BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 18, pp. 3503–3510, 1995

0032-3861/95/$10.00+0.00

Surface properties of copolymers and terpolymers of styrene as studied by inverse gas chromatography

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(Received 15 November 1994)

Inverse gas chromatography has been used for the determination of the glass transition temperatures of amorphous polymers and the thermodynamic functions for adsorption of n-alkanes (C_7 to C_{10}), n-butanol, di-n-butyl ether and 1,4-dioxane in the Henry region onto the surface of polystyrene, styrene–nonyl methacrylate (4:1) copolymer, and styrene–maleic anhydride–methacrylic acid (1:1:1) and styrene–nonyl methacrylate (4:1) with 2 wt% *p*-phthalimidinoxymethacrylic acid terpolymers. The data were compared with the thermodynamic functions of test solutes in polymer solution at infinite dilution. The influence of modification of polymer structure on the ability of polymer functional groups to interact with non-polar, donor or acceptor molecules of sorbates or solvents has been established.

(Keywords: inverse gas chromatography; glass transition temperature; adsorption)

INTRODUCTION

The study of the thermodynamic functions for adsorption of test compounds onto the surface of polymers and their dependence on the molecular structure of the adsorbate gives an insight into the physicomechanical and adhesive properties of new polymers. Several co- and terpolymers of polystyrene are widely used, for example, as materials for optical disc manufacturing. Their durability depends on the ability of the functional groups to interact with residual solvent molecules, etc. Inverse gas chromatography is extensively used in the investigation of adsorption thermodynamics on polymer surfaces in the Henry region[1,2]. In the present study this method was used for the determination of the thermodynamic functions for adsorption of test compounds onto polymer surfaces in the Henry region and the thermodynamic functions of their solution at infinite dilution as well as of glass transition temperatures. The following amorphous polymers have been studied: polystyrene (PS), styrene–nonyl methacrylate (4:1) (SNM) copolymer, and styrene–maleic anhydride–methacrylic acid (1:1:1) (SMAM) and styrene–nonyl methacrylate (4:1) with 2% (w/w) *p*-phthalimidinoxymethacrylic acid (SNMP) terpolymers.

The aim of this work was to determine the influence of polymer structural modifications on the glass transition temperature and on the ability of polymer functional groups to interact with non-polar, donor or acceptor molecules of sorbates on the surface and in the bulk.

EXPERIMENTAL

Synthesis of polymers

Polystyrene was synthesized by radical polymerization of styrene with benzoyl peroxide as initiator in ethyl acetate solution at 84°C for 10 h. This polymer was purified by precipitation from acetone solution into methanol. The molecular weight was determined by viscosimetry and is equal to 14500.

The copolymer of styrene with nonyl methacrylate was synthesized by radical polymerization of a mixture of styrene and nonyl methacrylate in a mole ratio of 4:1 in the presence of benzoyl peroxide in ethyl acetate solution at 84°C for 10 h. Purification was performed by precipitating the obtained copolymer into propan-2-ol with addition of 10% (w/w) water. The molecular weight is 29000.

The terpolymer of styrene–nonyl methacrylate in 4:1 mole ratio with 2% (w/w) *p*-phthalimidinoxymethacrylic acid was synthesized by radical polymerization of a mixture of these reactants at 80°C for 10 h. Purification was performed by precipitating the copolymer into propan-2-ol and drying *in vacuo* at 50°C. The molecular weight of this polymer is 8100.

The styrene–maleic anhydride–methacrylic acid terpolymer in 1:1:1 mole ratio was synthesized by the addition of a mixture of 0.15 M styrene to 400 ml toluene

