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Solution properties of amorphous co- and terpolymers of styrene as examined by inverse gas chromatography

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Abstract

Inverse gas chromatography was used for determination of thermodynamic functions of solution of C_7–C_{10} *n*-alkanes, *n*-butanol, di-*n*-butyl ether and 1,4-dioxane in amorphous polystyrene and its copolymers [styrene–nonyl methacrylate (4:1), styrene–maleic anhydride–methacrylic acid (1:1:1) and styrene–nonyl methacrylate (4:1) with addition of 2% (w/w) *p*-phthalimidinoxymethacrylic acid] at infinite dilution and also the glass transition temperatures of these polymers. The influence of modification of the polymer structure on the glass transition temperature and on ability of the polymer functional groups to interact with non-polar, donor or acceptor sorbates was established.

1. Introduction

Inverse gas chromatography (GC) is extensively used in investigations of the thermodynamics of polymer solutions at infinite dilution [1–26]. A knowledge of the thermodynamic functions of solution of test organic compounds in polymers [12–25], glass transition temperatures of amorphous polymers [1–11] and their dependence on the molecular structure of sorbates gives an insight into the physico-chemical properties of new polymers.

In this work, inverse GC was used for the determination of thermodynamic functions of solution at infinite dilution and the glass transition temperatures for the following amorphous polymers: polystyrene (PS), styrene–nonyl methacrylate (4:1) (SNM), styrene–maleic anhydride–methacrylic acid (1:1:1) (SMAM) and styrene–nonyl methacrylate (4:1) with 2% (w/w) *p*-phthalimidinoxymethacrylic acid (SNMP). These copolymers are widely used in, e.g., the manufacture of photoresists.

The aim of this work was to determine the influence of modification of the polymer structure on the glass transition temperature and on the ability of copolymer functional groups to interact with non-polar, donor or acceptor molecules.

2. Experimental

2.1. Materials

Polystyrene was synthesized by radical poly-

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merization of styrene with benzoyl peroxide as initiator in the ethyl acetate solution at 84°C for 10 h. This polymer was purified by precipitation from acetone solution into methanol. The molecular mass is 14 500.

The copolymer of styrene with nonyl methacrylate was synthesized by the radical polymerization of mixture of styrene and nonyl methacrylate in a 4:1 ratio in the presence of benzoyl peroxide in ethyl acetate solution at 84°C for 10 h. Purification was performed by precipitating the copolymer obtained into 2-propanol with addition of 10% (w/w) water. The molecular mass is 29 000.

The terpolymer styrene–nonyl methacrylate (4:1) plus 2% (w/w) *p*-phthalimidinoxymethacrylic acid was synthesized by radical polymerization of a mixture of these reagents at 80°C for 10 h. Purification was performed by precipitating the copolymer into 2-propanol followed by drying under vacuum at 50°C. The molecular mass is 8100.

The terpolymer styrene–maleic anhydride–methacrylic acid (1:1:1) was synthesized by addition of 0.15 *M* styrene to 400 ml of a toluene solution of 0.15 M maleic anhydride, 0.15 M metacrylic acid and dinitroazobutyrate as polymerization initiator [2% (w/w) of monomers mixture], followed by heating and stirring at 80°C for 10 h. The molecular mass is 28 000.

The composition of the co- and terpolymers was confirmed from their ^{1}H NMR spectra in perdeuterated dimethyl sulfoxide solvent (Bruker WP-100 SU high-resolution NMR spectrometer). The molecular masses of the polymers were determined by viscosimetry and calculated from the Mark–Houwink equation. We used benzene as the solvent for PS at 283 K and acetone for SNM and SNMP and ethyl acetate for SMAM at 303 K. The molecular volumes of the polymers were calculated on the basis of their density from dilatometric data above their glass transition temperature.

2.2. IGC experiments

The test compounds used were non-polar *n*-heptane, *n*-octane, *n*-nonane and *n*-decane, acceptor *n*-butanol (BuOH) and donor di-*n*-butyl ether (DBE) and 1,4-dioxane (DO). All the compounds were of chromatographic or analytical-reagent grade and were used as received.

