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Determination of interaction parameters of block copolymers containing aromatic polyesters from solubility parameters obtained from solution viscosities

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Abstract Flory–Huggins interaction parameters of polymeric systems including polysulfone and aromatic poly(ester imides) were calculated using solubility parameters in order to estimate the tendency of phase separation of the respective block copolymers. The scope of the work was to compare χ values based on δ calculated by means of increment tables as well as obtained experimentally using the solubility behavior in different solvent mixtures. It was found that χ parameters based on experimentally determined δ are generally at least 1 order of magnitude smaller than values calculated with increment tables. However, the experimental data sets for χ allowed the establishment of a general order of phase separation in the block copolymers investigated almost independently of the method of obtaining the solubility parameters (i.e., from the increment table used). The tendency of phase separation correlates with the tendency found by investigation of the respective block copolymers.

Keywords Solubility parameters · Flory–Huggins interaction parameters · Solution viscosity · Multiblock copolymers · Segmented block copolymers

Introduction

The synthesis of block copolymers is one of the most important tools of polymer science to design materials with tailor-made property profiles. Block copolymers offer the opportunity to combine properties of different parent homopolymers in a new material (e.g., combination of proper processability with high mechanical performance and thermostability) or give rise to synergistic properties, as in thermoplastic elastomers. Owing to the thermodynamic immiscibility of most polymers [1], block copolymers show the special feature of microphase separation between the incorporated blocks [2]. One important parameter to predict microphase separation is the interaction parameter, χ. It was introduced by Flory [1] to describe semiempirically the energetic interactions between different polymers and is a measure for the degree of phase separation in a given system of polymers according to Eq. (1):

$$\Delta G_m = RTV_c[(\phi_A/N_A)\ln\phi_A + (\phi_B/N_B)\ln\phi_B + \chi_{AB}\phi_A\phi_B], \quad (1)$$

where ΔG_m is the Gibbs free energy of mixing, ϕ_A and ϕ_B are the volume fractions of polymers A and B ($\phi_A + \phi_B = 1$) and N_A and N_B are the number of reference units with the molar volume V_c of a given reference unit.

There are a number of methods to obtain χ_{AB}; namely

1. Direct determination from the phase diagram (i.e., plot of N versus ϕ), [3, 4].
2. From the small-angle X-ray scattering (SAXS) and light scattering behavior of a blend or block copolymer consisting of A and B [5].

3. From the interaction between the polymers and a solvent [6].
4. By determination of contact angles and segregation isotherms [7].

The correlation of the parameters measured by methods 2–4 is given by mean-field theory [8, 9]. Although method 1 is the most reliable, it is difficult to apply because it requires, first, the knowledge of the whole phase diagram, including a binodal equation, and, second, from an experimental point of view extended efforts in synthesizing series of polymers with varying N. Method 2 assumes a distinct scattering behavior (appearance of a SAXS scattering maximum, order on a certain length scale) of the system and is therefore restricted to block copolymers with specific architecture, particularly to block copolymers with a small number of blocks and low polydispersity. Method 3 uses the interaction between one (or two) polymers with a solvent, finally obtaining the solubility parameters, δ, for each polymer. The solubility parameters of two polymers A and B are correlated to the respective interaction parameter, χ_{AB}, according to Eq. (2) [10]:

$$\chi_{\mathrm{A,B}} = (\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 V_{\mathrm{c}}/RT, \tag{2}$$

where T is the temperature, R is the gas constant, and V_{c} is the molar volume of the reference unit, which is often arbitrarily set to 100 cm^3/mol.

Experimental methods to determine δ include calculation from thermal expansion coefficients and isothermal compressibilities obtained by pVT measurements [11] and calculations based on solvents with known solubility parameters; the interaction with a polymer can be evaluated by using different specific parameters, for example, swelling [12], cloud point [13], and solution viscosity [14]. Here, δ of the polymers follows directly from δ of the solvent with the most intensive interaction to the polymer. On the other hand, several concepts were developed to predict solubility parameters on the basis of the correlation between cohesive energy density and δ (Eq. 3) [15]:

$$\delta = (E_{\mathrm{coh}}/V_{\mathrm{m}})^{1/2}, \tag{3}$$

where E_{coh} is the cohesive energy and V_{m} is the molar volume of the repeating unit.

The concepts of cohesive energy density as well as the calculation of χ from δ are often criticized for their lack of precision. Additionally, Eq. (2) cannot explain negative values of χ. However, these concepts are largely applied to predict miscibility of polymers as well as their thermophysical and mechanical properties [12]. Thus, there is still a need for scientific investigations to correlate predicted and experimental results.

In this work, we calculate χ parameters between polysulfone (PSU) and aromatic poly(ester imides) (PEI) from solubility parameters obtained by incremental methods and in experiments. The applicability of solution viscosity measurements to obtain solubility parameters of these aromatic polymers was evaluated and the results were compared to the results calculated by different incremental methods, in order to answer the question how the relatively simple theories used to obtain χ and δ would describe the phase separation behavior of segmented block copolymers having segments with rather complex chemical structure. Phase diagrams of such block copolymers have been obtained before by mean-field calculations [16] and could be refined by using χ parameters based on the experimentally obtained solubility parameters. Thus, a contribution to the understanding of structure–property relationships in block copolymers with segments of high-performance polymers, recently reported [16, 17], would be possible.

The solubility and interaction parameters obtained for PSU and three aromatic PEI in different combinations of solvent mixtures are discussed in the following. The general chemical structures of the homopolymers and segmented block copolymers discussed are given in Fig. 1.

Experimental

Sample preparation and chemical characterization

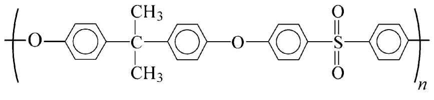
PSU (molecular weight $M_{\mathrm{n,NMR}}$ = 30,000 g/mol; $M_{\mathrm{n,SEC}}$ = 38,600 g/mol; $M_{\mathrm{w,SEC}}$ = 63,200 g/mol) was supplied by Polyscience. The PEI under investigation were synthesized by a melt transesterification procedure as described in Ref. [17]. They were chemically characterized by their solution viscosities in a mixture from trifluoroacetic acid/$\mathrm{CHCl_3}$ (1/1 vol/vol), at 25 °C, as well as by size-exclusion chromatography (SEC). The SEC measurements were performed with a modular chromatographic equipment containing a high-pressure liquid chromatography pump, a refractive index detector, PL-mixed three separation columns (Polymer Laboratories, UK) and a manual injection valve (Knauer, Berlin, Germany) at ambient temperature. A mixture of pentafluorophenol (PFP)/$\mathrm{CHCl_3}$ (1/1 vol/vol) was used as an eluant, the polymer concentration was 1.6 g/l, the injection volume was 20 µl, and the flow rate was 0.3 ml/min. The molecular weights were calculated by polystyrene calibration using narrowly distributed polystyrene standards, thus giving relative values. The chemical characterization of the samples is given in Table 1.