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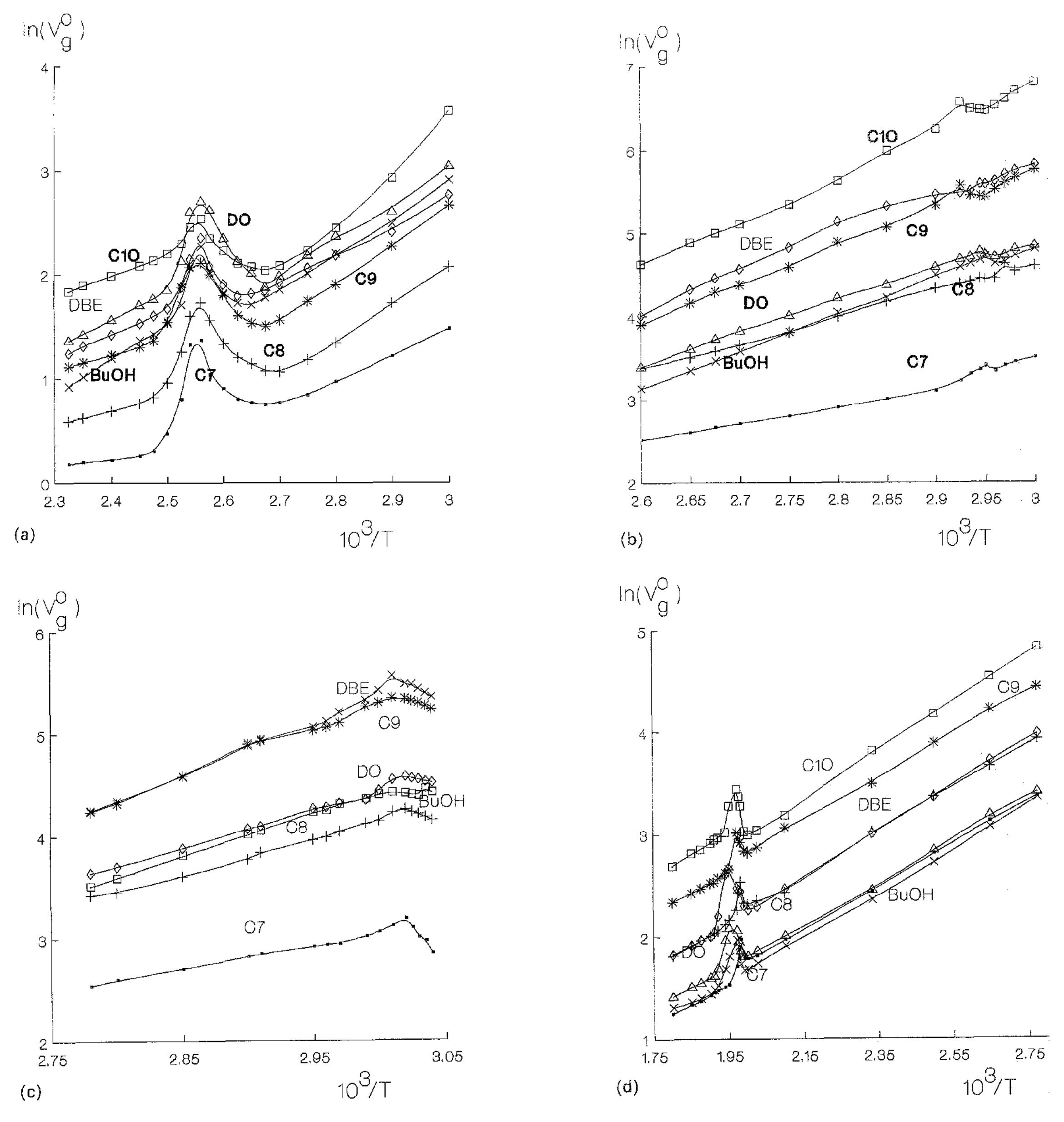

Figure 1 Dependences of logarithm of specific retention volume for test sorbates in polymers on the inverse temperature: (a) polystyrene; (b) styrene–nonyl methacrylate (4 : 1); (c) styrene–nonyl methacrylate (4 : 1) + 2% (w/w) *p*-phthalimidinoxymethacrylic acid; (d) styrene–maleic anhydride–methacrylic acid (1 : 1 : 1)

Table 1 Glass transition temperatures (K) of polymers as determined with use of different test compounds

	Polymer			
Compound	PS	SNM	SNMP	SMAM
n-Heptane	392.2	333.3	331.1	503.8
n-Octane	392.2	336.7	332.2	506.3
n-Nonane	391.4	341.3	331.7	507.6
n-Decane	391.4	341.4	–	510.2
n-Butyl alcohol	391.4	340.1	331.7	507.6
Di-n-butyl ether	391.4	342.5	332.0	512.8
1,4-Dioxane	391.4	337.3	331.0	508.9

Table 2 Enthalpy H_1^S (kJ mol^{-1}) and entropy S_1^S (J mol^{-1} K^{-1}) of test compounds in polymer solution at infinite dilution

	Polymer							
	PS		SNMP		SMAM		SNM	
Compound	$-H_1^S$	$-S_1^S$	$-H_1^S$	$-S_1^S$	$-H_1^S$	$-S_1^S$	$-H_1^S$	$-S_1^S$
n-Heptane	5.1	9	19.3	31	14.5	15	15.9	20
n-Octane	11.4	21	26.6	44	16.7	14	25.3	37
n-Nonane	12.5	19	45.6	91	14.9	7	39.6	69
n-Decane	16.3	21	–	–	18.1	9	40.9	67
n-Butyl alcohol	29.3	59	34.7	66	10.7	8	37.7	71
Di-n-butyl ether	19.1	33	44.3	87	15.1	11	45.6	94
1,4-Dioxane	22.8	41	29.9	51	14.8	14	33.8	59

solution of 0.15 M maleic anhydride, 0.15 M methacrylic acid and dinitroazobutyrate as initiator (2% of weight of monomer mixture), with subsequent heating and stirring at 80°C for 10 h. The molecular weight of this polymer is 28 000.

Test compounds

The following test compounds were used in this study as sorbates or solvents—*non-polar*: n-heptane (C_7), n-octane (C_8), n-nonane (C_9) and n-decane (C_{10}); *acceptor*: n-butanol (BuOH); and *donor*: di-n-butyl ether (DBE) and 1,4-dioxane (DO). All the compounds were chromato-quality or reagent-grade and were used without further purification.

