indicated that the components were compatible, and the T_g values were higher than the additive values. As in the previous studies, the authors explained this fact by the formation of the N–H–N hydrogen bonds. This was confirmed experimentally by FT-IR spectroscopy.

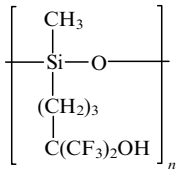
Based on the aforesaid, the following practically significant conclusion can be drawn, *viz.*, the compatibility of polymers in a blend can be improved by introducing a small number of functional groups (*e.g.*, hydroxyl groups) into one of the blend components; this will lead to the formation of hydrogen bonds between the blend components. In this case, domains of different size can be formed. To reduce the size of domains, it is sufficient to introduce a certain number of hydroxyl groups. For instance, compatibility of PS with poly(n-butyl acrylate) is achieved by introducing 4.4 mol. % of hydroxyl groups. Relaxation times and domain size were assessed by NMR spectroscopy.[47–52]

Complexes based on poly(4-hydroxystyrene) and poly-*N*,*N*-dimethylacrylamide were studied by ^{13}C CPMAS NMR spectroscopy. The size of inhomogeneous domains determined by this method was ~ 2.5 nm.[51] Analogous study of inhomogeneous domains in IPN has shown that the domain size in this case is smaller (~ 2.2 nm).[50]

The effect of microtacticity of PMMA on its compatibility with poly(styrene-*co*-4-hydroxystyrene) was studied by NMR

spectroscopy.[48] It turned out that syndiotactic PMMA possesses better compatibility with the above copolymer and that the blend based on both methyl methacrylates is homogeneous over a wide range of compositions. The size of inhomogeneous domains for most blends established by NMR spectroscopy was ~ 2 nm. Analogous studies of poly[(4-vinylphenyl)dimethylsilanol] (PVPDMS) and its copolymers with styrene[49, 50] also showed a strong effect of hydrogen bonding between the phenol and phosphate groups, which was confirmed by IR and ^{13}C and ^{31}P NMR spectroscopy.[53]

Blends were studied[54] of PEO and poly(butyl methacrylate) with modified poly(butyl methacrylate) that contained groups capable of forming hydrogen bonds.[55–60] Introduction of 4-hydroxy-4,4-bis(trifluoromethyl)butyl group even in the siloxane polymer

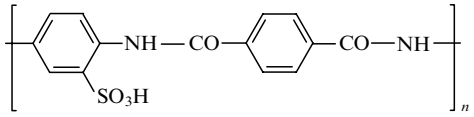


possessing low surface energy, makes it possible to prepare compatible blends with PEO and PBMA.

The parameter of the polymer–polymer interaction was assessed on the basis of studies of steam diffusion and solubility in blends.[61] In all cases its value was negative and became more negative on introduction of hydroxyl groups into the polymer, thus indicating better compatibility. Correlations between the diffusion coefficient and the specific free volume of the polymer were found.

Functionalisation of polystyrene due to introduction of hydroxyfluoroalkyl (or hydroxyl) groups enhances its thermal stability, oxidation stability, retards combustion and improves compatibility with other polymers.[62]

The compatibility of a number of polyamides in blends was studied.[63–65] Huang *et al.*[64] studied the sulfonated poly(*p*-phenyleneterephthalamide)



Based on its blends with poly(vinylpyrrolidone), poly(4-vinylpyridine) and poly(vinyl alcohol) (PVA), the so-called molecular composites were prepared in which the rigid-chain sulfonated polyamide was used as reinforcing element. It was established that hydrogen bonding between the elements of the molecular composite has a strong effect on its properties. The glass transition temperatures of blends with poly(vinylpyridine) and PVA were lower than the additive values, which, according to the authors' opinion, indicates a small number of contacts between the macromolecules.

Modifications of nylon-6, *viz.*, its blends with small amount of PF resins, were studied.[65] The addition of 1.2% of PF resins results in an increase in the modulus of elasticity and in lowering of moisture absorption. In this case, spherolites of larger size are formed. Further increase in the content of PF resins in the blend does not improve its properties. It was thus concluded that the compatibility of nylon-6 with PF resins is limited (to 3% of PF resins).

The mechanism was studied[63] of polymer-analogous reactions of poly(trichlorobutadiene) (PTCB) with aliphatic amines, *viz.*, *tert*-butylamine, diethylamine and triethylamine, which simulate chemical processes occurring in individual fragments of polymer chains in the reaction of PTCB with branched poly(ethyleneimine).

Using FT-IR and electronic spectroscopy, it was shown that hydrogen-bonded ionic charge-transfer complexes are formed in the reaction of poly(1,1,2-trichlorobutadiene) with amines in parallel to the substitution reactions of the chlorine atom of the allyl group by the amino group and dehydrogenation reactions. The contribution of each of these processes to the overall conversion of functional groups of the polymer depends on the nature of the amine (the degree of N-substitution) and on the type of the solvent. Primary and secondary amines are more prone to form stable hydrogen-bonded complexes with the polymer, whereas the tertiary amine causes mostly dehydrochlorination of the polymer and the formation of polyene fragments of various length. If dioxane is used as solvent, then dehydrochlorination predominates, whereas substitution and complexation predominate in chloroform.

A model in the framework of the Flory theory was developed[66] that makes it possible to describe self-association and inter-association of the molecules of the components in the case of hydrogen bonding between them. This model was experimentally tested in studies of poly(4-hydroxystyrene)–PMMA blends. These studies have been extended.[67] This model uses the equilibrium constants that are determined from the IR spectral data, so there is no need to use fitting parameters for the description of the phase properties.

In studies of compatibility of poly(vinylpyridine) and a polyethylene–PVA copolymer, this model was used to analyse the equilibrium association of hydroxyl groups present in the copolymer with the pyridine fragment.[68]

Thus, to predict compatibility of polymers and to establish the reasons for the compatibility, one should pay attention not only to the properties of individual components, but also to the specific intermolecular interaction between them.

IV. The effect of hydrogen bonding and strong dipole–dipole interactions on the glass transition temperature of compatible polymer blends

If no specific intermolecular interaction occurs between cross-linked polymers, the glass transition temperature of a homogeneous blend of compatible polymers is calculated using Eqn (15) in which the glass transition temperatures of homopolymers based on the components 1 and 2 (T_{g1} and T_{g2}, respectively) appear. The T_g value of the blend can be assessed using either calculated or experimental values of T_{g1} and T_{g2}. Equation (15) can be written in another form

$$T_g^0 = \left[\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times \times \left[\alpha_1\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1 + \alpha_2\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_2 + 2\alpha_1\alpha_2 \times 0.03\right]^{-1}, \quad (26)$$

where a_i and b_j are constants related to the energy of the weak dispersion forces and strong intermolecular interaction (dipole–dipole interaction, hydrogen bonding), respectively.

Let us assume that the addition of polymer 2 to polymer 1 gives rise to hydrogen bonding.

Then, the term $\left(\sum_i a_i \Delta V_i + \sum_j b_j\right)_1$ should contain an addend (a constant) characterising the contribution of hydrogen bonds, *viz.*,

$$b_h = -140 \times 10^{-3}\ \text{Å}^3\ \text{K}^{-1},$$

since a portion of repeating units of the polymer 1 becomes bonded to the component 2 by hydrogen bonds. In this case we have

$$T_g = \left[\alpha_1\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times \left[\alpha_1\left(\sum_i a_i\Delta V_i + \sum_j b_j + 2\alpha_2 b_h\right)_1 + \alpha_2\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_2 + 2\alpha_1\alpha_2 \times 0.03\right]^{-1}. \quad (27)$$

This equation was derived assuming that two repeating units (one unit of the polymer 1 and one unit of the polymer 2) are bonded by hydrogen bonds. Taking into account Eqn (15) and the relationship $\alpha_1 = 1-\alpha_2$, we obtain

$$T_g = \left[(1-\alpha_2)\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times \left[(1-\alpha_2)\frac{\left(\sum_i \Delta V_i\right)_1}{T_{g1}} + 2(1-\alpha_2)\alpha_2 b_h + \alpha_2\frac{\left(\sum_i \Delta V_i\right)_2}{T_{g2}} + 2(1-\alpha_2)\alpha_2 \times 0.03\right]^{-1}. \quad (28)$$

Let us analyse the dependence of the glass transition temperature on the blend composition, which is described by Eqns (27) and (28). Let us consider three cases.