Determination of solution viscosities

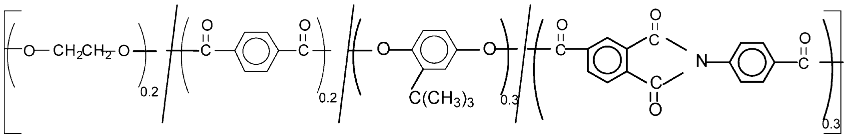
The sample to be investigated was dissolved in the solvent mixture and filtered before measurement. To determine the solubility parameters, the solution viscosities were measured with an automatic Ubbelohde-type viscometer (Schott, Germany), capillary I (capillary Ic with PFP/$\mathrm{CHCl_3}$), using different polymer concentrations and different compositions of the solvent mixture at constant temperature (20 °C). As solvent mixtures were used hexafluoroisopropanol (HFIP)/$\mathrm{CHCl_3}$ and PFP/$\mathrm{CHCl_3}$. Concentration-independent reduced viscosities, η_{red}, [$\eta_{\mathrm{red}} = (\eta_{\mathrm{rel}} - 1)/c_{\mathrm{pol}}$)] were used for all the plots. The experimental error for the viscosity measurements was about 1% for the relative and reduced viscosities of PSU, poly(ethylene terephthalate) (PET)/PEI and PEI(t-But), and 1–4%

Fig. 1. Chemical structures of the aromatic polymers and block copolymers investigated in this work

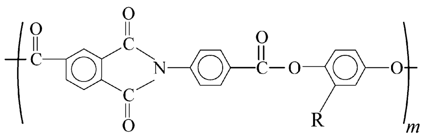
a



Polysulfone (**PSU**)



Poly(ethylene terephthalate-*co*-polyester imide) (**PET/PEI(t-but)**)



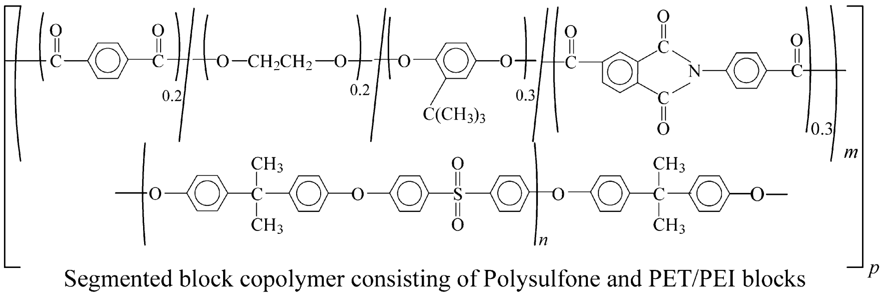
Poly(p-phenylene-N-(4-carboxyphenylene)-4,4‘-(carboxyphenoxy) phthalimide)

poly(ester imide, (PEI)

R= $-C(CH_3)_3$: **PEI(t-but)**

R = - Ph : **PEI(Ph)**

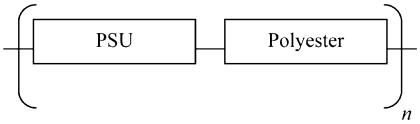
b



Segmented block copolymer consisting of Polysulfone and PET/PEI blocks

(**PSU-PET/PEI MBCP**)

General chemical structure of segmented block copolymers:



Segmented block copolymer consisting of Polysulfone and Poly(ester imide) blocks

(**PSU-PEI MBCP**)

for PEI(Ph). The errors for the determination of the viscosity maxima in the solvent mixtures were about 2% for PSU, PET/PEI and PEI(*t*-But), but up to 6% for PEI(Ph).

Headspace gas chromatography

Solvent mixtures (HFIP/$CHCl_3$ and PFP/$CHCl_3$, respectively) with different compositions and polymers dissolved in these solvent mixtures were examined using headspace gas chromatography (GC). A solution (100 µl) was placed in a sample vial and equilibrated for 15 min in the heating chamber of the headspace sampler (HP 7694) at 50 °C. After that time, the gaseous phase was analyzed by GC/mass spectrometry using a HP 5890 gas chromatograph equipped with a mass-selective detector (HP 5971, quadrupole mass spectrometer, ionization 70 eV, split 1:50) with helium as a carrier gas (2 ml/min), and an HP-5MS capillary column. The GC temperature program was 50 °C for 2 min, and heating was up to 150 °C at a rate of 12 °C/min. The loop- and transferline temperature was 60 °C. As a result, the amounts of the

Table 1. Chemical characterization of the polymers under investigation: polysulfone (*PSU*), poly(ethylene terephthalate) (*PET*), poly(ester imides) (*PEI*), pentafluorphenol (*PFP*)

Polymer	Inherent viscosity (dl/g)[a]	$M_{\mathrm{n,GPC}}$ (g/mol)[b]	$M_{\mathrm{w,GPC}}$ (g/mol)[b]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[b]
PSU	0.57	35,400	58,700	1.66
PET/PEI	0.48	12,800	38,300	2.99
PEI(*t*-Bu)	1.77	26,700	65,300	2.45
PEI(Ph)	1.60	23,500	98,000	4.17

[a] Ubbelohde viscometer, capillary I, 20 °C, $c_{\mathrm{pol}} = 0.5$ g/dl; solvent: trifluoroacetic acid/$CHCl_3$ (1/1 v/v), (except for PSU: CHCl3)

[b] Gel permeation chromatography using a Knauer GPC; eluant: PFP/$CHCl_3$ (except for PSU: $CHCl_3$); separation columns: Waters Styragel HT3/HT6; molecular weights relative to polystyrene standard

solvent components in the gas phase were compared with the composition of the liquid phase to detect interactions between the components of the solvent mixture and between solvents and polymers. The results were expressed as percental portions of HFIP and PFP, respectively, in mixtures with $CHCl_3$ with $x_{\mathrm{a,HFIP}} = A_{\mathrm{HFIP}}/(A_{\mathrm{HFIP}} + A_{\mathrm{CHCl3}})$ and $x_{\mathrm{a,PFP}} = A_{\mathrm{PFP}}/(A_{\mathrm{PFP}} + \mathrm{A}_{\mathrm{CHCl3}})$, where A corresponds to the peak area of the component in the chromatogram. The relative failure of the method was about 4%.