Table 3 Enthalpy H_1^E (kJ mol^{-1}) and entropy S_1^E (J mol^{-1} K^{-1}) of test compounds and polymer mixing at infinite dilution

	Polymer							
	PS		SNMP		SMAM		SNM	
Compound	H_1^E	S_1^E	H_1^E	S_1^E	H_1^E	S_1^E	H_1^E	S_1^E
n-Heptane	21.6	24	12.2	14	16.0	25	14.0	22
n-Octane	19.0	17	9.8	9	13.3	22	9.3	12
n-Nonane	22.2	25	−4.1	−29	15.2	28	0.0	−13
n-Decane	22.8	29	–	–	12.8	24	3.6	−2
n-Butyl alcohol	6.2	−10	12.0	13	22.9	36	5.2	−1
Di-n-butyl ether	14.5	11	−4.5	−27	15.9	26	−7.5	−29
1,4-Dioxane	7.5	1	5.3	3	12.5	21	0.3	−9

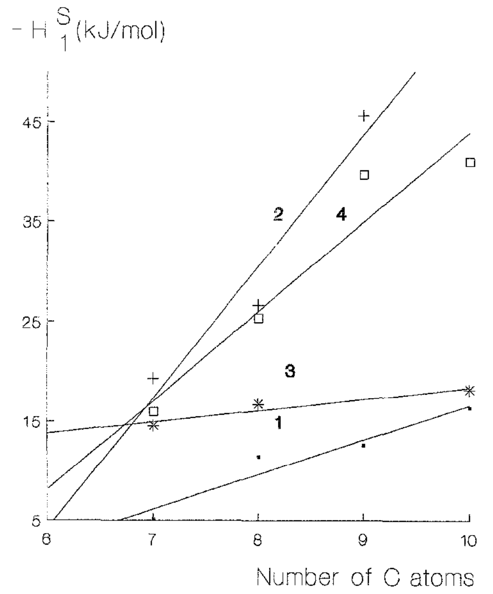

Figure 2 Dependences of heats of solution of n-alkanes in the PS (1), SNMP (2), SMAM (3) and SNM (4) polymers at infinite dilution on the alkane carbon number

Preparation of chromatographic columns

In each column, polymer was deposited onto Chromosorb W (AW-DMCS treated, 80/100 mesh) from a chloroform or acetone solution by continuous stirring and slow evaporation of the solvent. The coated support was dried *in vacuo* at 293 K in order to remove traces of solvent. Such filling was packed into a stainless-steel column (1 m long and 4 mm i.d.). The column loading was 10% (w/w) for SMAM and 20% for the other polymers.

Instrumentation

The gas chromatographic measurements were carried out with the use of an LHM-80 modification 6 (Russia) gas chromatograph equipped with a katharometer 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-interactive marker, was used to measure the dead volume of the column. The injection of the test sorbate 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. Flow rate was measured at the end of the column with a bubble flow meter and its value was maintained at 15 ml min^{-1}. The molecular probes were injected manually with a 1 μl Hamilton syringe. The volume of injected liquid probe was 0.1–0.3 μl. The columns were conditioned at temperatures above 150–200°C for 12 h under helium before use.

Primary data reduction

Net retention volume was computed from the following equation[2]:

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

where

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

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

Here, P_{H_2O} is the saturated vapour pressure of water at temperature T; T is the temperature of the chromatographic column; T_{room} is room temperature; P_i is the inlet pressure of the carrier gas; P_o is the outlet pressure of the carrier gas; t_0 is the retention time of the non-sorbed gas (air); t_R is the retention time of the probe at temperature T; F_{meas} is the flow rate of the carrier gas measured at room temperature; and J is the James–Martin correction factor for gas compressibility.

Specific retention volumes at temperature T were calculated as the ratio of the net retention volumes and the mass of the polymer in the chromatographic column[2]:

$$V_g = V_N/w \qquad (3)$$

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 as[2]:

$$V_g^\circ = V_N 273.13/(wT) \qquad (4)$$

The first step in the experiments was to determine the glass transition temperature of the polymers (T_g). Further measurements were then carried out:

(i) below T_g—adsorption in the Henry region and evaluation of the surface properties of the polymers;

(ii) above T_g—bulk properties of the polymers, determination of the solubility parameters and thermodynamic functions of the test compounds for transition from gas phase to polymer solution at infinite dilution.