1. The van der Waals volumes of repeating units of the polymers 1 and 2 are approximately equal

$$\left(\sum_i \Delta V_i\right)_1 \approx \left(\sum_i \Delta V_i\right)_2. \quad (29)$$

2. The van der Waals volume of the repeating unit of polymer 1 is much smaller than that of the repeating unit of the polymer 2

$$\left(\sum_i \Delta V_i\right)_1 < \left(\sum_i \Delta V_i\right)_2. \quad (30)$$

3. The van der Waals volume of the repeating unit of the polymer 1 is much larger that of the repeating unit of the polymer 2

$$\left(\sum_i \Delta V_i\right)_1 > \left(\sum_i \Delta V_i\right)_2. \quad (31)$$

The initial values of $\left(\sum_i \Delta V_i\right)_1$, $\left(\sum_i \Delta V_i\right)_2$, T_{g1}, T_{g2}, $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_1$ and $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_2$ for blends corresponding to all three cases are listed in Table 2.

Table 2. Initial parameters for calculation of the glass transition temperature of a compatible blend of two homopolymers (T_{g1} = 376 K, T_{g2} = 426 K).

Curve number	$\left(\sum_i \Delta V_i\right)_1$ /Å^3	$\left(\sum_i \Delta V_i\right)_2$ /Å^3	I	II
For dependences shown in Fig. 5 *a*				
1	110	115	293	260
2	250	260	665	588
3	350	360	931	814
4	450	460	1197	1041
For dependences shown in Fig. 5 *b*				
1	105	240	279	543
2	105	340	279	769
3	105	440	279	995
4	105	540	279	1222
For dependences shown in Fig. 5 *c*				
1	225	115	598	260
2	340	115	904	260
3	440	115	1170	260
4	540	115	1436	260

Note. Here and in Table 3 the parameters $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_1 \times 10^3$ and $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_2 \times 10^3$ are denoted as I and II, respectively; both parameters have dimensions of Å^3 K^{-1}.

The dependences of the glass transition temperature of blends on the content of the component 2 shown in Fig. 5 *a* correspond to the first case. The blends were chosen so that $T_{g1} \approx T_{g2}$, whereas the van der Waals volumes vary over a wide range. If the van der Waals volume of a repeating unit is small, the sum $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_2$ is also small. In this case the value of the b_h constant is rather large. From Eqns (27) and (28) it can be seen that the smaller the van der Waals volume, the higher the glass transition temperature of the blend and the larger the difference between T_g of the blend and that of a blend in which no additional specific interaction between components occurs [see Eqns (15) and (26), *i.e.*, $T_g > T_g^0$]. This affects the shape of the dependences of T_g on α_2 (see Fig. 5 *a*). If the van der Waals volumes of repeating units of both components increase, the effect of additional interaction

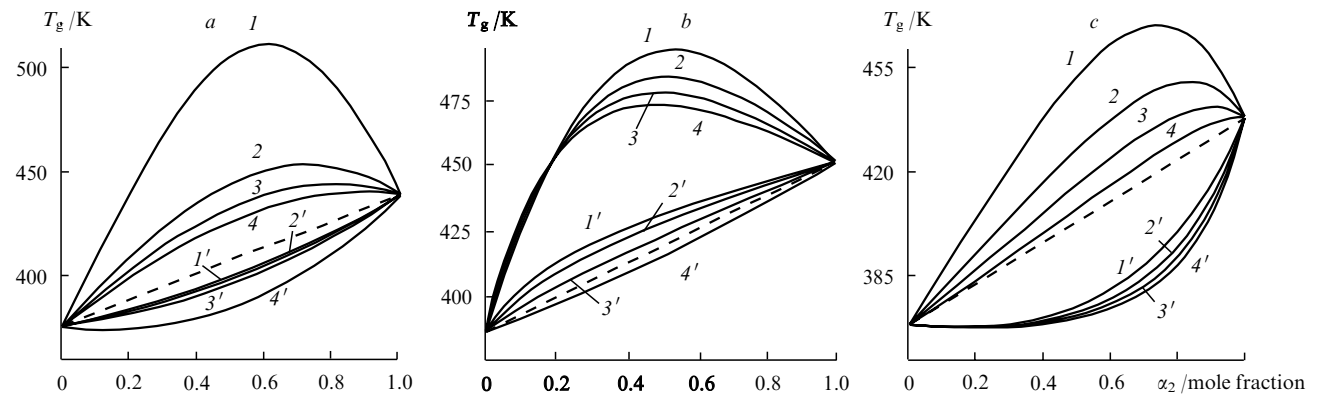


Figure 5. Dependences of the glass transition temperatures on the content of the second component for blends of compatible polymers in which the components are bonded by hydrogen bonds. Relationship (29) (*a*), (30) (*b*) and (31) (*c*) holds.
The values of initial parameters for constructing curves (*1*–*4*) are listed in Table 2. Curves (*1′*–*4′*) correspond to the case where no additional hydrogen bonding between the components occurs.

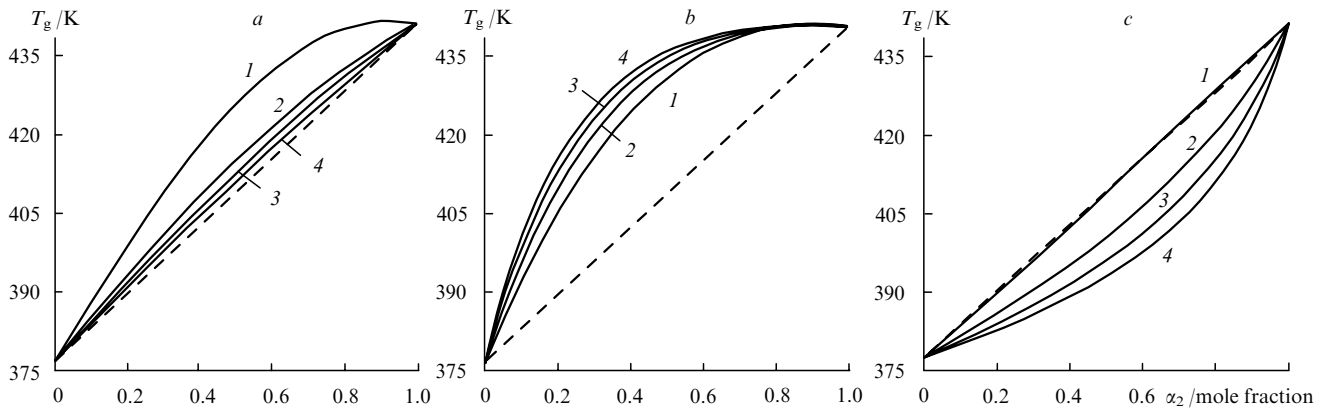


Figure 6. Dependences of the glass transition temperature on the content of the second component for blends of compatible polymers in which dipole–dipole interaction between the components occurs.
Relationship (29) (*a*), (30) (*b*) and (31) (*c*) holds.

decreases and the glass transition temperatures of blends are only slightly higher than the T_g values calculated using Eqns (15) and (26).

The dependences shown in Fig. 5 *b* illustrate the second case. Here $T_g > T_g^0$. Even if no additional hydrogen bonding occurs, the T_g values are higher than those of blends calculated on the basis of the mole fractions of the components.