Polymers were deposited on Chromosorb W AW DMCS (80–100 mesh) from a chloroform or acetone solution by continuous stirring and slow evaporation of the solvent. The coated support was dried under vacuum at 293 K to remove traces of solvent. The fillings were packed into a stainless-steel column (1 m × 4 mm I.D.). The column loading was 10% (w/w) for SMAM and 20% (w/w) for the other polymers.

GC measurements were carried out with the use of an LHM-80 modification 6 gas chromatograph equipped with a katharometer as detector. The column temperature was controlled to ±0.2 K over the measured temperature range. Helium was used as the carrier gas. Air, as a non-interacting marker, was used to measure the dead volume of the column. Injection of the test sorbates was repeated at least three times. The pressures at the inlet and outlet of the column were used to compute corrected retention volumes by the usual procedures. The flow-rate was measured at the end of the column with a bubble flow meter and its value was maintained at 15 ml/min. The molecular probes were injected manually with a 1-μl Hamilton syringe. The volume of liquid probe injected was 0.1–0.3 μl. The columns were conditioned at 150–200°C for 12 h under helium before the measurements.

The net retention volume was calculated with the following equation [2]:

$$V_N = F_{corr} J (t_R - t_0) \quad (1)$$

where

$$J = \frac{3}{2}\left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right]$$

and

$$F_{corr} = F_{meas} T (1 - P_{H_2O}/P_o)/T_{room} \quad (2)$$

P_{H_2O} is the water-saturated vapour pressure at the temperature of the chromatographic column T (K), T_{room} is room temperature (K), P_i is the inlet pressure of the carrier gas (atm), P_o is the

outlet pressure of the carrier gas (atm), t_0 is the retention time of non-sorbed gas (air) (s), t_R is the retention time of the probe at temperature T (s), F_{meas} is the flow-rate of the carrier gas measured at room temperature (cm^3/s) and J is the James–Martin correction factor for gas compressibility.

The specific retention volume, i.e., the net retention volume of a probe at column temperature T, per gram of polymer, adjusted to a standard state of 273.13 K, was calculated from the well known equation [2]

$$V_g^\circ = V_N \times 273.15/wT \quad (3)$$

The first step in our experiments was to determine the glass transition temperature of the polymers (T_g) using retention diagrams. Further measurements and calculations of bulk properties of polymers and their solutions were carried out above these T_g values.

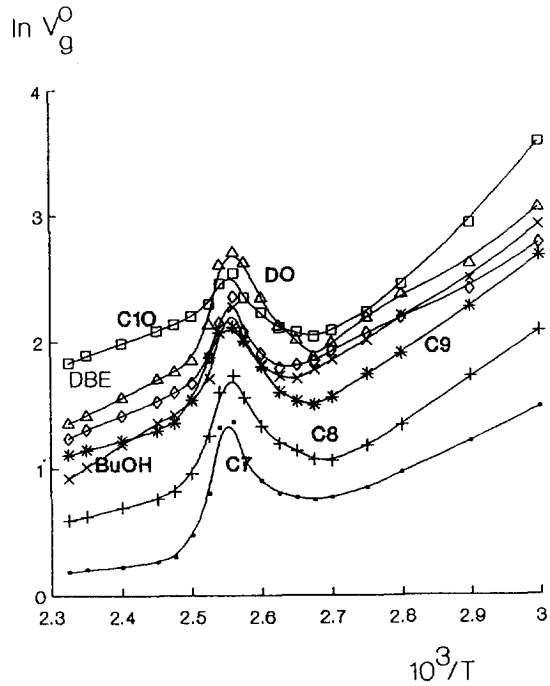

Fig. 1. Relationships $\ln V_g^\circ$ vs. $1/T$ (retention diagrams) for test compounds on styrene–nonyl methacrylate (4:1) copolymer.

3. Results and discussion

The relationships $\ln V_g^\circ$ vs. $1/T$ (retention diagrams) for the test compounds are presented in Fig. 1. Similar relationships were obtained for all polymers studied.