RESULTS AND DISCUSSION

Glass transition temperatures

The obtained dependences of ln V_g° for the test compounds on the surface and in the bulk of the studied polymers *versus* the $1/T$ value (retention diagrams) are presented in *Figure 1*. The apparent glass transition temperature of an amorphous polymer can be determined using a retention diagram. The T_g value is located at the maximum of the dependence of ln V_g° vs. $1/T$. It is well established that sigmoidal-type retention diagrams are related to a transition from a surface to a bulk retention mechanism in the vicinity of the T_g of the polymer[3]. The values of apparent glass transition

Table 4 Partition adsorption coefficients (K_1^S), free adsorption energies (G_1^A) and their polar interaction components estimated from correlation of G_1^A with heat of evaporation ($G_{A,1}^{sp}$) or molar deformation polarization ($G_{A,2}^{sp}$) at 333.5 K on the surface of polymers

Compound	K_1^S (ml m^{-2})	G_1^S (kJ mol^{-1})	$G_{A,1}^{sp}$ (kJ mol^{-1})	$G_{A,2}^{sp}$ (kJ mol^{-1})
		PS		
n-Heptane	0.894	−15.50	−0.71	0.360
n-Octane	1.612	−17.14	−0.48	−0.015
n-Nonane	2.909	−18.77	−0.14	−0.410
n-Decane	7.155	−21.27	1.13	0.125
n-Butyl alcohol	3.698	−19.44	−2.68	10.259
Di-n-butyl ether	3.215	−19.05	−0.03	1.180
1,4-Dioxane	4.254	−19.83	1.20	10.299
		SNM		
n-Heptane	6.862	−21.15	−1.861	−0.335
n-Octane	20.614	−24.20	−0.813	−0.158
n-Nonane	65.758	−27.42	0.554	0.149
n-Decane	186.044	−30.30	1.690	0.227
n-Butyl alcohol	25.178	−24.76	−6.677	11.812
Di-n-butyl ether	69.824	−27.59	0.482	2.196
1,4-Dioxane	26.206	−24.87	−1.586	11.424
		SMAM		
n-Heptane	6.738	−21.10	−1.861	−0.335
n-Octane	20.242	−24.15	−0.815	−0.162
n-Nonane	64.570	−27.37	0.555	0.151
n-Decane	182.684	−30.25	1.894	0.234
n-Butyl alcohol	24.724	−24.71	−6.667	11.788
Di-n-butyl ether	68.563	−27.54	0.484	2.195
1,4-Dioxane	25.733	−24.82	−1.585	11.401
		SMNP		
n-Heptane	4.341	−19.88	0.071	0.028
n-Octane	12.784	−22.88	−0.149	−0.055
n-Nonane	40.374	−26.07	0.075	0.027
n-Butyl alcohol	16.580	−23.60	−9.707	12.857
Di-n-butyl ether	45.521	−26.40	0.029	2.368
1,4-Dioxane	17.256	−23.71	−1.621	12.435

temperatures determined by using the various 'probe' molecules are presented in *Table 1*. It can be seen that the T_g values of SNM and SMAM polymers depend on the size and polarity of the penetrating solute molecules. This dependence is due to the fact that their diffusion coefficient is a function of the chemical potentials of diffusant and polymer. Thus, the inverse gas chromatography method has enabled the determination of the apparent glass transition temperatures for the polymers studied.

Thermodynamic functions for solution of test compounds in the polymers at infinite dilution

Also, thermodynamic functions for solution of test compounds in the polymers at infinite dilution as well as excess thermodynamic functions of the solutions were calculated from the dependences of the logarithms of specific retention volumes and activity coefficients *versus* the inverse temperature[2]. The data are presented in *Tables 2* and *3*. The physicochemical parameters of test sorbates (vapour pressure, second virial coefficient, molar volume, etc.) required for computation of the functions were taken from ref. 4. Linear relationships were obtained between the heat of solution ($-H_1^S$) and the number of carbon atoms in the homologous alkane series used as solute probes (*Figure 2*). The contribution of the methylene group in this series to the H_1^S value was attributed to van der Waals dispersive forces between the alkane molecule and the polymer. As can be seen from *Table 3*, there is no significant variation of the excess enthalpy of mixing at infinite dilution with the n-alkane series in PS solution. With the other polymers this value decreased with increasing number of carbon atoms in the n-alkane molecule.

Free surface energy of polymers

In the case of adsorption of test compound from the gas phase onto the polymer surface, the partition coefficient was determined by the use of the following equation[2]:

$$K_1^S = V_N/(wS_p) \tag{5}$$

where S_p is the polymer specific adsorption area in the solid state, which approximately equals the specific adsorption area of the chromatographic solid support, and w is the weight of polymer in the chromatographic column.