Results and discussion

Calculations of solubility parameters for the solvents and for the polymers investigated (PEI and PSU)

The Hildebrand solubility concept correlates the total solubility parameter with the cohesive energy density. This concept is, strictly speaking, only applicable to low-molecular-weight substances, like the solvents that are used in this work. It cannot be applied to polymers owing to their lack of vaporization. Therefore, several concepts were developed to calculate the solubility parameter of polymers, for example, by summing up all the molar attraction constants, F_i, (Eq. 4) of the polymer structural units, correlated to δ by Eq. (5) [15]:

$$F = (E_{\mathrm{coh}}/V_{\mathrm{m}})^{1/2}, \tag{4}$$

where F is the molar attraction constant, E_{coh} the cohesive energy, and V_{m} the molar volume of the repeating unit at 298 K and

$$\delta = \rho \sum F_i / M_0, \tag{5}$$

where ρ is the density and M_0 the molar mass of the repeating unit of the polymer.

Here, the solubility parameters were calculated using F_i of three different increment tables (Van Krevelen [15, p. 195], Small [18] and Hoy [19]). The molar volumes of the repeating units of the polymers were calculated by adding the molar volume increments of all the structural units [15, p. 87, values recommended by Van Krevelen]. The increment tables for molar volumes and cohesive energy increments based on the same assumptions were used.

The total solubility parameters of solvents can be obtained directly from the heat of vaporization, ΔH_{v}, (Eq. 6):

$$\delta = (E_{\mathrm{coh}}/V_{\mathrm{m}})^{1/2} = [(\Delta H_{\mathrm{v}} - RT)/V_{\mathrm{m}}]^{1/2}. \tag{6}$$

Partial solubility parameters were introduced by Hansen to take intermolecular interactions in polar substances into account [20]. The total solubility parameter, δ_{t}, was split into three parts considering atomic dispersion forces, δ_{d}, dipole–dipole forces, δ_{p}, and molecular hydrogen bonding, δ_{h}. Hansen parameters are correlated to the total (Hildebrand) solubility parameters δ_{t} as shown in Eq. (7):

$$\delta_{\mathrm{t}} = \left(\delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2\right)^{1/2}. \tag{7}$$

δ_{d}, δ_{p}, and δ_{h} can be calculated as follows:

$$\delta_{\mathrm{d}} = \sum F_{\mathrm{d},i}/\mathrm{V}_{\mathrm{m}}, \tag{8}$$

$$\delta_{\mathrm{p}} = \left(\sum F_{\mathrm{p},i}^2\right)^{1/2}/V_{\mathrm{m}}, \tag{9}$$

and

$$\delta_{\mathrm{h}} = \left(\sum E_{\mathrm{coh}}^2\right)^{1/2}/V_{\mathrm{m}}^{1/2}, \tag{10}$$

where $F_{\mathrm{d},i}$ and $F_{\mathrm{p},i}$ are the group contributions for dispersive and polar forces and E_{coh} is the group contribution for the hydrogen bonding in the polymer.

The copolymers (PET/PEI) were calculated using the molar contents of copolymer repeating units according to the miscibility rule (Eq. 11):

$$\delta_{\text{block copolymer}} = x_{\mathrm{v},1}\delta_1 + x_{\mathrm{v},2}\delta_2. \tag{11}$$

Hansen's approach is often considered more realistic for polar compounds and was thus also used for the polymers under investigation. The repeating chemical structures of PSU and the aromatic PEI are rather complex and the heteroatoms S, N, O, and their specific interactions have to be taken into account with respect to F_i. The molar volume of the repeating units were also calculated by increment tables.

The δ computed for the solvents used in the experiments are summarized in Table 2. The solubility parameters calculated by using the heat of vaporization, ΔH_{v}, should give the real, defined δ (Eq. 6). The values obtained by Hoy, Small, and Van Krevelen do not consider specific interactions. As expected, the δ obtained by Hansen's approach match the δ from ΔH_{v} best. Nevertheless, Van Krevelen's concept describes less polar compounds, like $CHCl_3$ and HFIP, also pretty well.

Table 2. Solubility parameters, δ, of solvents calculated by different methods [15, 18, 19, 20]: hexafluoroisopropanol (*HFIP*)

Solvent	Molar volume (cm^3/mol)	δ (MPa$^{1/2}$) obtained by different calculation methods							
		Small	Hoy	Van Krevelen	Hansen				ΔH_v
					δ_d	δ_p	δ_h	δ_t	
$CHCl_3$	80.9^a	21.32	21.31	19.33	17.80	0	0	17.80	18.88^c
HFIP	102.6^a	11.21	14.79	17.88	14.17	2.41	13.89	19.99	17.98^c
PFP	76.4^b	14.97	13.91	16.80	35.86	1.70	16.20	39.39	32.05^d

[a] Calculated by density data
[b] Calculated according to Fedors' increments, see Ref. [15]
[c] Evaporation enthalpies taken from Merck catalog [23]
[d] Calculated from cohesive energy density (Eq. 3), group increments from [15]

The calculated δ for the polymers examined are given in Table 3. An example for the detailed calculation is given in the Appendix. The different increment tables give for PSU values from 19.62 to 21.79 MPa$^{1/2}$, whereas the values obtained for the aromatic PEI are higher (up to 23.73 MPa$^{1/2}$). The differences between PSU, on the one hand, and the PEI, on the other hand, are more obvious in the partial Hansen parameters. According to these, PSU is less polar, which seems to reflect the real situation. However, the values for each polymer obtained using the different increment tables are significant and differ less than those of the solvents which might be caused by the rather similar and complex chemical structure of the repeating units.