The T_g value is located at the maximum point of the plot $\ln V_g^\circ$ vs. $1/T$. It is well established that sigmoidal-type retention diagrams are related to a transition from surface to bulk retention mechanism in the vicinity of T_g in polymers [1–11]. The values of the apparent glass transition temperatures determined by using different test molecules are presented in Table 1. Thus, inverse GC allows the determination of apparent glass transition temperatures for the copolymers studied. The observed dependence of T_g on the structure of the test molecules in the case of SNM and SMAM copolymers is due to the fact that their diffusion coefficient is a strong function of the chemical potentials of the diffusant and polymer. Hence it is obvious that the introduction of maleic anhydride into polystyrene copolymer, in the case of SMAM, causes a significant increase in its glass transition temperature in comparison with the other polymers studied.

Flory–Huggins parameters characterizing the interaction of a solute with the polymer at infinite dilution were determined from the following expression [2]:

Table 1
Glass transition temperatures (K) for the polymers studied, determined with the use of different test compounds

Test solute	Polymer			
	PS	SNM	SNMP	SMAM
n-Heptane	392	333	331	504
n-Octane	392	337	332	506
n-Nonane	391	341	332	508
n-Decane	391	341	–	510
n-Butanol	391	340	332	508
Di-*n*-butyl ether	391	343	332	513
1,4-Dioxane	391	337	331	509

$$\kappa_{12}^{\infty} = \ln\left(\frac{273.15R}{P_1^{\circ}V_g M_1}\right) - \frac{P_1^{\circ}}{RT}(B_{11} - V_1^{\circ}) + \ln\left(\frac{\rho_1}{\rho_2}\right) - \left(1 - \frac{V_1^{\circ}}{V_2^{\circ}}\right) \quad (4)$$

where M_1, P_1°, B_{11}, V_1°, ρ_1 and V_g° are the molecular mass, saturated vapour pressure, second virial coefficient, molar volume and specific retention volume of the solute, respectively, ρ_2 and V_2° are the density and molar volume of the stationary phase, T is the column temperature and R is the gas constant. The P_1 value was calculated from Antoine's equation [27]. The B_{11} values for polar test molecules were calculated from the following equations [27]:

$$B_{11} = (RT_c/P_c)(g_0 + \omega g_1 + \omega_p g_2) \quad (5)$$

where

$$g_0 0.1145 - 0.330/T_r - 0.1385/T_r^2 - 0.0121/T_r^3$$

$$g_1 = 0.073 + 0.46/T_r - 0.50/T_r^2 - 0.097/T_r^3 - 0.0073/T_r^8$$

$$g_2 = 0.1042 - 0.2717/T_r + 0.2388/T_r^2 - 0.0716/T_r^3 + 0.0001502/T_r^8$$

$$T_r = T/T_c$$

and the acentric factor (ω) was calculated from [27]

$$\omega = T_b^{1.72}/M_1 - 263 \quad (6)$$

where T_c and T_b are the critical and boiling temperatures of the test solute, respectively, and P_c is the critical pressure. If ω_{calc} was lower than 0, then ω was rounded up to zero.

The solubility parameter of a test molecule was determined from the following equation [1,2]:

$$\delta_1 = \left(\frac{H_v - RT}{V_1}\right)^{1/2} \quad (7)$$

The solubility parameter δ_2 for the polymers examined was calculated from the slope of the linear relationship for a series of test solutes having different δ_1 values:

$$\frac{\delta_1^2}{RT} - \frac{\kappa_{12}^{\infty}}{V_1} = \frac{2\delta_2}{RT}\cdot\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\kappa_s^{\infty}}{V_1}\right) \quad (8)$$

where κ_{12}^{∞} is the Flory–Huggins interaction parameter [1].

The solubility parameter of a polymer may be also calculated from the partial molar free energy of mixing at infinite dilution (above the glass transition temperature of the polymer). The partial molar free energy of a probe (G_1^E) was determined from the mass fraction activity coefficient (a_1/w_1) at infinite dilution [2]:

$$\ln\left(\frac{a_1}{w_1}\right) = \ln\left(\frac{273.15R}{P_1^{\circ}V_g M_1}\right) - \frac{P_1^{\circ}}{RT}(B_{11} - V_1^{\circ}) - 1 \quad (9)$$

where M_1 is the molecular mass of the solute.

The relationships between the G_1^E, a_1/w_1 and δ values at infinite dilution are [1]

$$G_1^E = RT\ln(a_1/w_1) \quad (10)$$

$$G_1^E = V_1(\delta_1 - \delta_2)^2 \quad (11)$$

Plotting $\delta_1^2 - G_1^E/V_1$ value versus δ_1 gives a straight line with a slope equal to $2\delta_2$ and intercept $-\delta_1^2$.