In the case of the De Boer reference state for an adsorbed probe, the free adsorption energy may be calculated as follows[5]:

$$G_1^A = -RT \ln [V_N \times 2.99 \times 10^2/(S_p w)] \tag{6}$$

The dispersive component of the polymer free surface energy (γ_s^d) was determined by injection of n-alkane probes into the chromatographic column. The general equation is given by[5]:

$$RT \ln V_N = 2N_A(\gamma_s^d)^{1/2} a(\gamma_l^d)^{1/2} + K \tag{7}$$

where N_A is the Avogadro number, a is the surface area of the adsorbed test molecule, γ_l^d is the dispersive component of the free surface energy of the probe in the liquid state, and K is a constant depending on the chosen reference state, the temperature, the specific surface area and the weight of polymer in the column. The quantity $RT \ln V_N$ for n-alkanes varies linearly with their vapour pressure (P_l)[5]. Since $\ln P_l$ is connected with the heat of vaporization (H_v) by the well known relation:

$$\ln P_l = -H_v/RT + c \tag{8}$$

then

$$G_A = -a_1 H_v/RT + a_2 \tag{9}$$

Table 5 Dispersive components of free surface energy (γ_s^d) at 333.5 K and coefficients of correlation equations connecting free energies of adsorption and heat of evaporation (a_1 and a_2) of test compounds or molar deformation polarization (a_3 and a_4) and mean-square deviations of calculation on these equations (s_1 and s_2)

Polymer	γ_s^d (mJ m^{-2})	a_1	a_2 (kJ mol^{-1})	s_1	a_3	a_4 (kJ mol^{-1})	s_2
PS	9.80	0.518	−0.206	2.064	0.0436	0.0621	0.315
SNM	19.97	0.740	−0.426	7.266	0.0625	−0.1092	0.206
SMAM	19.90	0.738	−0.427	7.308	0.0624	−0.1120	0.216
SNMP	51.21	1.185	−17.717	0.033	0.0667	−3.1992	0.004

Table 6 Acceptor and donor components of free surface energy of polymers at 333.5 K from correlations of polar components of free adsorption energies of test compounds with their donor and acceptor numbers (equation (11))

Polymer	$(AN)_p$	$(DN)_p$
PS	0.237	0.219
SNM	0.294	0.227
SMAM	0.294	0.226
SNMP	0.219	0.248

Table 7 Enthalpy H_1^A (kJ mol^{-1}) and entropy S_1^A (J mol^{-1} K^{-1}) of test compounds adsorption on the polymer surface in the Henry region

	Polymer							
	PS		SNMP		SMAM		SNM	
Compound	$-H_1^A$	$-S_1^A$	$-H_1^A$	$-S_1^A$	$-H_1^A$	$-S_1^A$	$-H_1^A$	$-S_1^A$
n-Heptane	17.1	5	16.3	-11	13.8	-24	24.5	10
n-Octane	25.7	26	23.7	3	14.7	-27	18.6	-18
n-Nonane	27.4	26	42.7	49	14.0	-33	41.3	42
n-Decane	38.4	52	–	–	16.6	-29	50.8	61
n-Butyl alcohol	25.8	19	31.8	24	14.3	-23	42.5	53
Di-n-butyl ether	19.6	2	41.4	45	15.1	-26	29.9	7
1,4-Dioxane	25.2	16	26.6	9	14.1	-24	28.0	10

[a] The H_1^A and S_1^A values are calculated from data obtained in the solution region

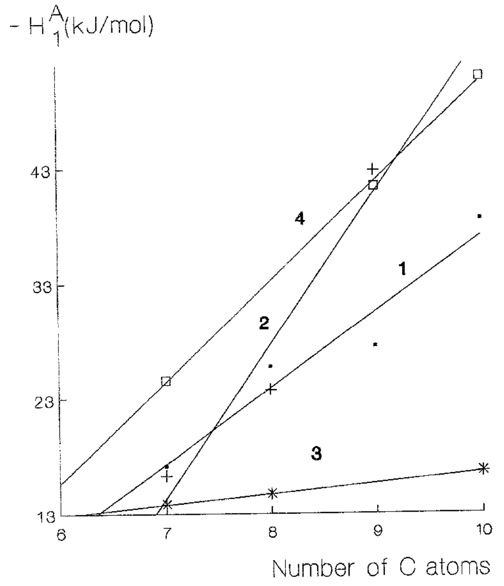

Figure 3 Dependences of heats of adsorption of n-alkanes on the surface of PS (1), SNMP (2), SMAM (3) and SNM (4) in the Henry region *versus* alkane carbon number

Here c is a constant to be determined by empirical fitting knowing P_1 and H_v for different liquids, while a_1 and a_2 are given by:

$$a_1 = 3RT(\gamma_s^d)^{1/2}/[\chi(\gamma_0)^{1/2}] \qquad (10)$$

$$a_2 = K[\chi/(3\mu) + c - 1] \qquad (11)$$

The parameter χ describes the number of 'bonds' that a molecule exchanges with its neighbours ($\chi = 3.5$ for n-alkanes), γ_0 is the surface energy of a non-polar solid that is homologous to the series of n-alkanes, e.g. polyethylene ($\gamma_0 = 36.5$ mJ m^{-2}), and μ is a coefficient describing the packing density of molecules of liquids adsorbed on the reference solid surface ($\mu = 0.6$ for n-alkanes on polyethylene)[5].