In the third case [see relationship (31) and Fig. 5 *c*], the effect of additional hydrogen bonding decreases, since the total energy of dispersion interaction is appreciably higher than that of the hydrogen bonding.

A similar situation is observed when mixing of blend components gives rise to additional dipole–dipole intermolecular interaction due to the presence of polar groups in repeating units. This interaction is characterised by the b_d constant. In this case, to calculate the T_g values of the blend, one should use the b_d constant instead of b_h in Eqns (27) and (28).

If relationship (29) is valid, the effect of additional intermolecular interaction on the dependence of T_g on composition is much weaker than in the case of hydrogen bonding between the components (Fig. 6 *a*), since $b_d < b_h$.

If inequality (30) holds, the deviation of T_g of blends from the average values is positive (Fig. 6 *b*); however, it is not as large as in the case of hydrogen bonding. If condition (31) is met, the effect of additional intermolecular interaction is not so strong (Fig. 6 *c*) and the T_g of blends are rather close to T_g^0.

The curves of dependences of the glass transition temperature on the blend composition may have maxima, minima and be *S*-shaped (Fig. 7). This is due to the fact that one of the blend components is a copolymer containing a limited number of polar groups capable of forming hydrogen bonds. Let us assume that the copolymer 2 whose formula is as follows

$$-\left[\mathrm{A}\right]_m-\left[\mathrm{B(OH)}\right]_n-,$$

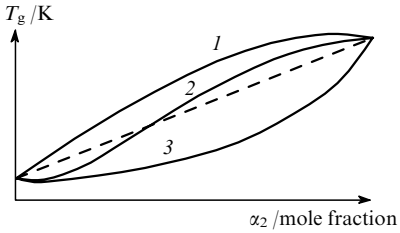


Figure 7. Dependences of the glass transition temperature on the composition of blends of compatible polymers: convex (*1*), *S*-shaped (*2*) and concave (*3*) curves.

contains a limited number of the $-[\mathrm{B(OH)}]-$ repeating units capable of forming hydrogen bonds.

Let us denote the mole fraction of repeating units of the type $-[\mathrm{B(OH)}]-$ by β. Let us assume that the second polymer (polymer 1) is capable of forming hydrogen bonds with the repeating units of the type $-[\mathrm{B(OH)}]-$, contained in the copolymer 2. Taking into account the notation introduced, Eqns (27) and (28) can be written in the form

$$T_g = \left[(1-\alpha_2)\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times \tag{32}$$

$$\times \left[(1-\alpha_2)\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_1 + 2(1-\alpha_2)\alpha_2 2\alpha_2\beta b_h + \right.$$

$$\left. + \alpha_2\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_2 + 2(1-\alpha_2)\alpha_2 \times 0.03\right]^{-1},$$

$$T_g = \left[(1-\alpha_2)\left(\sum_i \Delta V_i\right)_1 + \alpha_2\left(\sum_i \Delta V_i\right)_2\right] \times$$

$$\times \left[(1-\alpha_2)\frac{\left(\sum_i \Delta V_i\right)_1}{T_{g1}} + 4(1-\alpha_2)\alpha_2\alpha_2\beta b_h + \right. \tag{33}$$

$$\left. + \alpha_2\frac{\left(\sum_i \Delta V_i\right)_2}{T_{g2}} + 2(1-\alpha_2)\alpha_2 \times 0.03\right]^{-1}.$$

Let us consider the cases where conditions (29)–(31) are met.

If the van der Waals volumes of repeating units are approximately equal, the initial parameters for calculating the glass transition temperature of the blend are $T_g = 376$ and 426 K, $\sum_i \Delta V_i = 110$ and 115 Å^3, $\sum_i a_i\Delta V_i + \sum_j b_j = 293$ and 260 Å$^3 \times$ K^{-1} for the polymer 1 and the copolymer 2, respectively. The content of the $-[\mathrm{B(OH)}]-$ component in the copolymer 2 was varied in calculations. The results of calculations are shown in Fig. 8 *a*. The *S*-like shape of the dependences of the glass transition temperature of blends on composition is observed as β varies from 0.1 to 0.4.[23, 26, 27, 38, 46, 54, 56]

If strong dipole–dipole interactions occur between the copolymer 2 and the polymer 1 [the condition (30) is met], the glass transition temperature is calculated using Eqns (32) and (33); however, the b_d constant is used in this case instead of b_h. The initial parameters required to calculate the dependence of T_g on the composition are the same as in the former case. The results of calculations are shown in Fig. 8 *b*. It should be noted that the

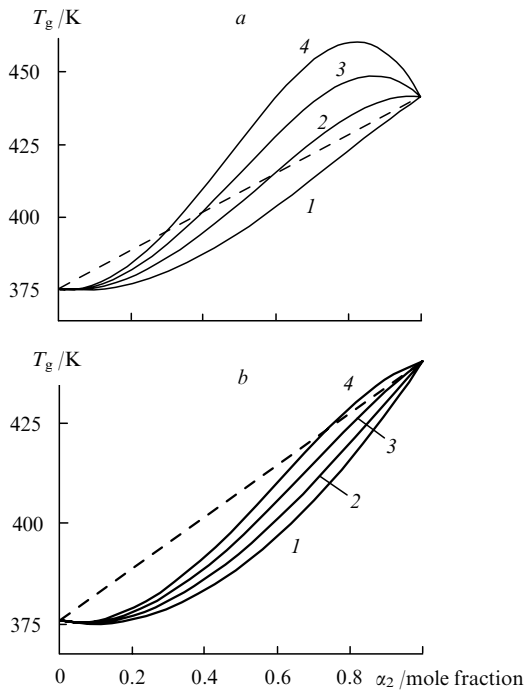


Figure 8. Dependence of the glass transition temperature on the content of the second component for a blend of compatible homopolymer and copolymer in the case of hydrogen bonding (*a*) and strong dipole – dipole interaction (*b*) between the blend components; β: (*1*) 0.1; (*2*) 0.2; (*3*) 0.3; and (*4*) 0.4.

S-like shape of the curves is observed only if the content of the —[B(OH)]— component in the copolymer 2 is high. In all cases, these dependences differ from those obtained without consideration of an additional dipole – dipole interaction between the blend components. Calculations of changes in glass transition temperatures due to the additional intermolecular interaction between the components show that these interactions play a significant role. The T_g values differ from the T_g^0 values. It should be emphasised that the equations used for analysing the dependences of the glass transition temperature on the blend composition contain no fitting parameter and all calculations are performed using only the data on the chemical structure of the blend components.

Let us consider particular blends of compatible polymers taking PBMA – poly(styrene-*co*-VPDMS) blends [56] as the first example.

It is required to calculate the glass transition temperature of poly(styrene – VPDMS) at different content of the second component. The results of calculations performed using Eqn (15) and experimental T_g values are listed in Table 3. To calculate the glass transition temperatures of blends of PBMA with this copolymer, one should know the $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{\text{PBMA}}$ and $\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)_{\text{styrene-VPDMS}}$ values, which can be determined using the following equation [10]

$$T_g = \frac{\sum_i \Delta V_i}{\left(\sum_i a_i\Delta V_i + \sum_j b_j\right)}, \qquad (34)$$

where $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit.

These values for copolymers of different compositions are also listed in Table 3. They were used to calculate the glass transition temperatures of a number of PBMA – poly(styrene-*co*-VPDMS) blends. The results of calculations for two blends are shown in Fig. 9 in the form of dependences of the glass transition temperature on the composition. These dependences for compatible blends containing poly(styrene-*co*-VPDMS-34) and poly(styrene-*co*-VPDMS-9) were obtained using Eqn (32). For each blend, the calculated values are in fairly good agreement with experimental data (see Figs 9 *a*,*b*). In addition, let us analyse the dependence of T_g on the composition for the PBMA – poly(styrene-*co*-VPDMS-9) blend using Eqn (33) and experimental T_g values. As a result, good agreement is observed between the calculated and experimental data (Fig. 9 *b*).