A high value of the Flory–Huggins interaction parameter denotes a poor solvent used for the polymer examined, whereas a low value reflects a good solubility capacity. The κ_{12}^{∞} values for polymer–solute systems studies are presented in Table 2. The solubility parameters of polymers calculated from Eqs. 8 and 11 are compared in Table 3. A polymer and solute having equal solubility parameters should be mutually soluble owing to the negative entropy factor. As the difference between δ_{solute} and $\delta_{polymer}$ increases, the tendency towards dissolution decreases. This is in accordance with the general rule that chemical and structural similarity favours solubility. The high values of κ_{12}^{∞} for the solutes in Table 2 indicate that the compounds studied are poor solvents for polystyrene. The negative κ_{12}^{∞} values found for the SMAM–*n*-alkane and SNMP–dioxane systems indicate good mutual solubility of the component. The results presented also indicate that these solute–polymer

Table 2
Specific retention volumes (V_g°), excess free energies of solution at infinite dilution (G_1^E) and Flory–Huggins residual free energy of interaction between solute and polymer (κ_{12}^∞) at 526.6 K for test compounds in the polymer solutions

Polymer	Test solute	V_g° (ml/g)	G_1^E (kJ/mol)	κ_{12}^∞
PS	*n*-Heptane	0.9	9.3	1.6
	n-Octane	1.1	9.8	1.7
	n-Nonane	1.6	9.6	1.7
	n-Decane	2.7	8.6	1.5
	n-Butanol	0.8	11.0	2.1
	Di-*n*-butyl ether	1.6	8.6	1.5
	1,4-Dioxane	1.7	6.1	1.2
SMAM	*n*-Heptane	4.1	2.6	0.0
	n-Octane	7.5	1.5	−0.2
	n-Nonane	12.4	0.6	−0.4
	n-Decane	18.4	0.3	−0.4
	n-Butanol	4.2	3.8	0.0
	Di-*n*-butyl ether	7.4	2.0	0.0
	1,4-Dioxane	4.9	1.3	0.2
SNM	*n*-Heptane	3.2	3.7	0.3
	n-Octane	4.5	3.8	0.3
	n-Butanol	1.5	8.4	1.5
	Di-*n*-butyl ether	1.6	8.5	1.5
	1,4-Dioxane	1.9	5.4	1.1
SNMP	*n*-Heptane	1.8	6.3	0.9
	n-Octane	2.9	5.7	0.8
	n-Nonane	4.9	4.8	0.6
	n-Butanol	1.8	7.6	1.4
	Di-*n*-butyl ether	1.8	8.4	1.5
	1,4-Dioxane	7.4	−0.5	−0.2

interaction parameters decrease with increase in temperature (Fig. 2a–d). The values of the Flory–Huggins interaction parameter vary from 2.2 to −0.4. In order to attain good polymer–solute miscibility, κ_{12}^∞ must be lower than the critical value of 0.5. It is apparent from comparison of the κ_{12}^∞ values that *n*-butanol, and in some cases di-*n*-butyl ether, are slightly less soluble in the polymers studied than 1,4-dioxane and *n*-alkanes.

Table 3
Hildebrand–Scatchard solubility parameters (at 526.6 K) for the polymers studied

Polymer	Solubility parameter [10^3 (J/m)$^{1/2}$]	
	δ_2 [a]	δ_2 [b]
SNM	13.1	13.2
PS	13.5	13.4
SMAM	15.2	15.1
SNMP	16.3	16.3

[a] Calculated from Eq. 8.
[b] Calculated from Eq. 11.

We also calculated thermodynamic functions of solution of the test compounds in the polymers at infinite dilution and the excess thermodynamic functions of the solutions on the basis of the dependences of logarithms of specific retention volumes and activity coefficients on the inverse temperature [2]. The enthalpy (H_1^S) and entropy (S_1^S) values of test compounds solutions in the polymers at infinite dilution are presented in Table 4.

Linear relationships were obtained between H_1^S and the number of carbon atoms in the homologous alkane series used as solutes. The contribution of the methylene group to the H_1^S values was attributed to Van der Waals dispersive forces between the alkane molecule and the polymer.