Specific interaction contribution in free surface energy

If polar probes are injected into the column, a specific interaction (G_A^{sp}) is established between these probes and the solid polymer surface in addition to the dispersive interaction (G_A^d) previously analysed. Since the variation of free energy is a consequence of both contributions, G_1^A is given by[5,6]:

$$-G_1^A = G_A^d + G_A^{sp} \qquad (12)$$

The experimental values of G_A for polar probes generally lie well above the straight line of $-G_A$ *versus* H_v corresponding to the series of n-alkanes. The difference of ordinates between the point corresponding to the polar probe and this straight line can therefore be considered equal to G_A^{sp}. The G_A^{sp} value depends on the acid–base behaviour of the polar sorbates, determined by their donor (DN) and acceptor (AN) numbers. The specific energy of adsorption G_A^{sp} can be easily determined as:

$$G_A^{sp} = G_p^A - a_1(H_v)_p - a_2 \qquad (13)$$

Therefore, the G_A^{sp} values of polar probes can be written as:

$$G_A^{sp} = (AN)_p(DN)_s + (DN)_p(AN)_s \qquad (14)$$

Another approach to the determination of the specific interaction contribution in free surface energy was proposed recently[7]. As the energy of dispersive interaction (U_A^d) determines the γ_s^d value (from measurements for the n-alkane series), the equation for the dispersive contribution to G_1^A is given by:

$$G_A^d = U_A^d = a_3RN + a_4 \qquad (15)$$

where the molar deformation polarization RN is calculated as:

$$RN = 10(n_R^2 - 1)M_1/[(n_R^2 + 2)\rho_1] \qquad (16)$$

The difference of ordinates between the point on the

Table 8 Polarization $(RN)_p$, donor $(DN)_p$ and acceptor $(AN)_p$ contributions of polymers to partial molar enthalpy of adsorption in the Henry region (a) and to the molar enthalpy of solution at infinite dilution (s) from equations (17) and (18)

	Adsorption				Solution				
Polymer	$(RN)_{pa}$	$(AN)_{pa}$	$(DN)_{pa}$	S_a	$(RN)_{ps}$	$(AN)_{ps}$	$(DN)_{ps}$	S_s	V_{ps}
PS	0.143	0.187	1.072	-31.97	0.076	0.776	0.686	-19.99	-0.0046
SNM	0.191	0.082	1.852	-41.98	0.188	1.448	0.596	-48.32	-0.0064
SMAM	0.020	0.053	0.089	6.99	0.025	0.056	0.066	6.28	-0.0014
SNMP	0.273	1.163	1.211	-79.72	0.303	1.312	1.328	-88.00	-0.0112

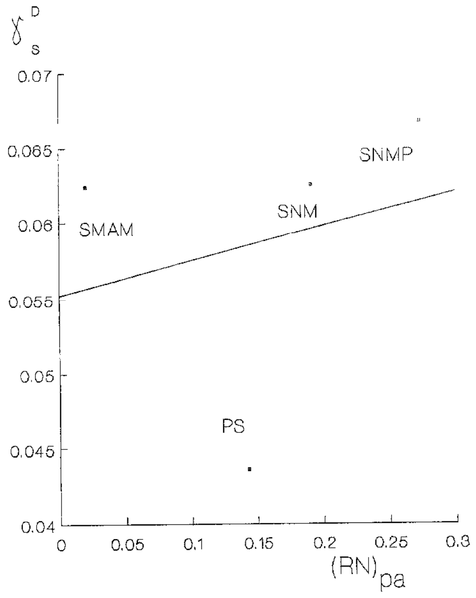

Figure 4 Dependence of dispersive component of polymer free surface energy on the polarization component of heat of adsorption in the Henry region

straight line of G_1^A vs. RN corresponding to the polar probe and the straight line for the n-alkane series can be considered equal to G_A^{sp}. The specific energy of adsorption G_A^{sp} of each probe p can be determined from the following equation, a_3 and a_4 being known:

$$G_A^{sp} = (G_A)_p - a_3(RN)_p - a_4 \qquad (17)$$

The partition adsorption coefficients, free adsorption energies and their polar interaction components, calculated from equations (13) ($G_{A,1}^{sp}$) and (17) ($G_{A,2}^{sp}$), are presented in *Table 4*, while the dispersive components and coefficients a_1, a_2, a_3 and a_4 for the polymers are listed in *Table 5*. As is seen from this table, the calculation of the polar component of free surface energy given by equation (13) leads to negative values of $G_{A,1}^{sp}$. In contrast to equation (13), the calculation in equation (17) furnishes the desired positive $G_{A,2}^{sp}$ values for n-butanol, di-n-butyl ether and 1,4-dioxane molecules. As is evident from *Table 6*, the ability of polymer surface groups to interact with electron-donor sorbates $(AN)_p$ (from equation (14)) decreases in the following order:

$$\text{SNM} \approx \text{SMAM} > \text{PS} > \text{SNMP}$$

and the donor ability of these polymers $(DN)_s$ varies as:

$$\text{SNMP} > \text{SMAM} \approx \text{SNM} > \text{PS}$$

These dependences correlate well with increasing polymer polarity induced by introduction of polar methacrylic acid, nonyl methacrylate, *p*-phthalimidinoxymethacrylic acid or maleic anhydride into the polystyrene matrix.

