Polymer Vol. 37 No. 19, pp. 4333–4344, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/\$15.00 + 0.00

S0032-3861(96)00280-7

Examination of surfaces of solid polymers by inverse gas chromatography: 2. Acid–base properties

Ewa Andrzejewska, Adam Voelkel*, Maciej Andrzejewski and Rajab Maga
Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl.M.Skłodowskiej-Curie, 60-965 Poznań, Poland

(Received 23 October 1995; revised 25 January 1996)

This paper deals with acid–base properties of the series of analogous poly(dimethacrylates) differing only by the presence and type of a heteroatom in the ester group and, for comparison, two reference polymers. These properties were quantified by K_A and K_D parameters, reflecting the ability of the surface to electrophilic and nucleophilic interactions, respectively. The parameters were calculated using various reference states for ΔG^{s} determination. It was found that the introduction of the sulfide, ether or amino functions into the polymer ester group causes both an increase in the nucleophilicity (K_D/K_A) and in the total ability of the surface to acid–base interactions ($K_D + K_A$). The greatest influence is exerted by the sulfide group. The increase in the $K_D + K_A$ parameter is associated with the decrease in the dispersive parameter γ_s^d. The influence of the polymer annealing at 80 and 160°C, both under helium and air, on the parameters determined is also discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: inverse gas chromatography; poly(dimethacrylates); surface acid–base characteristics)

INTRODUCTION

In the first paper of this series we described the surface properties of a series of analogous crosslinked polymethacrylates by dispersive force parameters determined by inverse gas chromatography (i.g.c.)[1]. The investigation included also the observation of changes occurring on the surface during annealing at various temperatures and atmospheres.

However, it is clear that the full description of the surface properties is possible only with the use of acid–base interaction parameters. This paper is devoted to the acid–base characteristics of the same series of polymethacrylates to complete the characterization of their surface properties given previously. The work gives also a short theoretical background in which various parameters proposed to describe the polar properties of polymer surfaces and calculated on the basis of the same i.g.c. data are presented.

Acid–base interactions are important components of polar forces and play a significant role in adhesion of organic substances to inorganic substrates[2–5]. However, the term 'polar' has been used most often in the description of adsorption adhesion phenomena and the properties of solvents. The reason is that intermolecular forces were studied first in dense gases, where dispersion forces, dipole–dipole interactions and dipole-induced dipole interactions explain most of the intermolecular interactions between pairs of molecules. These forces were assumed to explain intermolecular interactions in solids and liquids, even after the discovery of hydrogen bonds. Although it was evident that the strength of hydrogen bonds is independent of the magnitude of dipole moments[6] the word 'polar' is used to describe intermolecular interactions involving hydrogen bonds.

Lewis acids and bases

The electronic or Lewis acid–base definitions may be summarized as follows[7]:

(a) an acid is any species (molecule, ion or non-molecular solid) that can accept a share in a pair of electrons during the course of a chemical reaction;
(b) a base is any species (molecule, ion or non-molecular solid) that can denote a share in a pair of electrons during the course of a chemical reaction;
(c) neutralization is coordinate (heterogenic) bond formation between the acid and base:

$$A^{+} : B \leftrightarrow A : B \qquad (1)$$

The usage of the molecular orbital version of the Lewis definitions allows one to discuss donor and acceptor interactions, involving delocalized electron systems and localized but multicentred bonds. Moreover, one can take into account all degrees of electron donation ranging from nearly zero, in the case of weak intermolecular attractions and idealized ion association, to complete transfer of one or more electrons (redox).

The prediction and quantification of Lewis acid–base interactions may proceed in three different ways:

(a) full four-parameter acid–base scales;
(b) monotonic acid–base scales;
(c) undifferentiated polarity scale.