Experimental determination of solubility parameters in solvent mixtures

By definition, the solubility parameter of a given polymer is approximately the same as for a solvent in which the polymer dissolves in all concentrations without heat of mixing, without volume change, and without reaction or special association [21]. Thus, the observation of the solubility behavior can be used to get δ. Mangaraj et al. [6, 13, 14] proposed measurements of solution viscosities of polymers in solvents with different δ. In the plot of the concentration-independent parameter η_{red} versus δ of the solvent, the maximum viscosity value corresponds to the solubility parameter of the polymer. At this point the optimal solubility is reached, i.e., the hydrodynamic volume of the polymer coils in dilute solution is maximal. This method had to be modified for the present investigations owing to the poor solubility of these aromatic polymers in common organic solvents and the restricted number of solvents applicable. To extend the range of available solvents, mixtures of solvents with different dissolution power were utilized, assuming an additivity rule (Eq. 12) which is often applied for solvent mixtures [22]:

$$\delta_{\mathrm{mixture}}=x_{v,1}\delta_1+x_{v,2}\delta_2, \tag{12}$$

where $\delta_{\mathrm{mixture}}$ is the solubility parameter of a solvent mixture with volume fraction $x_{v,1}$ of polymer 1 with

Table 3. Comparison of solubility parameters of the polymers under investigation calculated by different methods [15, 18, 19, 20] and obtained by viscometry

Polymer		Molar volume (cm^3/mol)	δ (MPa$^{1/2}$) obtained by different calculation methods				
			Small	Hoy	Van Krevelen	Hansen^a	ΔH_v
PSU	From δ_{calc}	359.5	19.76	21.73	21.79	19.62^b	–
	From $\delta_{\mathrm{CHCl3–HFIP}}$		17.38	18.77	18.77	18.65	18.53
	From $\delta_{\mathrm{CHCl3–PFP}}$		18.18	17.54	18.04	28.81	25.60
PET/PEI	From δ_{calc}	272.1	22.77	22.41	23.73	20.24^c	–
	From $\delta_{\mathrm{CHCl3–HFIP}}$		14.14	16.68	18.30	19.35	18.24
	From $\delta_{\mathrm{CHCl3–PFP}}$		17.38	16.72	17.76	31.19	26.26
PEI(*t*-Bu)	From δ_{calc}	357.3	23.01^f	22.26	23.31	20.04^d	–
	From $\delta_{\mathrm{CHCl3–HFIP}}$		15.66	17.66	18.52	19.03	18.38
	From $\delta_{\mathrm{CHCl3–PFP}}$		17.76	17.18	17.96	29.89	26.26
PEI(Ph)	From δ_{calc}	369.0	23.31^f	23.05	23.27	20.04^e	–
	From $\delta_{\mathrm{CHCl3–HFIP}}$		16.16	17.98	18.59	18.92	18.42
	From $\delta_{\mathrm{CHCl3–PFP}}$		17.76	17.18	17.96	29.89	26.26

[a] $\delta=\delta_t$ from $\delta_d|\delta_p|\delta_h$
[b] 18.61|2.31|5.58
[c] 17.88|4.40|8.41
[d] 17.86|4.28|8.02
[e] 17.94|4.14|7.89
[f] Missing data for some structural units were taken from Van Krevelen's table

solubility parameter δ_1 and polymer 2 with volume fraction $x_{v,2}$ and solubility parameter $\delta 2$.

Strictly speaking, the solubility parameters of solvent mixtures have to be calculated correctly by averaging the cohesive energies of the structural units of both solvents divided by the averaged molar volume, which might be determined experimentally by density measurements of the mixture. These correct δ were computed for HFIP/$CHCl_3$ mixtures. It was found that the calculated results differed less than 1% from the values obtained by the simplified Eq. (12), which was therefore used in all the calculations of δ.

The solvents used in the experiments were mixtures of $CHCl_3$ (as a good solvent for PSU and a bad solvent for the PEI) with HFIP or PFP, respectively, which are good solvents for the PEI and bad solvents for PSU.

Here, interactions between polymer and both solvents as well as between the solvents themselves have to be taken into account. Thus, the first step was to examine the behavior of the solvent and solvent mixtures with different composition used in the viscosity measurements with respect to intermolecular interactions between the solvents.

Investigation of solvent mixtures

Headspace GC was applied to characterize the behavior of mixtures of HFIP/$CHCl_3$ and PFP/$CHCl_3$, respectively. The principle of headspace GC consists of the analysis of the composition of the gas phase above a liquid phase in order to characterize the mixture itself, assuming a system near the thermodynamic equilibrium. From this method, qualitative conclusions about specific interactions between the partners within the mixture (solvents, polymer) were expected.

The relative concentrations of HFIP and PFP, respectively, expressed as a percental part (area percent, $x_{a,HFIP}$, and $x_{a,PFP}$) in the vapor phase over the mixtures of HFIP/$CHCl_3$ and PFP/$CHCl_3$at a constant measuring temperature of 50 °C are shown in Fig. 2.

The difference between the contents of HFIP (Fig. 2a) and PFP (Fig. 2b) in the solvent mixture and the gaseous phase is obvious and can be explained easily with the higher (HFIP) and much lower (PFP) vapor pressure of these liquids compared to $CHCl_3$. Both solvent mixtures give S-shaped curves, which is a qualitative measure of a rather complex liquid system and a strong indication of nonideal behavior. However, in the range between 0.4 and 0.6, where the viscosity maximum of the polymers was expected to appear, the curves are approximately linear. That means, even if specific interactions exist, their strength does not change within this compositional region and there is no change in the principal behavior of the mixtures. Deviations from this linear curve are observed in compositions with higher or lower content of $CHCl_3$ ($x_{v,HFIP,PFP} = 0.3$ and 0.7), resulting in an asymmetrical shape of the curve and thus reflecting that asymmetric mixtures with low and high concentration of PFP and HFIP, respectively, have significantly changed specific interactions. The effect is suppressed or apparently compensated in the solvent mixtures with polymer (i.e., the polymer solutions), as also shown in Fig. 2. This might mean that the polymer when dissolved in the mixture might change the interactions between both solvents by its own interactions with them. However, the polymer does not alter the concentration of PFP or HFIP in the vapor phase significantly compared to the pure solvent mixture, i.e., there is no preferential solvation.

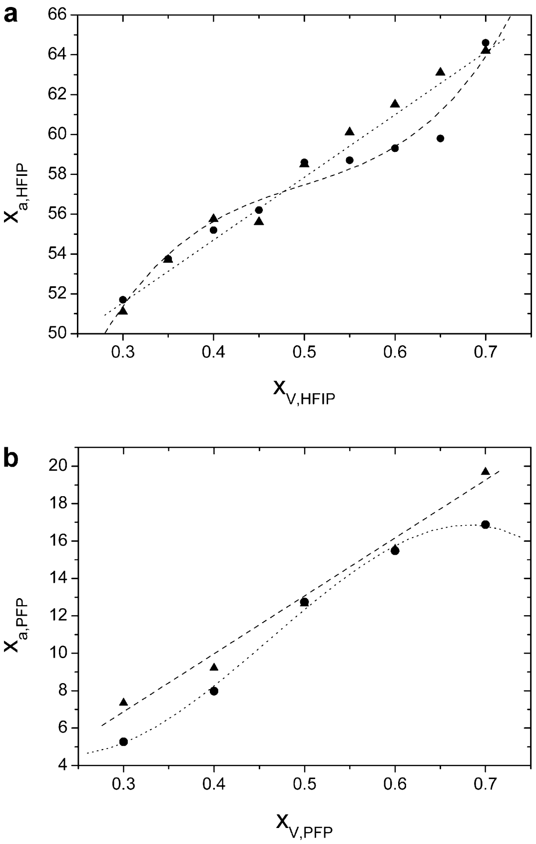


Fig. 2. Dependence of the vapor composition on the composition of the solvent mixture, obtained by headspace gas chromatography, for pure solvent mixtures (*circles*) and solvent mixtures with added polymer polysulfone (*PSU*) (*triangles*): **a** for hexafluoroisopropanol (*HFIP*)/$CHCl_3$, **b** for pentafluorophenol (*PFP*)/$CHCl_3$

This result suggests that the viscosity maxima found in the range $0.4 < x_{v,PFP,HFIP} < 0.6$ should not be influenced by the altered strength of specific interactions between solvents as well as solvents and polymer.