The enthalpy and entropy of mixing of test solutes with polymers at infinite dilution are presented in Table 5. There is no significant variation of H_1^E for the *n*-alkane series in PS solution. In the case of other polymer solutions the H_1^E values decrease with increase in carbon number in the *n*-alkane molecule.

The molar solution enthalpy at infinite dilution (H_1^S) is the most representative parameter for the interaction energies of test molecules with polymer groups in the solutions. It represents the combination of contributions of non-specific and specific interactions [6]:

$$-H_1^S = H_{1(nsp)}^S + H_{1(sp)}^S - A \quad (12)$$

where A is the work of hole formation in the volume of polymer. This value varies proportionally with the molar volume of the test solute (V_1). The contribution of non-specific interactions (mainly dispersive interactions) is proportional to the solute molar deformation polarization (RN), and the contribution of specific interactions is proportional to the electron-donor and

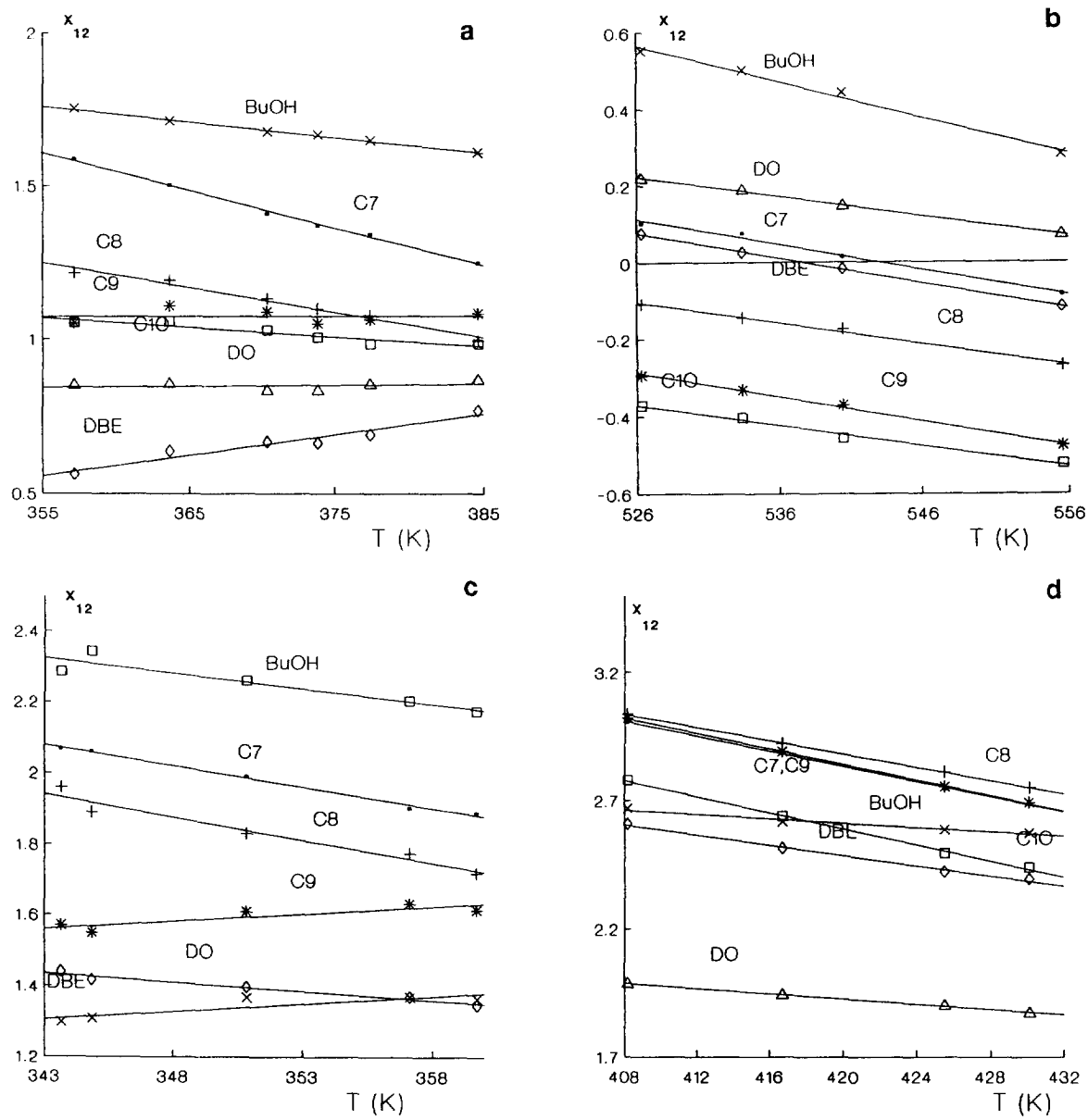

Fig. 2. Dependence of Flory–Huggins interaction parameter on temperature for the test solutes and polymers examined: (a) SNM; (b) SNAM; (c) SNMP; (d) PS.

electron-acceptor abilities of the molecule, i.e., its donor (DN) and acceptor (AN) numbers. Rewriting Eq. 12 in these terms, we obtain

$$-H_1^S = (\mathrm{RN})_{ps}RN + (AN)_{ps}DN + (DN)_{ps}AN + V_{ps}V_1 + S_S \quad (13)$$

where $(RN)_{ps}$, $(AN)_{ps}$ and $(DN)_{ps}$ are the parameters reflecting the ability of the polymer to interact with non-polar, electron-donor and electron-acceptor solutes, respectively, V_{ps} accounts for the cohesive ability of the polymer and S_S is a constant for the solutes studied. The coefficients

Table 4