Table 3. Composition and characteristics of PS – PVPDMS copolymers.

Specimen [a]	[PVPDMS] (mol. %)	T_g /°C		$\sum_i \Delta V_i$/ Å^3	I
		experiment	calculation		
PS	100	105	103	110	293
PBMA	100	29	14	148	516
PVPDMS-2	1.9	97	103	111	295
PVPDMS-4	4.1	98	103	113	301
PVPDMS-9	8.7	98	103	116	309
PVPDMS-11	11.4	99	103	117	311
PVPDMS-18	18.2	101	104	122	324
PVPDMS-34	33.9	115	109	133	348
PVPDMS-60	60	121	122	151	382
PVPDMS-100	100	—	153	178	418

[a] Figures denote the content of silanol groups (%) in PVPDMS.

If the content of modified polystyrene [*i.e.*, poly(styrene-*co*-VPDMS)] in the blend is low, the glass transition temperatures of blends are lower than the additive values. As the content of this component in the blend increases, the glass transition temperatures appear to be higher than the average values. This is explained by the formation of a large number of hydrogen bonds between the components on their mixing.

Blends of PBI and poly(4-vinylpyridine) have been studied.[46] It was shown that hydrogen bonds are formed between the 4-vinylpyridine residues and the NH groups in PBI. Therefore homogeneous blends based on these polymers are formed. The dependences of experimental and calculated glass transition temperatures on blend compositions are shown in Fig. 10. Glass transition temperatures of the blends are higher than the T_g values of the initial components. The calculated curve fits well the experimental points if the mole fraction of PBI in the blends does not exceed 0.3. Deviation of the experimental points from the calculated curve at high PBI content is associated with the fact that destruction of poly(4-vinylpyridine) begins above 375 °C. It should be noted once again that calculations were carried out using the equations containing no fitting parameters.

Thus, the aforesaid makes it possible to draw the following conclusions. In the case of compatible blends of two homopolymers, the shape of the dependence of the glass transition temperature on the blend composition can be different. If the van der Waals volumes of repeating units of the homopolymers are approximately equal and no additional strong intermolecular interaction between the components occurs, the glass transition temperature is lower than the average values. If the van der Waals volume of the unit of a homopolymer 1 is substantially smaller than that of the unit of a homopolymer 2, the glass transition temperature is slightly higher than the average values (even in the absence of additional intermolecular interactions). If these interactions occur, the T_g value of the blend is always higher than the average values.

For blends of a homopolymer with a copolymer containing a limited number of polar groups that can participate in strong intermolecular interaction with the other component (dipole – dipole interaction, hydrogen bonding), the dependences of T_g on

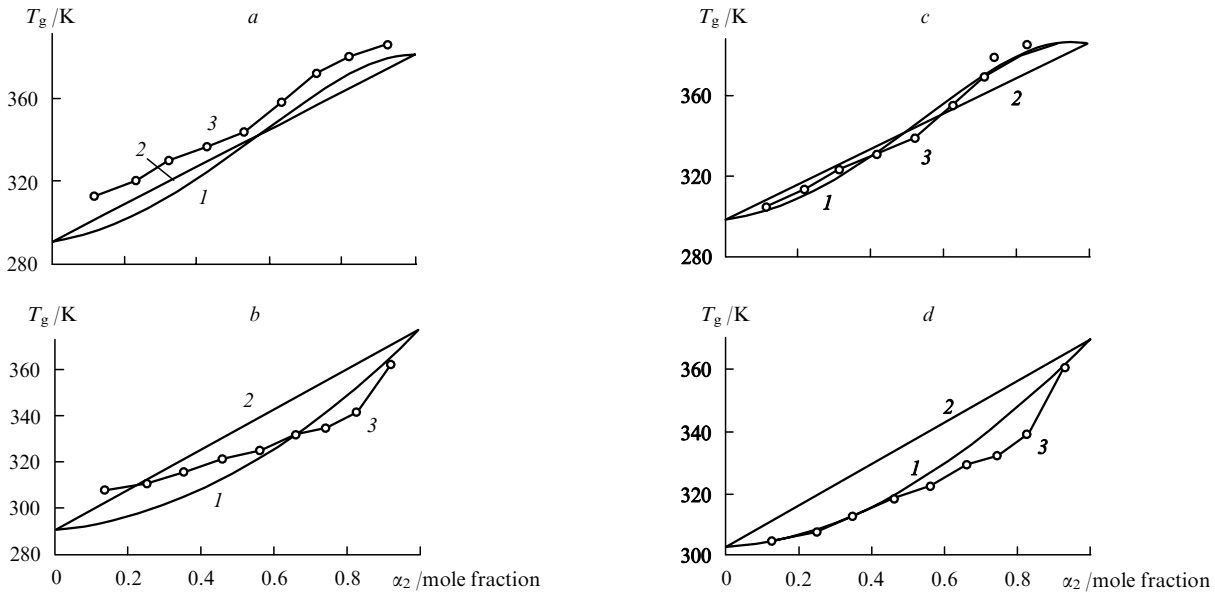


Figure 9. Dependences of the glass transition temperature on the content of the second component for compatible poly(styrene-*co*-VPDMS-34) – PBMA (*a*, *c*) and poly(styrene-*co*-VPDMS-9) – PBMA (*b*, *d*) blends; calculations using Eqns (32) (*a*, *b*) and (33) (*c*, *d*); (*1*) calculations; (*2*) average values; and (*3*) experiment.

composition are *S*-shaped. The above peculiarities of changes in the characteristics of compatible blends can be described by the equations given above which contain the parameters obtained using the data on the chemical structure of the components. It is needless to say that this approach is not versatile and further investigations are needed to understand how should, *e.g.*, the effects of various specific interactions and peculiarities of the structure of blend components on their thermomechanical behaviour be taken into account.

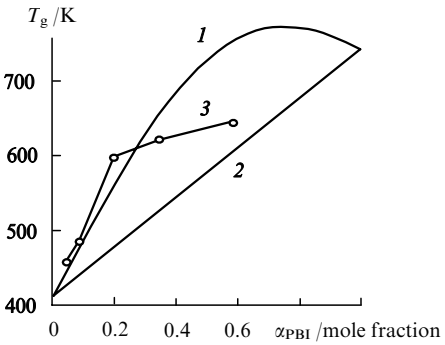


Figure 10. Dependence of the glass transition temperature for compatible polyvinylpyridine – polybenzoimidazole blends; (*1*) calculations; (*2*) average values; and (*3*) experiment.

V. Formation of chemical bonds between components of polymer blends

Processing of polymers often results in the formation of chemical bonds between the components, which improves their compatibility.[69] Let us consider a case of the so-called 'forced mixing' of two incompatible polymers by synthesising interpolymers.† The reaction is conducted in solution and repeating units of the polymers contain functional groups capable of chemical reaction with one another. Such an approach makes it possible to prepare macromolecules composed of finished polymers whose repeating units cannot be united in the course of synthesis.

In Fig. 11, the structures of various polymers are represented schematically. The difference between interpolymers and random copolymers is obvious and needs no special explanation. The difference between interpolymers and block copolymers lies in the fact that the chemical reaction between two unlike macromolecules (blocks), resulting in the addition of one block to another one, involves functional groups within the repeating units of macromolecular chains rather than the end functional groups.

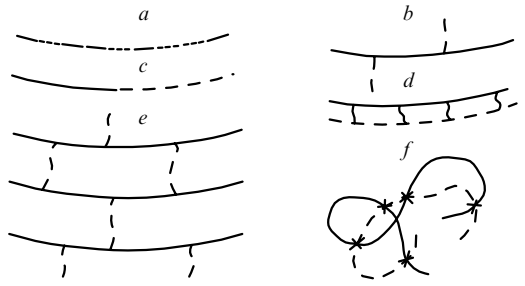


Figure 11. Different types of structures of polymers and copolymers: (*a*) random copolymer; (*b*) graft copolymer; (*c*) block copolymer; (*d*) a fragment of interpolymer; (*e*) a polymer network; and (*f*) a macromolecular interpolymer coil.