The flow behavior of the solvent mixtures investigated is shown in Fig. 3. The plot of the corrected flow times versus concentration of HFIP in the mixture with $CHCl_3$ does not show irregularities (i.e., deviation from

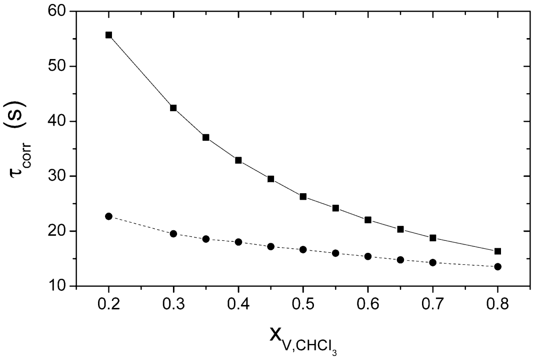


Fig. 3. Dependence of the flow time of solvent mixtures (corrected time τ_{corr}) on the composition of the mixture, obtained by viscometry: for the solvent mixture of HFIP/$CHCl_3$ (*circles*); for the solvent mixture of PFP/$CHCl_3$ (*squares*)

linearity). In contrast, PFP mixtures, particularly around $x_{v,PFP}$~0.5, show lower viscosities than expected from ideal linear behavior, suggesting increased specific interactions in that compositional region. This effect will counteract a possible viscosity maximum of the polymer solutions in that region and has therefore to be taken into account when discussing the results for the polymer solutions.

Figure 4 follows the question whether the polymer concentration in the solvent mixtures would increase specific interactions or not, illustrating the influence of the polymer concentration on the composition of the vapor for three polymer concentrations in HFIP/$CHCl_3$ mixtures. It can be noted that the polymer (PSU) concentration for a given solvent composition does not have a detectable effect, being almost within the limits of accuracy of headspace GC. A comparable result was obtained using PSU in PFP/$CHCl_3$ mixtures.

Viscosity measurements of polymer solutions

The influence of polymer concentration for solutions of PSU in different HFIP/$CHCl_3$ mixtures on the solution viscosity is shown in Fig. 5. Indeed, a maximum in the reduced viscosity over the compositional range is found at about $x_{v,HFIP}$~0.4, as expected from the concept. The position of this maximum is not influenced by the polymer concentration, only the height of the maximum rises with increasing concentration.

The plot of η_{spec}/c_{PSU} versus c_{PSU} (Huggins plot) for different PSU concentrations is displayed in Fig. 6 and also confirms the regular behavior of PSU in solvent mixtures (for $x_{v,HFIP}=0.5$). The same behavior was observed for all the PEI under investigation.

In conclusion, an intermediate polymer concentration of 5 g/l was used to determine the viscosity maxima of the other polymers.

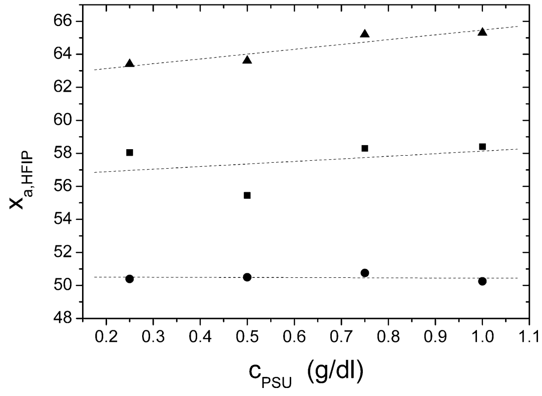


Fig. 4. Headspace gas chromatographic examination of solutions of PSU with different polymer concentration in solvent mixtures, dependence of the vapor composition on the polymer concentration and the mixture composition for HFIP/$CHCl_3$ mixtures: HFIP/$CHCl_3$ (30/70) (*circles*); HFIP/$CHCl_3$ (50/50) (*squares*); HFIP/$CHCl_3$ (70/30) (*triangles*)

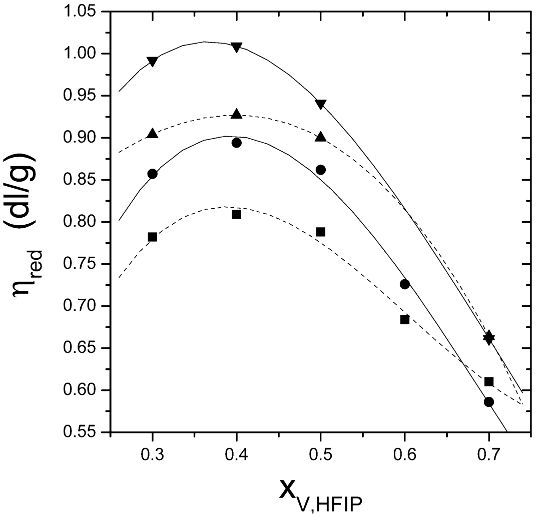


Fig. 5. Solution viscosities (η_{red}) of PSU solutions with different polymer concentration for the solvent mixture of HFIP/$CHCl_3$: 0.25 g/dl (*squares*); 0.50 g/dl (*circles*); 0.75 g/dl (*up triangles*); 1.00 g/dl (*down triangles*)

Further experiments concerned the influence of the size of the capillary used for the viscosity measurements. Only experiments with a proper flow time of the solution offer the possibility to get a distinct viscosity maximum. Thus, for PFP/$CHCl_3$ a different capillary (capillary Ic) than for HFIP/$CHCl_3$ (capillary I) had to be applied owing to the much longer flow time of PFP/$CHCl_3$. Another possibility to overcome this problem is to use the absolute kinematic viscosities instead of η_{spec} which gives for both capillaries the same curve.