Enthalpy (H_1^S, kJ/mol) and entropy S_1^S, J mol·K) of test compounds in polymer solution at infinite dilution

Test solute	Polymer							
	PS		SNMP		SMAM		SNM	
	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S
n-Heptane	5	9	19	31	15	15	16	20
n-Octane	11	21	27	44	17	14	25	37
n-Nonane	13	19	46	91	15	7	40	69
n-Decane	16	21	–	–	18	9	41	67
n-Butanol	29	59	35	66	11	8	38	71
Di-*n*-butyl ether	19	33	44	87	15	11	46	94
1,4-Dioxane	23	41	30	51	15	14	34	59

Table 5
Enthalpy (H_1^E, kJ/mol) and entropy (S_1^E, J mol·K) of test compounds and polymer mixing at infinite dilution

Test solute	Polymer							
	PS		SNMP		SMAM		SNM	
	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S	$-H_1^S$	S_1^S
n-Heptane	22	24	12	14	16	25	14	22
n-Octane	19	17	11	9	13	22	9	12
n-Nonane	22	25	−4	−29	15	28	0	−13
n-Decane	23	29	–	–	13	24	4	−2
n-Butanol	6	−10	12	13	23	36	5	−1
Di-*n*-butyl ether	15	11	−5	−27	16	26	−8	−29
1,4-Dioxane	8	1	5	3	13	21	0	−9

of Eq. 13 calculated for the polymers studied are presented in Table 6. The polarization contribution $(RN)_{ps}$ decrease in the order SNMP > SNM > PS > SMAM.

Table 6
Parameters reflecting the ability of polymers to interact with non-polar (RN_{ps}), electron-donor (AN_{ps}) and electron-acceptor (DN_{ps}) solutes, parameter accounting for cohesive ability of polymer (V_{ps}) and constant for solutes studied (S_{ps}), calculated from Eq. 13

Polymer	RN_{ps}	AN_{ps}	DN_{ps}	S_{ps}	V_{ps}
PS	0.08	0.78	0.69	−20.0	−0.005
SNM	0.19	1.45	0.60	−48.3	−0.005
SMAM	0.03	0.06	0.07	6.3	−0.001
SNMP	0.30	1.31	1.33	−88.0	−0.011

SNMP exhibits the highest donor ability $(DN)_{ps}$, whereas the highest acceptor ability $(AN)_{ps}$ was found for SNM. Thus, the introduction of *p*-phthalimidinoxymethacrylic acid into the polystyrene matrix causes a dramatic increase in the polarization and electron-donor ability of the terpolymer functional groups.