Thermodynamic functions for adsorption on the polymer surface in the Henry region

The adsorption enthalpy and entropy for the studied systems in the Henry region are presented in *Table 7*. Differential enthalpy of adsorption varies linearly with the number of carbon atoms in the n-alkanes (*Figure 3*). This is due to the increasing dispersive interaction of the

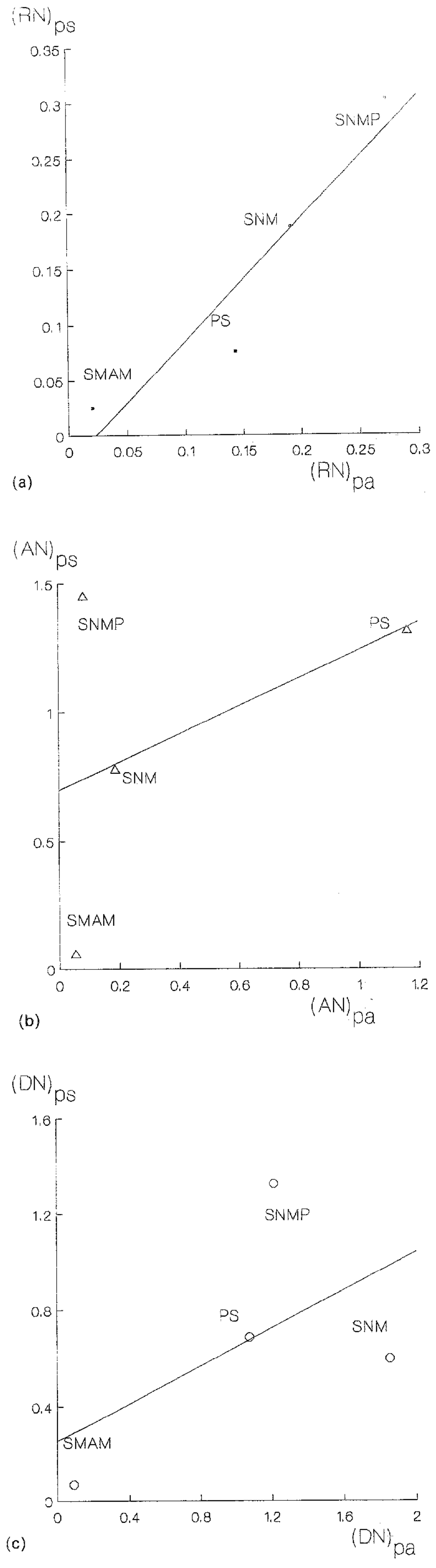

Figure 5 Dependences of components of polymer heat of solution at infinite dilution on the corresponding components of polymer heat of adsorption in the Henry region: (a) polarization; (b) acceptor; (c) donor

Table 9 The group contributions to the parachors and molecular volumes of polymers studied[a]

	Relative number of functional groups									
Polymer	$-CH_2-$	$CH\equiv$	C_6H_5	$C\equiv$	CH_3-	$=C=O$	$-O-$	$-OH$	$-C_6H_4-$	$N\equiv$
PS	1	1	1							
SNM	13	4	4	1	2	1	1			
SMAM	2	3	1	1	1	3	1	1		
SNMP	262	80	80	21	41	22	21	–	2	1
P_s (dyn cm^{-1})	40	24.5	189.6	9.0	55.5	17.3	20	29.8	174.1	17.5
V (cm^3 mol^{-1})	22.2	18.5	107.3	14.8	25.9	24.7	9.9	15.7	103.6	12.0

[a] P_s and V values are taken from ref. 4

Table 10 Experimental and estimated solubility parameters and free surface energies of polymers

Polymer	$(P_s/V_2)^{4a}$	δ_{est}[b]	δ_{exp}[c]	γ_{est}[d]	γ_s^d
PS	13.32	8.65	13.40	23.0	9.80
SNM	14.42	9.18	13.15	23.3	19.97
SMAM	6.26	4.91	15.13	28.1	19.90
SNMP	11.54	7.77	16.29	31.0	51.21

[a] Estimated from group contributions of P_s and V_2 values
[b] Estimated from $(P_s/V_2)^4$ values
[c] Data from ref. 9
[d] Calculated from the δ_{exp} values[9]

sorbate molecule with the polymer surface. Thermodynamic functions that account for the energy of interaction of probe molecules with a polymer surface or in its bulk are the partial molar enthalpy of adsorption in the Henry region (H_1^A) and the partial molar enthalpy of solution at infinite dilution (H_1^S). These functions are combinations of non-specific and specific interaction contributions:

$$-H_1^A = H_{1(nsp)}^A + H_{1(sp)}^A \qquad (18)$$

$$-H_1^S = H_{1(nsp)}^S + H_{1(nsp)}^S - A \qquad (19)$$

where A is the work of hole formation in the polymer volume. This value varies proportionally with probe molar volume (V_1). The non-specific interaction contributions are proportional to the sorbate molar deformation polarization (RN) and the specific interaction contributions are proportional to the Gutmann donor (DN) and acceptor (AN) numbers of the sorbate. Rewriting equations (18) and (19) in these terms we obtain:

$$-H_1^A = (RN)_{pa}RN + (AN)_{pa}DN + (DN)_{pa}AN + S_a \qquad (20)$$

$$-H_1^S = (RN)_{ps}RN + (AN)_{ps}DN + (DN)_{ps}AN + V_{ps}V_1 + S_s \qquad (21)$$

where S_a and S_s are constants for the given sorbates. The regression coefficients of equations (20) and (21) for the polymers studied are presented in *Table 8*.