It should also be noted that the position of the viscosity maximum is not influenced by the molecular weight of the polymer which was investigated for some

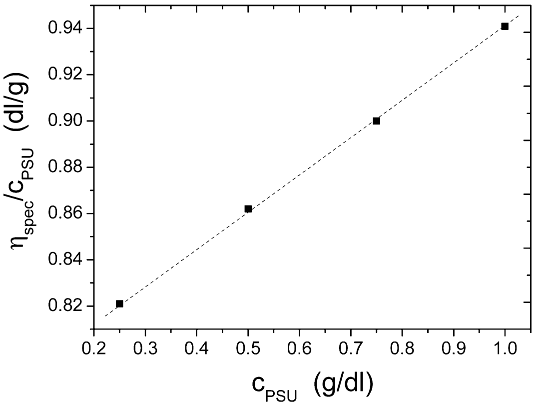


Fig. 6. Huggins plots of viscometric measurements of solutions with different PSU concentrations (η_{spec}/c_{PSU} versus c_{PSU}) in HFIP/CHCl$_3$ (50/50 v/v)

of the samples. The molecular weight of the sample does not change the position of the maximum significantly. However, higher η_{red} of the polymers, i.e., higher molecular weight, results in a more distinct maximum in the viscosity curve and thus in a more accurate determination of δ.

The plots of the reduced viscosities of PEI(*t*-But) in both solvent mixtures, HFIP/CHCl$_3$ and PFP/CHCl$_3$, are shown in Fig. 7 as examples. Both curves allow, as in the case of all the other polymer solutions, the determination of the solvent composition at the viscosity maximum of the polymer solution. The solvent composition at the maximum yields, finally, the solubility parameter of the polymer using Eq. (11). If the viscosities are plotted versus the solubility parameter of the solvent mixture, the solubility parameter of the polymer can directly be deduced from the plots, as demonstrated in Fig. 8 for PET/PEI solutions in HFIP/CHCl$_3$. It has to be noted which increment tables were applied for the base solubility parameters of the solvents.

All the results of viscometrical investigations of the polymers in both solvent mixtures are summarized in Tables 4 and 5. All the solubility parameters obtained experimentally using the different solvent mixtures and the calculated values based on Small, Hoy, Van Krevelen, and Hansen increment tables are compared in Table 3. The error range in the experimental determination of δ by using the viscosity maximum is 1–3% for PSU, PET/PEI, and PEI(*t*-But) and about 2–6% for PEI(Ph). On the basis of the experimental error of δ, only the first decimal place is significant; however, the second decimal place is given in Table 3 additionally because these values were used for the calculation of the χ parameters to avoid an artificial enlargement of the error for χ.

It has to be emphasized that the δ values obtained using HFIP/CHCl$_3$ differ significantly from those obtained with the PFP/CHCl$_3$solvent system. The reason is obvious: the viscosities are plotted between the values of δ_{CHCl3} and δ_{HFIP} or δ_{PFP}, respectively, and the maximum can only be found within these limits. Because δ_{HFIP} and δ_{PFP} are very different from each other, the position of the maximum and, hence, the resulting solubility parameters of the polymer also diverge, which strikingly shows the limitation of the viscosity method to get meaningful solubility parameters, particularly in the case of aromatic polymers that do not allow the use of a

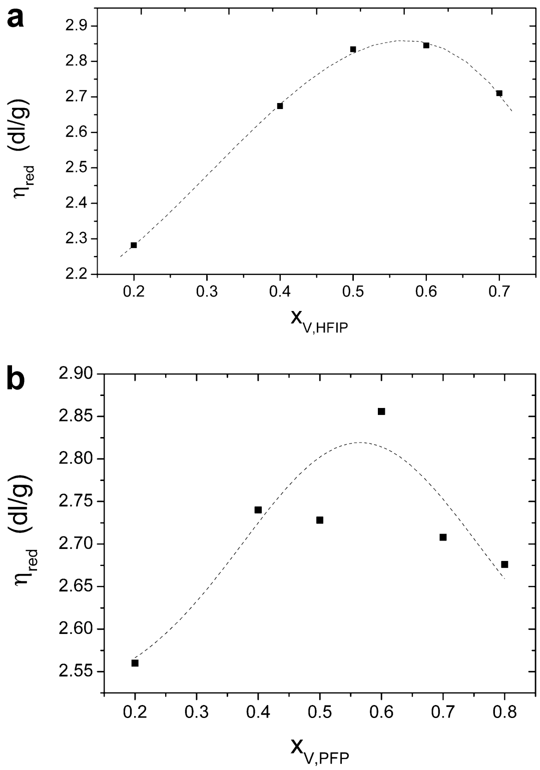


Fig. 7. Reduced solution viscosities (η_{red}) of poly(ester imides) (*PEI*) (*t*-But) in solvent mixtures: **a** HFIP/CHCl$_3$, **b** PFP/CHCl$_3$

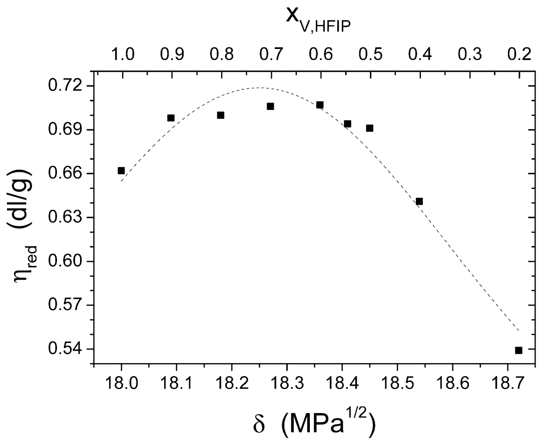


Fig. 8. Dependence of the reduced solution viscosities (η_{red}) of poly(ethylene terephthalate)/PEI in HFIP/CHCl$_3$ mixtures on the solubility parameters (δ) of the mixture and the HFIP content ($x_{v,HFIP}$)

Table 4. Summary of solution viscosities (η_{rel}, η_{red}) of all the polymers investigated in mixtures of HFIP/$CHCl_3$ with different composition, at 20 °C ($c_{\mathrm{pol}} = 5$ g/dl)