4. Conclusions

Inverse GC was used for the determination of the thermodynamic functions of C_7–C_{10} *n*-alkanes, *n*-butanol, di-*n*-butyl ether and 1,4-dioxane in solutions of polystyrene and its co- and terpolymers: styrene–nonyl methacrylate (4:1), styrene–maleic anhydride–methacrylic acid (1:1:1) and styrene–nonyl methacrylate (4:1)

with 2% (w/w) of *p*-phthalimidinoxymethacrylic acid at infinite dilution and also the glass transition temperatures of these amorphous polymers. The dependence of the apparent glass transition temperature on the structure of the test molecules is due to the fact that their diffusion coefficients are a function of the chemical potentials of the diffusant and polymer. The introduction of maleic anhydride into polystyrene copolymer, in the case of SMAM, causes a large increase in its glass transition temperature in comparison with other polymers. Values of the Flory–Huggins interaction parameter for the polymer–solute systems studied range from 2.2 to −0.4. The influence of modification of the polymer structure on the glass transition temperature and on the ability of the polymer functional groups to interact with non-polar, donor or acceptor molecules of solutes was established. The introduction of 2% of *p*-phthalimidinoxymethacrylic acid into the polystyrene matrix causes a dramatic increase in the polarization and electron-donor ability of the terpolymer functional groups.

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References

[1] A. Voelkel, CRC Crit. Rev. Anal. Chem., 22 (1991) 411.
[2] J.R. Conder and C.L. Young, Physicochemical Measurements in Gas Chromatography, Wiley-Interscience, New York, 1979.
[3] J.E. Guillet and M. Galin, J. Polym. Sci., Polym. Lett. Ed., 11 (1973) 233.
[4] A. Lavoie and J.E. Guillet, Macromolecules, 2 (1969) 443.
[5] D.G. Gray and J.E. Guillet, Macromolecules, 7 (1974) 244.
[6] G.J. Courval and D.G. Gray, Macromolecules, 8 (1975) 328.
[7] G.J. Courval and D.G. Gray, Macromolecules, 8 (1975) 916.
[8] J.M. Braun and J.E. Guillet, Macromolecules, 9 (1976) 340.
[9] J.M. Braun and J.E. Guillet, Macromolecules, 9 (1976) 617.
[10] G.J. Courval and J.E. Guillet, Can. J. Chem., 54 (1976) 3496.
[11] C. Beldie, O. Auo, G. Borceanu and J.C. Poinescu, Eur. Polym. J., 21 (1985) 443.
[12] R.D. Newman and J.M. Prausnitz, J. Phys. Chem., 76 (1972) 1492.
[13] F.H. Covitz and J.W. King, J. Polym. Sci., Part A-1, 10 (1972) 689.
[14] L.J. Stiel and D.F. Harnish, AIChE J., 22 (1976) 117.
[15] Y. Jwai, M. Nagatuji and Y. Arai, J. Jpn. Pet. Inst., 23 (1980) 215.
[16] M.T. Ratzsch, G. Jlling and Ch. Wohlfatrth, Acta Polym., 33 (1982) 89.
[17] S. Gunduz and S. Dincer, Polymer, 21 (1980) 1041.
[18] P.J.T. Tait and A.M. Abushihada, Polymer, 18 (1977) 810.
[19] P.J.T. Tait and A.M. Abushihada, Macromolecules, 11 (1978) 918.
[20] M. Galin and M.S. Ruprecht, Polymer, 19 (1978) 506.
[21] O. Olabisi, Macromolecules, 8 (1975) 316.
[22] R.H. Schuster, H. Grater and H.J. Cautow, Macromolecules, 17 (1984) 619.
[23] L. Bonifaci and G.P. Ravanetti, J. Chromatogr., 641 (1993) 301.
[24] M. Castun, I. Kaya and E. Ozdemir, J. Macromol. Sci., Pure Appl. Chem., A30, Suppl. 5 (1993) 425.
[25] E. Ozdemir, Z. Ilter, M. Castun and S. Celik, J. Macromol. Sci., Pure Appl. Chem., A30, Suppl. 5 (1993) 391.
[26] J.I. Irrebarren, M. Iriarte and J.J. Iruin, J. Appl. Polym. Sci., 37 (1989) 3459.
[27] R.C. Reid, J.M. Prausnitz and T.K. Sherwood, The Properties of Gases and Liquids, McGraw-Hill, New York, 1977.