Graft copolymers and interpolymers differ not only in the structure, but also in the procedure for preparation. Grafting of chains in solution is due to the interactions of the end functional groups in repeating units of the polymers. Grafting from the gas phase on the surface of a polymeric product is carried out by polymerisation of a monomer on this surface and the product obtained has nothing to do with an interpolymer.

Additional explanation is required as to cross-linking reactions, even in the case where one polymer is cross-linked by the other polymer (*e.g.*, curing of epoxide resin with polyanhydride belongs to this type of reaction). In this case, branched products are formed in the first stage of curing due to the interaction of one

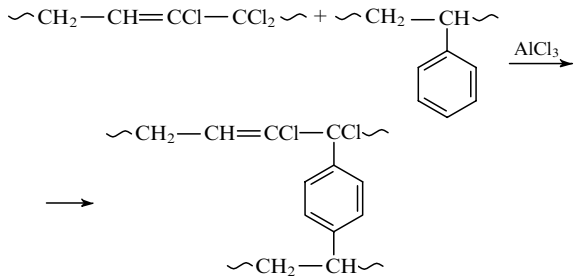
† Interpolymers are polymacromolecular compounds formed in a chemical reaction occurring in a solution of two polymers.[70–78]

or several polymer (or oligomer) macromolecules with those of the curing agent, whereas in the second stage the reaction proceeds in such a way that an increase in the degree of conversion leads to an increase in the degree of cross-linking up to complete insolubility of the product.

In the synthesis of interpolymers, chemical reactions between functional groups in repeating units of unlike macromolecules occur in a different manner. The conditions of reaction in solution are chosen so that the increase in the degree of conversion is due to consumption of functional groups in the chemically bonded macromolecules rather than to the formation of cross-links. In this case, conversion of functional groups is not accompanied by an increase in the molecular weight of the system and the reaction occurs in the region of mutual penetration of unlike coils (see Fig. 11*d*). Such a reaction results in the formation of soluble products, *viz*., interpolymers. It should be noted that the degree of conversion of functional groups does not exceed 10%.

Without dwelling on peculiarities of chemical reactions between two unlike polymers in dilute solutions, we should note that the degree of conversion of the same functional groups in the case of two polymers is always much lower than in the case of one polymer and a low-molecular weight substance. Chemical reaction between polymers can occur only in the region of their mutual penetration and the role of excluded volume is of particular importance in those cases where functional groups are arranged in the repeating units along the chain.

Preparation of interpolymers can be exemplified taking the reaction of PTCB with PS. It should be noted that if $AlCl_3$ is used as catalyst, PTCB readily reacts with the aromatic nuclei of low-molecular weight compounds, *e.g*., with benzene and its derivatives, and the degree of conversion can be very high. In the reaction of PTCB with PS using the same catalyst, interaction with the aromatic nucleus of PS also occurs



The reaction between PTCB and PS is carried out in nitrobenzene at a low blend concentration (from 0.5 to 5 g dl^{-1}). Fractionation of the interpolymer obtained gives several fractions (A – D) that can be isolated and characterised. Fractions A and B are soluble in the same solvents as the initial polymers; however, unlike fraction A, fraction B is insoluble in carbon tetrachloride. Fraction C is soluble only in tetrachloroethane and nitrobenzene on heating. Finally, fraction D is insoluble.

It should be noted that the increase in the degree of conversion is virtually not accompanied by the increase in the molecular weight of the product, which indicates that the chemical process occurs in the region of mutual penetration of two bonded macromolecules formed in the first reaction stage. In other words, interpolymers are the products of reactions between two or several unlike macromolecules; the molecular weight of the interpolymer is approximately equal to the sum of those of the macromolecules that had reacted.

The aforesaid can be contrasted with the following. First, the molecular weight mentioned above is the apparent molecular weight rather than the true molecular weight, since the experiments have been carried out in one solvent.[73, 74] However, the true molecular weight can only be lower than the apparent molecular weight; therefore, one cannot say that the process occurs as conventional chaotic branching resulting in a considerable increase in the molecular weight.

Second, it can be assumed that in the case of polydisperse specimens, substantial enlargement of individual macromolecules can be accompanied by a slight increase in the weight-average molecular weight. This issue requires a special consideration. Let us perform such an analysis in the general form.

The weight-average molecular weight is determined from the relationship

$$M_w^0 = \left(\sum_1^n n_i M_i^2\right)\left(\sum_i^n n_i M_i\right), \tag{35}$$

where n_i is the number of macromolecules with the molecular weight M_i.

Let us assume that both reacting polymers have equal molecular weights, which can be calculated using formula (35), and the same molecular weight distributions (MWD). Different variants of chemical reactions can be considered. Let small macromolecules of different types react respectively in pairs with one another and let the same be true for medium-size and large macromolecules. Then the formula for calculating the M_w of the reaction product will have the form

$$M_w = \left[\sum_1^n n_i (2M_i)^2\right]\left[\sum_i^n n_i (2M_i)\right]^{-1} = 2M_w^0, \tag{36}$$

i.e., the M_w value becomes doubled as compared to the initial M_w^0 value. If n macromolecules of each type react in the same way, then

$$M_w = \left[\sum_1^n \frac{2n_i}{n}(n_i M_i)^2\right]\left[\sum_i^n \frac{2n_i}{n}(n_i M_i)\right]^{-1} = n_i M_w^0, \tag{37}$$

i.e., the weight-average molecular weight of the reaction product is equal to the number of macromolecules that had reacted multiplied by the initial molecular weight. In other words, in this case the weight-average molecular weight of the reaction product is equal to the sum of those of the initial macromolecules.

If the smallest and the largest macromolecules react in pairs (cross reaction), the formula for calculating the M_w of the product has the form

$$M_w = \frac{n_1(M_1 + M_x)^2 + n_2(M_2 + M_{x-1})^2 + \ldots}{n_1(M_1 + M_x) + n_2(M_2 + M_{x-1}) + \ldots}, \tag{38}$$

where M_x is the molecular weight of the final fraction x.

The dependence of the molecular weight of a fraction on its number can be linear: $M_i = M_1 i$, where M_1 is the molecular weight of the first fraction and i is the fraction number. In this case, from Eqn (38) it follows that

$$M_w = M_1 + M_x,$$

i.e., a monodisperse specimen is obtained.

Thus, in all cases considered above, the weight-average molecular weight of the reaction product is equal to the sum of the molecular weights of the macromolecules that had reacted. Clearly, if initial specimens and reaction products are monodisperse, the M_w of the reaction product will be equal to nM_w^0, where n is the number of the macromolecules that had reacted.

Experiments shows that the reaction product has a very broad MWD.[73, 74]

Let us consider a case of exaggerately broad MWD where all fractions are present in equal proportions, *i.e*., each fraction also contains an equal number of macromolecules ($n_1 = n_2 = \ldots = n_x = n$). In this case, the weight-average molecular weight M_w^0 of the initial products is

$$M_w^0 = \left(\sum_1^x n M_i^2\right)\left(\sum_1^x n M_i\right)^{-1} = \left(\sum_1^x M_i^2\right)\left(\sum_1^x M_i\right)^{-1}, \tag{39}$$

where x is the number of fractions.