Solvent		PSU		PET/PEI		PEI(*t*-But)		PEI(Ph)	
$x_{\mathrm{v,CHCl3}}$	$x_{\mathrm{v,HFIP}}$	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)
0.20	0.80			1.350	0.700			2.346	2.692
0.30	0.70	1.293	0.586	1.353	0.706	2.355	2.710	2.335	2.670
0.35	0.65							2.333	2.667
0.40	0.60	1.363	0.726	1.354	0.707	2.422	2.845	2.369	2.738
0.45	0.55			1.347	0.694			2.357	2.704
0.50	0.50	1.431	0.862	1.346	0.691	2.417	2.834	2.390	2.779
0.55	0.45							2.380	2.560
0.60	0.40	1.447	0.894	1.321	0.641	2.337	2.674	2.379	2.758
0.65	0.35							2.373	2.745
0.70	0.30	1.428	0.857					2.353	2.706
0.80	0.20			1.269	0.539	2.141	2.282	2.255	2.509
$x_{\mathrm{v,CHCl3,max}}$		0.60 ± 0.06		0.29 ± 0.02		0.44 ± 0.06		0.49 ± 0.06	

Table 5. Summary of solution viscosities (η_{rel}, η_{red}) of all the polymers investigated in mixtures of PFP/$CHCl_3$ with different composition, at 20 °C (viscometer Ic, $c_{\mathrm{pol}} = 5$ g/dl)

Solvent		PSU		PET/PEI		PEI(*t*-Bu)		PEI(Ph)	
$x_{\mathrm{v,CHCl3}}$	$x_{\mathrm{v,PFP}}$	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)	η_{rel}	η_{red} (dl/g)
0.20	0.80			1.334	0.668	2.338	2.676		
0.30	0.70	1.424	0.848	1.335	0.670	2.354	2.708	2.358	2.715
0.35	0.65	1.424	0.848					2.378	2.756
0.40	0.60	1.425	0.850	1.341	0.682	2.428	2.856	2.393	2.786
0.45	0.55	1.434	0.867					2.390	2.780
0.50	0.50	1.444	0.888	1.339	0.678	2.384	2.728	2.391	2.782
0.55	0.45	1.440	0.880					2.361	2.722
0.60	0.40	1.433	0.866	1.324	0.648	2.370	2.740	2.346	2.691
0.65	0.35	1.436	0.872					2.315	2.629
0.70	0.30	1.429	0.858					2.290	2.580
0.80	0.20	1.356	0.711	1.288	0.576	2.281	2.562		
$x_{\mathrm{v,CHCl3,max}}$		0.49 ± 0.02		0.38 ± 0.02		0.44 ± 0.02		0.44 ± 0.02	

large number of solvents with different solubility parameters. The values determined with solvent mixtures can, however, be regarded as relative values which can be used to calculate the interaction parameters of block copolymers according to Eq. (2), where the difference term $(\delta_A - \delta_B)^2$ converts the relative values to χ which are then comparable. Thus, the apparent failure of the viscosity method and the kind of the solvent mixture is eliminated.

The relative error in χ originating from the law of error propagation is given in Eq. (13):

$$\frac{\Delta\chi}{\chi} \times 100 = \frac{\sqrt{8}}{1} \frac{\Delta\delta_{\mathrm{rel}}\delta}{\left|\delta_i - \delta_j\right|}. \tag{13}$$

Using this equation and the δ values from Table 3, we estimated the errors in χ for the most favorable and the least favorable cases. Values of $(\Delta\chi/\chi)\times 100$ of 50% were obtained for favorable cases (χ parameters > 1) and of 200% in least favorable cases, particularly for small differences of δ, as in the case of PSU–PEI(Ph). However, we believe that the order of magnitude of the χ obtained is suitable for discussion.

The χ values for the block copolymers consisting of PSU and aromatic PEI segments (with significant decimal places originating from error estimation) calculated and obtained from viscosity measurements using for each solvent mixture the solubility parameters from the respective increment table are given in Table 6. χ sets with Hoy's, Small's, Van Krevelen's, Hansen's, and ΔH_v-based solubility parameters are displayed.

In the following, the data sets are analyzed with respect to general tendencies that can be concluded from the investigations.

1. From the calculated (theoretical) χ of the block copolymers, the following general tendency was found with δ of each increment table: χ[PSU– PEI(Ph)] > χ(PSU–PET/PEI) > χ[PSU–PEI(*t*-But)], whereby $\chi_{\mathrm{Small}} > \chi_{\mathrm{VanKrevelen}} > \chi_{\mathrm{Hoy}}$. The tendency for phase separation increases in the same direction as χ increases. Although the χ values with Small's table were higher than those with Van Krevelen's table and the lowest were obtained using Hoy's table, the trend between the polymers was the same for each increment table.

Table 6. χ parameters of segmented block copolymers calculated by the solubility parameter method, comparison of calculated and experimental values

Block copolymer	χ obtained by different calculation methods						
		Small	Hoy	Van Krevelen	Hansen		ΔH_v
					a	b	
PSU–PET/PEI	From δ_{calc}	3.3	1.2	1.6	0.05	1.6	–
	From $\delta_{CHCl3–HFIP}$	1.3	0.6	0.03	0.06	2.6	0.01
	From $\delta_{CHCl3–PFP}$	0.1	0.1	0.01	0.7	0.9	0.05
PSU–PEI(*t*-But)	From δ_{calc}	1.7	0.2	0.8	0.03	1.5	–
	From $\delta_{CHCl3–HFIP}$	0.5	0.2	0.001	0.02	0.8	0.004
	From $\delta_{CHCl3–PFP}$	0.03	0.02	0.002	0.2	0.2	0.06
PSU–PEI(Ph)	From δ_{calc}	4.4	1.5	2.4	0.03	1.3	–
	From $\delta_{CHCl3-HFIP}$	0.2	0.1	0.005	0.01	0.4	0.002
	From $\delta_{CHCl3-PFP}$	0.03	0.02	0.002	0.2	0.2	0.06

[a] the values were calculated from the total $\delta = \delta_t$

[b] the values were calculated from the individual $\delta = \delta_d$, δ_p, δ_h

2. The χ values obtained in the experiments are at least 1 order of magnitude lower than the theoretical values, whereby the tendencies of χ follow those pointed out for the theoretical χ (i.e., values calculated using Small's and Van Krevelen's δ for solvents are higher than those using Hoy's and Hansen's δ). In most cases, χ resulting from $\delta_{\Delta H_v}$ and δ_{Hansen} are the lowest ones which can be discussed as a result of interactions between the polymers. These two approaches are able to reflect the polar nature of the polymers.
3. χ parameters obtained using PFP/CHCl$_3$ mixtures are up to 1 order of magnitude less than χ parameters obtained from δ from HFIP/CHCl$_3$.
4. The tendency for phase separation within the block copolymers with the experimental χ sets is changed compared to the theoretical order and is as follows: χ(PSU–PET/PEI) > χ[PSU–PEI(*t*-But)] ≥ χ[PSU–PEI (Ph)] with a small number of deviations [changes in the order between PSU–PEI(*t*-But) and PSU–PEI(Ph)] which might be caused by the very small differences in χ. For these polymers, the strength of phase separation obtained from the onset of phase separation with increasing segment molecular weight is as follows [16]: PSU–PEI(*t*-But) > PSU–PET/PEI > PSU–PEI(Ph)
5. The same tendency was found experimentally for block copolymers with comparable PSU segment molecular weight for a series of block copolymers [16]. The most significant difference between the theoretical and the experimental tendency was found for PSU–PET/PEI, on the one hand, and PSU–PEI (*t*-But) and PSU–PEI(Ph), on the other hand, and is reflected correctly by the experimentally obtained χ.