One would expect a correlation between the dispersive interaction component of polymer free surface energy and the non-specific interaction contribution of the polymer surface to the heat of adsorption, calculated from equation (20). The dependence between these parameters for the polymers studied is presented in *Figure 4*. As is shown, some correlation is evident between these parameters. It is believed that deviation from a linear dependence is caused by an entropy effect associated with change of conformation of the polymer chains at liquid–solid polymer phase transition.

It would appear reasonable that some correlation remain between parameters $(RN)_{pa}$, $(AN)_{pa}$ and $(DN)_{pa}$ for adsorption ability of polymer functional groups at the surface and parameters $(RN)_{ps}$, $(AN)_{ps}$ and $(DN)_{ps}$ for these groups in solution. The dependences between these parameters are shown in *Figure 5*. Unsatisfactory correlations are found between polar components of the discussed parameters for the studied polymers. The deviations from linear relationships may be explained by the change of conformations of polymer chains on transition from the liquid to the solid state. Good linear dependence is observed between polarization components of adsorption on the polymer surface and heat of polymer solution. This is in general agreement with the weak sensitivity of dispersive interaction to conformational transitions on the polymer surface and in the bulk. In both phases polarization contributions decrease in the following order:

$$\text{SNMP} > \text{SNM} > \text{PS} > \text{SMAM}$$

On the surface, SNM has the highest donor ability among the polymers studied, and PS has the highest acceptor ability; whereas in solution, SNMP exhibits the highest donor ability and SNM has the best acceptor properties.

Estimation of polymer free surface energy from molar parachor

The free surface energy (γ) as well as the solubility parameter (δ) of polymers can be estimated from an additive function, for example, from the molar parachor $(P_s)^8$. If the group contributions of P_s and V_2 are known, free surface energy γ results from the expression:

$$P_s = \gamma^{1/4}M_2/\rho_2 = \gamma^{1/4}V_2 \qquad (22)$$

where M_2 and ρ_2 are the molecular weight and density of the polymer, respectively. The group contributions to the parachor and molecular volume of polymers studied are presented in *Table 9*. Free surface energies for polymers, calculated from equation (22), are presented in *Table 10*. Also, the free surface energy can be estimated on the basis of the solubility parameter (δ):

$$\gamma = 0.75\delta^{4/3} \qquad (23)$$

As is shown from *Table 10*, a trend exists between changes in the calculated γ and experimental γ_s^d values. The correlations between estimated and experimental δ

parameters are inadequate. This is due to the contribution of polar and specific interactions between polymer functional groups and sorbate molecules to the observed δ value, as well as the contribution of the change of polymer conformations to this parameter. It is therefore concluded that specific interactions between polymer functional groups and adsorbates or solutes, as well as conformational transition of the polymer, can have a significant influence on the distinctions between adsorptive or adhesive properties of the polymer surface and on the properties of the polymer solution[9].

CONCLUSION

Inverse gas chromatography was used for the determination of the thermodynamic functions for adsorption of non-polar, donor and acceptor test sorbates in the Henry region on the surface of polystyrene and its copolymer and terpolymers, thermodynamic functions for solution in the polymers at infinite dilution as well as their glass transition temperatures. The influence of polymer structural modification on the glass transition temperature and on the polymer functional group's ability to interact with non-polar, donor or acceptor molecules of sorbates or solvents has been established. The donor, acceptor and polarization solution and surface parameters of the polymers studied have been estimated. The calculation of the polar component of the free surface energy from the dependence of free adsorption energy on heat of vaporization of polar sorbates leads to negative values of this parameter. In contrast to the above, the calculation from the dependence of free adsorption energy on the molar deformation polarization gives the desired positive values. It is found that, in contrast to the correlations between polar components, a good linear dependence between polarization components of heats of adsorption on the polymer surface and polymer heats of solution is observed. The free surface energies and solubility parameters of the polymers were estimated from parachor values. A trend exists between changes in the calculated free surface energies and their experimental dispersive components. The correlations between estimated and experimental solubility parameters of the polymers are poor. This may be due to: (i) the contribution of polar and specific interactions between polymer functional groups and sorbate molecules; and (ii) the contribution of the change of polymer conformations to the observed parameters.

ACKNOWLEDGEMENT

One of the authors (V.I.B.) thanks Sharwin-Williams Co. (Ohio, USA) for financial support of this work.

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