The number-average molecular weight M_n^0 of the initial product is

$$M_n^0 = \left(\sum_1^x nM_i\right)(nx)^{-1} = \left(\sum_1^x M_i\right)x^{-1}. \quad (40)$$

The polydispersity index of such a system is

$$\frac{M_w^0}{M_n^0} = x\left(\sum_1^x M_i^2\right)\left(\sum_1^x M_i\right)^{-2}. \quad (41)$$

Let us assess the polydispersity of the initial system, which is characterised by a linear dependence of the molecular weight of a fraction on the fraction number, $M_i = M_1 i$. The formulae for calculating the M_w^0 and M_n^0 values will take the form

$$M_w^0 = \sum_1^x (iM_1)^2\left(\sum_1^x iM_1\right)^{-1} = \quad (42)$$

$$= M_1\sum_1^x i^2\left(\sum_1^x i\right)^{-1} = M_1\frac{2x+3}{3},$$

$$M_n^0 = M_1\sum_1^x \frac{i}{x} = M_1\frac{x+1}{2}. \quad (43)$$

The polydispersity index is

$$\frac{M_w^0}{M_n^0} = \frac{x\sum_1^x i^2}{\left(\sum_1^x i\right)^2} = \frac{x \times x(x+1)(2x+1)4}{6(1+x)^2x^2} = 1.33 \ (x\to\infty). \quad (44)$$

Therefore, if the condition $M_i = M_1 i$ is met, the polydispersity index cannot be high and for $x \to \infty$ its value approaches 1.33. This also holds for the reaction products. The polydispersity index can be high (as is observed in the experiment) if the dependence of the molecular weights fractions on their numbers is nonlinear.

Let us consider the modes of reactions between unlike polymers to form highly polydisperse specimens, assuming that the initial specimens are monodisperse.

If the products of reaction between such polymers also are monodisperse, their weight-average molecular weights will be equal to the sum of the molecular weights of the chains that had reacted with one another. This statement requires no special proofs.

To prepare specimens with high polydispersity index, it is necessary that the molecular weights of the final fractions be markedly different. Let us consider the exaggerately broad MWD once again. Let us assume that the number of chemically bonded macromolecules in each fraction is $n_1 \times 10^i$, where n_1 is a constant for each fraction and i is the fraction number. Then the molecular weight of the macromolecules in the first fraction will be $M_1 n_1 \times 10$, that of the macromolecules in the second fraction will be $M_1 n_1 \times 10^2$, *etc.*, where M_1 is the weight-average molecular weight of the initial monodisperse specimens. Then the weight-average molecular weight of specimens obtained will be

$$M_w = \left[\sum_1^x (M_1 n_1 \times 10^i)^2\right]\left(\sum_1^x M_1 n_1 \times 10^i\right)^{-1} = \quad (45)$$

$$= \left(M_1 n_1 \sum_1^x 10^{2i}\right)\left(\sum_1^x 10^i\right)^{-1}.$$

After simplification of this formula we get (to some approximation) $M_w \approx M_1 n_1 \times 10^x$.

If $M_w^0 = M_1$, then $M_w/M_w^0 \approx n_1 \times 10^x$, *i.e.*, this ratio is equal to the number of chemically bonded macromolecules in each fraction. Therefore, the weight-average molecular weight of the reaction products must be equal to the sum of the molecular weights of the macromolecules constituting the interpolymer.

Let the dependence of the molecular weight of a fraction on its number be of power type, which means that the number of bonded macromolecules in each fraction is n_1^i. Then, the molecular weight of a fraction is

$$M_i = M_1 n^i,$$

and the weight-average molecular weight is

$$M_w = \left[\sum_1^x (n_1^i M_1)^2\right]\left(\sum_1^x n_1^i M_1\right)^{-1} = \left(M_1\sum_1^x n^{2i}\right)\left(\sum_1^x n^i\right)^{-1}. \quad (46)$$

After simplification of this equation we get (to a certain approximation)

$$M_w = M_1 n^x,$$

i.e., in this case the weight-average molecular weight of the reaction product is also equal to that of the initial specimen M_1 multiplied by the number of macromolecules in each fraction.

Let us assume now that the initial specimens of two polymers are polydisperse. The weight-average molecular weight of a blend of such macromolecules is calculated using relationship (35). A polydisperse reaction product can be prepared using different procedures. One of them was considered above, *viz.*, small macromolecules should react in pairs with one another and large macromolecules should react in pairs with large macromolecules. In this case the weight-average molecular weight of the reaction products formed is higher than that of the initial specimens. The ratio of these weights is equal to the number of macromolecules which react with one another and bind to form the interpolymer.

Let us consider an exaggerated case where all large macromolecules in the fraction x, as well as all other macromolecules in other fractions, react with one another. As a result, only two giant macromolecules are formed. Analogous situation is also observed upon completion of the network formation. The weight-average molecular weight of such a reaction product will be

$$M_w = \left[\left(\sum_1^{x-1} n_i M_i\right)^2 + (n_x M_x)^2\right]\left(\sum_1^{x-1} n_i M_i + n_x M_x\right)^{-1}. \quad (47)$$

The ratio of this weight to that of the initial specimens, M_w^0, is

$$\frac{M_w}{M_w^0} = \left[\left(\sum_1^{x-1} n_i M_i\right)^2 + (n_x M_x)^2\right]\left(\sum_1^x n_i M_i^2\right)^{-1}. \quad (48)$$

For an exaggerately broad MWD, $n_1 = n_2 = \ldots = n_x = n$. After several transformations, we get

$$\frac{M_w}{M_w^0} = n\left[\left(\sum_1^{x-1} M_i\right)^2 + M_x^2\right]\left(\sum_1^x M_i^2\right)^{-1}. \quad (49)$$

Let us assume that $M_i = M_1 \times 10^i$, where i is the fraction number. Then

$$\frac{M_w}{M_w^0} = n\left[\left(\sum_1^{x-1} 10^i\right)^2 + 10^{2x}\right]\left(\sum_1^x 10^{2i}\right)^{-1} \approx n, \quad (50)$$

i.e., in this case the ratio of the weight-average molecular weight to that of the initial specimens is also equal to the number of macromolecules that are chemically bound to one another.

Thus, in both cases of (i) initially monodisperse and exaggerately polydisperse specimens and (ii) monodisperse and exaggerately polydisperse reaction products, the ratio of the weight-average molecular weights of the reaction products to those of the initial specimens is equal to the number of macromolecules in the interpolymer.

In studies of fractions A and B of interpolymers by dynamic mechanical analysis [75] it was shown that the formation of chemical bonds between the macromolecules decreases the mobility of each macromolecule. In the plot of temperature dependence of the loss factor $\tan\delta$ the peaks or their 'shoulders', characteristic of PTCB and PS, are shifted toward higher temperatures as compared to those of the mechanical mixture. The interpolymer is characterised by a large storage modulus E' and a higher glass transition

temperature as compared to that of each of the polymers and of their mechanical mixture.

Studies of thermomechanical properties of interpolymers [76] have shown that their glass transition temperatures increase from 58 to 100 °C as the polymer blend is converted into the polymer A and then into the polymer B. This effect is analogous to that observed at the formation of a ladder polymer the glass transition temperature of which is higher than that of the strands that form the ladder. The T_g value decreases to 30 °C in the later reaction stages, *i.e.*, as the polymer B is converted into the polymer C and then into the polymer D. In the case of formation of conventional polymer networks, the T_g value monotonically increases as the number of cross-links increases.

Blends of PTCB with PS form transparent solutions up to a concentration of 10%; however, in studies of these blends by electron microscopy it was found [75] that phase separation of blend components occurs even in dilute solution. The interpolymer solution is also transparent; however, unlike the polymer blend, no indications of phase separation are observed in this case. Uniformly distributed large spherical particles are clearly seen when analysing the interpolymer using electron microscopy.