Conclusion

In this work, solubility parameters of aromatic PEI and PSU were determined by means of two methods: first, the calculation of δ by using group contributions given in increment tables and, second, experimentally by using viscometric measurements. It has to be concluded that calculated and experimentally determined solubility parameters, and, consequently, χ interaction parameters for block copolymers (A–B)$_n$ consisting of PSU and the aromatic PEI differ widely. The viscometric method gave only relative values for δ because solvent mixtures with different composition instead of a wide range of chemically different solvents had to be used owing to the restricted solubility of the aromatic polymers examined. Nevertheless, the relative values illustrated principal relationships between the polymers.

The theoretical Flory–Huggins interaction parameters calculated from solubility parameters originating from increment tables differ by at least 1 order of magnitude from the experimental ones. Moreover, the experimentally found χ are much lower than the calculated ones. However, the data sets allow the establishment of a general order of phase separation in the block copolymers investigated almost independently of the method of obtaining the solubility parameters (i.e., from the increment table used). The tendency of phase separation obtained correlates with the tendency found by investigation of the respective block copolymers and the measurements are therefore very useful to understand the phase separation of block copolymers. These results will be compared in future with δ and χ parameters determined by *pVT* measurements (work in progress) to give a further correlation between calculated and experimental values of δ and χ.

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Appendix

Calculation of solubility parameters by group increments for PEI(*t*-But) as an example

1. According to Hoy, Small, Van Krevelen [15]

PEI(*t*-But)	Number[a]	F_i Small	F_i Hoy	F_i van Krevelen	Calculation of V_m	Number[a]	V_i (cm^3/mol)
p-Phenylene	3	1,346	1,442.2	1,377	*p*-Phenylene	2	65.5
> COO	2	634	668.2	512	–COO–	1	23
> C = O	1	563	538.1	685	–O–	1	8
–CH_3	3	438	303.4	420			
> C <	1	−190	65.5	0	*t*-But	1	65.28
–CO–NH–	1	1,228	906.4	1,228	Imide	1	130
ΣF_i		8,221	7,952.2	8,328			
δ $(J/cm^3)^{1/2}$		23.01	22.26	23.31	ΣV_i (cm^3/mol)		357.28

The superscript a denotes the number of structural units

2. According to Hansen [15, 20]

PEI(*t*-But)	Number[a]	$F_{d,i}$ ($MPa^{1/2}$/mol)	$F_{p,i}$ ($MPa^{1/2}$/mol)	$E_{h,i}$ (J/mol)	Calculation of V_m	Number[a]	V_i (cm^3/mol)
p-Phenylene	3	1,270	110	0	*p*-Phenylene	2	65.5
> C = O	2	290	770	2,000	–COO–	1	23
> COO	2	390	490	7,000	–O–	1	8
–CH_3	3	420	0	0			
> C <	1	−70	0	0	*t*-But	1	65.28
> N-	1	20	800	5,000	Imide	1	130
ΣF_i		6,380	1,530.46	23,000			
δ $(J/cm^3)^{1/2}$		$\delta_d = 17.86$	$\delta_p = 4.28$	$\delta_h = 8.02$	ΣV_i (cm^3/mol)		357.28

The superscript a denotes the number of structural units

References

1. Flory PJ (1953) Principles of polymer chemistry. Cornell University Press, Ithaca, NY
2. Bates FS, Fredrickson GH (1999) Phys Today 2:32
3. Bates FS, Fredrickson GH (1990) Annu Rev Phys Chem 41:525
4. Flory PJ (1942) J Chem Phys 10:51
5. Mori K, Tanaka H, Hasegawa H, Hashimoto T (1989) 30:1389
6. Mangaraj D, Bhatnagar SK, Rath SB (1963) 67:75
7. Clarke CJ, Eisenberg A, La Scala J, Rafailovich MH, Sokolov J, Li Z, Qu S, Nguyen D, Schwarz SA, Strzhemechny Y, Sauer BB (1997) Macromolecules 30:4184
8. de Gennes P-G (1979) Scaling concepts in polymer physics. Cornell University Press, Ithaca, NY
9. Leibler L (1980) Macromolecules 13:1602
10. Hildebrand JH, Scott, RL (1950) The solubility of nonelectrolytes, 3rd edn, Van Nostrand-Reinhold, Princeton, NJ
11. Maier RD, Suhm J, Kressler J, Mülhaupt R (1998) Polym Bull 40:337
12. Deslandes N, Bellenger V, Jaffiol F, Verdu J (1998) J Appl Polym Sci 69:2663
13. Mangaraj D (1963) Makromol Chem 65:29
14. Mangaraj D, Bhatnagar SK, Rath SB (1963) Makromol Chem 67:75
15. Van Krevelen, DW (1990) Properties of polymers, their correlation with chemical structure; their numerical estimation and prediction from additive group contributions. Elsevier, Amsterdam
16. Pospiech D, Häußler L, Eckstein K, Komber H, Voigt D, Jehnichen D, Friedel P, Gottwald A, Kollig W, Kricheldorf HR (2001) High Perform Polym 13:275
17. Pospiech D, Häußler L, Voit B, Böhme F, Kricheldorf HR (1998) In: Hunt M, Long T (eds) Solvent-free polymerizations and processes: Minimization of conventional organic solvents. ACS symposium series 713, American Chemical Society, Washington, DC, pp 8
18. Small PA (1953) J Appl Chem 3:71
19. Hoy KL (1970) J Paint Technol 42:76
20. Hansen CM (2000) Hansen solubility parameters, a user's handbook. CRC, Boca Raton, FL
21. Barton AFM (1983) CRC handbook of solubility parameters and other cohesion parameters. CRC, Boca Raton, FL
22. Burke J (1984) AIC book and paper group annual
23. Merck Eurolab GmbH (2001) Der Laborkatalog Merck, Chemikalien und Reagenzien. Merck Eurolab, Darmstadt