Interpolymer films are transparent and display no indications of phase separation, whereas films of PTCB–PS blends are turbid, with distinct phase separation. However, indications of microphase separation were found in the studies of interpolymer films by physical methods.[75] Two separated peaks characteristic of PTCB and PS and shifted toward higher temperatures are observed in the plot of the temperature dependence of the loss factor tan δ of the interpolymer. Two maxima characteristic of PS are also seen in the X-ray diffraction patterns of interpolymers isolated in the initial reaction stages; however, their intensities decrease as the extent of reaction increases. In the latest stage (polymer D), the maximum completely disappears.[76] Most likely, microaggregation of PS and PTCB fragments occurs on solution casting; however, the size of domains built of unlike fragments is small and therefore the films retain transparency.

It was also shown [79] that poly(vinyl chloride) (PVC) also can enter into the Friedel–Crafts reaction with PS; however, it is less reactive than PTCB. From the data in Tables 4 and 5 it can be seen that the mechanical properties of films and moulded blocks of interpolymers based on PVC (and PTCB) with PS depend largely on their composition. The characteristics of mechanical properties of interpolymers are intermediate between those of the initial polymers and in some instances even surpass them. Particularly large is the increase in the impact strength of PVC–PS interpolymers in the range of compositions close to the equimolar composition. The strength of interpolymers is much higher than that of mechanical mixtures of the initial polymers of the same composition (Table 6).

Table 4. Tensile strength (σ_t) and percentage elongation at rupture (ε) of films of interpolymers based on PTCB and PS.

Parameter	PTCB : PS (mol. %)					
	100 : 0	75 : 25	50 : 50	34 : 66	10 : 90	0 : 100
σ_t /MPA	2.6	11.0	32.0	29.0	36.0	32.0
ε (%)	1190	8	4	4	5	5

Table 5. Specific impact strength (γ) and bending strength (σ_b) of moulded monolithic specimens of interpolymers based on PVC and PS.

Parameter	PVC : PS (mol. %)						
	100 : 0	78 : 22	54 : 46	30 : 70	15 : 85	10 : 90	0 : 100
γ /kJ m^{-2}	2.1	1.7	3.0	4.0	2.2	1.1	1.3–2.1
σ_b /MPa	—	—	30.0	36.0	25.2	29.0	—

Table 6. Mechanical properties of interpolymers of equimolar composition.

Initial polymers	Characteristic	Polymer blend	Interpolymer
PTCB + PS	σ_t/MPa	10.8	32.0
PVC + PS	γ/kJ m^{-2}	1.2	3.0
	σ_b/MPa	6.7	30

Chemical reaction between two unlike macromolecules in solution was theoretically analysed using the Monte Carlo dynamic simulation.[74] The major conclusion drawn on the basis of results of the computer experiment is that the reaction between unlike macromolecules occurs by a mechanism of disordered formation of chemical bonds between the macromolecules of the 'coil-in-coil' type. The reacting macromolecules are 'drawn into' each other (the distance between their centres of gravity is shortened), and the reaction proceeds inside the region of interpenetration.

In actual experiments, changes in the number of chemical bonds between macromolecules were monitored using a specially developed precise refractometric method.[80] In the first stage, a very small number of chemical bonds between the macromolecules is formed; however, most of the macromolecules become bonded in pairs. In the second stage, the reaction proceeds in the macromolecular coils formed in the first stage and consists in an increase in the number of chemical bonds between macromolecules already bonded, *i.e.*, it is an intramolecular reaction of the first kind. Acceleration of this reaction compared to the interchain reaction is due to the appreciably lower activation energy, which is equal to 96.6 and 37.4 kJ mol^{-1} in the first and in the second stage, respectively.

Thus, preparation of interpolymers is an efficient method for the preparation of compatible polymers from initially incompatible ones. Such a compatibility can be called 'forced compatibility'. Interpolymers should be considered as individual class of polymers which possess the same and even improved properties compared with those of the initial polymers.

VI. Conclusion

The results of numerous studies show that there are several methods for the improvement of compatibility of polymers.

First, it is selection of polymer pairs or modification of polymers. These are performed to give rise to strong intermolecular interaction (*e.g.*, hydrogen bonding) between unlike polymer chains. This issue was analysed in detail above.

Second, it is conducting of chemical reactions between blend components that result in the formation of interpolymers.

Third, it is introduction of compatibilisers into the system. Compatibilisers are low-molecular weight and high-molecular weight compounds whose molecules contain functional groups capable of strengthening specific intermolecular interactions between the chains. Copolymers can be used as compatibilisers.

Analysis of compatibility of polymers showed that the dependences of the glass transition temperature of blends on the composition vary in shape and can be described by relationships that require no fitting parameters; only the chemical structure of the components needs to be known to perform such an analysis. It is needless to say that this approach does not cover all possible cases of compatibility of polymers. Further investigations, including those in the framework of the approach considered, are required in order to take into account all peculiarities of the chemical structure of polymers that strongly affect their compatibility and properties.

References

1. D R Paul, S Newman (Eds) *Polymer Blends* Vol.1 (London: Academic Press, 1987)
2. V N Kuleznev *Smesi Polimerov* (Polymer Blends) (Moscow: Khimiya, 1980)
3. V N Kuleznev *Kolloid. Zh.* **49** 881 (1987) [a]
4. D R David, T F Sincock *Polymer* **33** 4505 (1992)
5. S J Krause *Polymer Blends* Vol. 1 (Eds D R Paul, S Newman) (London: Academic Press, 1987) p. 27
6. A G Shvarts, B N Dinzburg *Sovmeshchenie Kauchukov s Plastikami i Sinteticheskimi Smolami* (Combining of Caoutchoucs with Plastics and Synthetic Resins) (Moscow: Khimiya, 1972)
7. A A Askadskii, Yu I Matveev, M S Matevosyan *Vysokomol. Soedin., Ser. A* **32** 2157 (1990) [b]
8. Yu I Matveev, A A Askadskii A A *Vysokomol. Soedin., Ser. A* **36** 436 (1994) [b]
9. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **31** 526 (1989) [b]
10. A A Askadskii *Physical Properties of Polymers, Prediction and Control* (New York: Gordon and Breach, 1996)
11. A A Askadskii *Vysokomol. Soedin., Ser. A* **41** (1999) [b]
12. V N Kuleznev *Vysokomol. Soedin., Ser. B* **35** 391 (1993) [b]
13. M Bank, J Leffingwell, C Thiess *Macromolecules* **4** 43 (1971)
14. T K Kwei, T Nishi, R F Roberts *Macromolecules* **7** 667 (1974)
15. H A Schneider, N J Brekner *Polym. Bull.* **14** 73 (1985)
16. H E Yang, Ph D Thesis, University of Massachusetts, 1985
17. H A Schneider, B Leikauf *Thermochim. Acta* **114** 165 (1987)
18. J L Halary, F B C Larbi, P Oudin, L Monnerie *Makromol. Chem.* **189** 2117 (1988)
19. K Schmidt-Rohr, J Clauss, H W Spiess *Macromolecules* **25** 273 1992)
20. W M Prest Jr, R S Porter *J. Polym. Sci., Polym. Phys., Part A-2* **10** 1639 (1972)
21. A R Shultz, B M Gendron *J. Appl. Polym. Sci.* **16** 461 (1972)
22. T K Kwei, H L Frish *Macromolecules* **11** 1267 (1978)
23. S P Ting, E M Pearce, T K Kwei *J. Polym. Sci., Polym. Lett. Ed.* **18** 201 (1980)
24. M Kryszewski, J Jachowicz, M Malanga, O Vogl *Polymer* **23** 271 (1982)
25. X Yang, P C Painter, M M Coleman, E M Pearce, T K Kwei *Macromolecules* **25** 2156 (1992)
26. S P Ting, B J Bulkin, E M Pearce, T K Kwei *J. Polym. Sci.* **19** 1451 (1981)
27. E M Pearce, T K Kwei, B Y Min *J. Macromol. Sci., Chem.* **A21** 1181 (1984)
28. D L Kotzev, E M Pearce, T K Kwei *J. Appl. Polym. Sci.* **29** 4443 (1984)
29. J R Pennacchia, E M Pearce, T K Kwei, B J Bulkin, J-P Chen *Macromolecules* **19** 973 (1986)
30. K Ogawa, F Tanaka, J Tamura, K Kadowaki, K Okamura *Macromolecules* **20** 1172 (1987)
31. T K Kwei, E M Pearce, B Y Min *Macromolecules* **18** 2326 (1985)
32. T K Kwei, E M Pearce, F Ren, J P Chen *J. Polym. Sci., Part B, Polym. Phys.* **24** 1597 (1986)
33. P Lin, C Clash, E M Pearce, T K Kwei *J. Polym. Sci., Part B, Polym. Phys.* **26** 603 (1988)
34. Y Y Chien, E M Pearce, T K Kwei *Macromolecules* **21** 1616 (1988)
35. E M Pearce, T K Kwei *Macromolecules* **22** 573 (1989)
36. F-L Chen, E M Pearce, T K Kwei *Polymer* **29** 2285 (1988)
37. H Park, E M Pearce, W H Starnes Jr , T K Kwei *J. Polym. Sci., Part A, Polym. Chem.* **28** 1079 (1990)
38. T P Yang, E M Pearce, T K Kwei, M L Yang *Macromolecules* **22** 1813 (1989)
39. L F Wang, E M Pearce, T K Kwei *J. Polym. Sci., Part C, Polym. Lett.* **28** 317 (1990)
40. L F Wang, E M Pearce, T K Kwei *J. Polym. Sci., Part B, Polym. Phys.* **29** 619 (1991)
41. H-I Kim, E M Pearce, T K Kwei *Macromolecules* **22** 3374 (1989)
42. H-I Kim, E M Pearce, T K Kwei *Macromolecules* **22** 3498 (1989)
43. K J Zhu, S F Chen, T Ho, E M Pearce, T K Kwei *Macromolecules* **23** 150 (1990)
44. H-i Kim, T K Kwei, E M Pearce *Macromolecules* **22** 687 (1989)
45. E M Pearce, T K Kwei, S Lu *Polym. Adv. Technol.* **5** 600 (1994)
46. S Makhija, E M Pearce, T K Kwei, F Liu *Polym. Eng. Sci.* **30** 798 (1990)
47. L Jong, E M Pearce, T K Kwei, L C Dickinson *Macromolecules* **23** 5071 (1990)
48. T Suzuki, E M Pearce, T K Kwei *Polymer* **33** 198 (1992)
49. E M Pearce, T K Kwei *Polymer Solutions, Blends and Interfaces* (Eds I Noda, D N Dublingh) (Amsterdam: Elsevier, 1992) p. 133
50. L Jong, E M Pearce, T K Kwei *Polymer* **34** 48 (1993)
51. S Lu, E M Pearce, T K Kwei *Macromolecules* **26** 3514 (1993)
52. H Zhuang, E M Pearce, T K Kwei *Macromolecules* **27** 6398 (1994)
53. H Zhuang, E M Pearce, T K Kwei *Polymer* **36** 2237 (1995)
54. E Y Chu, E M Pearce, T K Kwei, T F Yeh, Y Okamoto, *Macromol. Chem., Rapid Commun.* **12** 4 (1991)
55. E M Pearce, T K Kwei *J. Polym. Sci., Part A, Polym. Chem.* **32** 2597 (1994)
56. S Lu, E M Pearce, T K Kwei *J. Macromol. Sci., Part A, Pure Appl. Chem.* **31** 1535 (1994)
57. S Lu, M M Melo, J Zhao, E M Pearce, T K Kwei *Macromolecules* **28** 4908 (1995)
58. S Lu, E M Pearce, T K Kwei *Polym. Eng. Sci.* **35** 1113 (1995)
59. S Lu, E M Pearce, T K Kwei *Polym. Adv. Technol.* **7** 553 (1996)
60. S Lu, E M Pearce, T K Kwei, E Chu *J. Polym. Sci., Part A, Polym. Chem.* **34** 3163 (1996)
61. T C Gsell, E M Pearce, T K Kwei *Macromolecules* **23** 1663 (1990)
62. E M Pearce, T K Kwei *J. Macromol. Sci., Part A, Pure Appl. Chem.* **28** 1207 (1991)
63. Y K Dao, E Y Chu, Z S Xu, E M Pearce, Y Okamoto, T K Kwei *J. Polym. Sci., Part A, Polym. Chem.* **32** 397 (1994)
64. M W Huang, K J Zhu, E M Pearce, T K Kwei *J. Appl. Polym. Sci.* **48** 563 (1993)
65. I I Vointseva, A A Askadskii *Interpolymers (Paired Polymers) (Sov. Sci. Rev., B. Chem.)* Vol. 16, Part 2 (Ed. M E Vol'pin) (Chur: Harwood Academ. Publ., 1991)
66. P C Painter, B Veytsman, M Coleman *J. Polym. Sci., Part A, Polym. Chem.* **32** 1189 (1994)
67. P C Painter, M Coleman, in *European Symposium on Polymer Spectroscopy (ECOPS-11) (Abstracts of Reports), Valladolid, 1994* p. 17
68. J K Isasi, L C Cesteros, I Katime, in *European Symposium on Polymer Spectroscopy (ECOPS-11) (Abstracts of Reports), Valladolid, 1994* p. 79
69. A O Baranov, A V Kotova, A N Zelenetskii, E V Prut *Usp. Khim.* **66** 917 (1997) [*Russ. Chem. Rev.* **66** 877 (1997)]
70. USSR P. 717 077: *Byull. Izobr.* (7) (1980)
71. V V Korshak, A A Askadskii, I I Vointseva, B B Mustafaeva, A P Suprun, G L Slonimskii *Vysokomol. Soedin., Ser. A* **23** 1002 (1981)
72. V V Korshak, A A Askadskii, I I Vointseva, B B Mustafaeva, G L Slonimskii, A P Suprun *Dokl. Akad. Nauk SSSR* **265** 1147 (1982) [c]
73. B B Mustafaeva, Candidate Thesis in Chemical Sciences, Institute of Organoelement Compounds, Academy of Sciences of the USSR, 1983
74. V V Korshak, A P Suprun, I I Vointseva, B B Mustafaeva, G L Slonimskii, A A Askadskii, T M Birshtein, E N Kaneva *Vysokomol. Soedin., Ser. A* **26** 111 (1984) [b]
75. V V Korshak, G L Slonimskii, A A Askadskii, O G Nikol'skii, A P Suprun, I I Vointseva, B B Mustafaeva, E M Belavtseva, L G Radchenko *Vysokomol. Soedin., Ser. A* **26** 1929 (1984) [b]
76. V V Korshak, I I Vointseva, A P Suprun, A A Askadskii, G L Slonimskii *Vysokomol. Soedin., Ser. A* **29** 140 (1987) [b]
77. V V Korshak, A P Suprun, I I Vointseva, I I Evstifeeva, G L Slonimskii, A A Askadskii *Vysokomol. Soedin., Ser. A* **29** 1257 (1987) [b]
78. V V Korshak, A P Suprun, G L Slonimskii, A A Askadskii, T M Birshtein, I I Vointseva, B B Mustafaeva, O G Nikol'skii *Makromol. Chem.* **187B** 2153 (1986)
79. V V Korshak, A P Suprun, I I Vointseva, B B Mustafaeva, G L Slonimskii, A A Askadskii, K A Bychko *Vysokomol. Soedin., Ser. B* **26** 376 (1984) [b]
80. A A Askadskii, I I Vointseva, B B Mustafaeva, V V Kazantseva, G L Slonimskii *Vysokomol. Soedin., Ser. A* **24** 2447 (1982) [b]

[a] — *Colloid. J. (Engl. Transl.)*
[b] — *Polym. Sci. (Engl. Transl.)*
[c] — *Dokl. Chem. Technol., Dokl.Chem. (Engl. Transl.)*