---

* To whom correspondence should be addressed

Drago's four-parameter equation

A double-scale enthalpy equation proposed by Drago and co-workers to correlate (and predict) the enthalpy of adduct formation in gas-phase or poorly solvating media[8,9] is given by

$$-\Delta H_{AB} = E_A E_B + C_A C_B \qquad (2)$$

Empirically determined parameters, E_A and C_A, are assigned to an acid, while E_B and C_B are assigned to a base. When substituted into equation (2), they give the enthalpy of adduct formation for the acid–base pair. E_A and E_B parameters supposedly represent the electrostatic contributions to adduct stability, while C_A and C_B parameters are the susceptibility of the acid and base, respectively, to form covalent bonds. With increasing amount of reliable enthalpy data, the E&C model was extended to many different acids and bases.

Jensen[7] indicated that there is no evidence that Drago's parameters reflect the relative electrostatic and covalent contributions to the bonding in resulting adducts. They were not correlated with either a physical property (dipole moment, ionization potential) or with a quantum-mechanically calculated index. Drago's approach is a purely empirical method of calculating enthalpy of formation for molecular adducts.

Donor and acceptor numbers

The donor number (DN) as the measure of Lewis basicity[10] was defined as the negative of the molar enthalpy of formation for the adduct formed between the base in question (donor D) and reference Lewis acid $SbCl_5$ (acceptor) in a 10^{-3} M solution of dichloroethane:

$$B + SbCl_5 \leftrightarrow B * SbCl_5 \; (-\Delta H_{B*SbCl_5} \equiv DN) \qquad (3)$$

The acceptor number was defined as a dimensionless number related to the relative chemical ^{31}P n.m.r. shift in triethylphosphine oxide $(C_2H_5)_3PO$ in the particular acceptor solvent:

$$(C_2H_5)_3P = O \rightarrow \text{Acceptor} \qquad (4)$$

This was further scaled by assigning a value of 0 (zero) to the shift induced by hexane and a value of 100 to the shift produced by $SbCl_5$ upon interacting with $(C_2H_5)_3PO$ in a diluted 1,2-dichloroethane solution:

$$AN \equiv \frac{\partial_{corr.} \times 100}{\partial_{corr.(C_2H_5)_3PO \cdot SbCl_5)]}} = \partial_{corr.} \times 2.348 \qquad (5)$$

Gutman further proposed[10] that the enthalpy of a given acid–base interaction could be approximated by a two-parameter equation of the form:

$$-\Delta H_{AB} = \frac{AN_A \times DN_B}{100} \qquad (6)$$

Where the factor of 100 converts the AN values from percentage into a decimal fraction.

Riddle and Fowkes[11] have shown that dispersion-only liquids, such as hexane, produce a significant ^{31}P shift in $(C_2H_5)_3PO$. Hence, AN values should be corrected for this dispersion effect. In many cases, this correction is quite substantial. Thus, 13.7 of the original 14.2 AN units assigned to pyridine appear to be due to dispersion rather than to specific electron-pair donor–acceptor interactions, lowering its measure of 'true' Lewis acidity from 14.2 to 0.5. Riddle and Fowkes have found that these dispersion-corrected AN values correlate well with the enthalpies of formation of the adducts formed between $(C_2H_5)_3PO$ and the examined acid. They proposed to use this enthalpy as the true measure of Lewis acidity for a species, which allows one to express both the DN and AN* (modified AN parameter) numbers in the same units

$$AN^* = -\Delta H[A \leftarrow (C_2H_5)_3PO] = 0.288(AN - AN^d) \qquad (7)$$

where the AN values are the original values reported by Gutman, AN^d is the dispersion contribution given by Riddle and Fowkes[11], and A denotes acceptor.

Determination of acid–base interactions

On the basis of the i.g.c. data one can calculate the free energy of adsorption, ΔG^0 being the sum of energies of adsorption attributed to dispersive and specific interactions:

$$\Delta G^0 = \Delta G^d + \Delta G^s = -RT \times \ln V_N + \text{const} \qquad (8)$$

where ΔG^d and ΔG^s are the dispersive and specific components of the free energy of adsorption, respectively, and V_N is the net retention volume of the testing probe.

For n-alkanes, $\Delta G^0 = \Delta G^d$ and changes with the number of carbon atoms in their molecules. On plotting ΔG^0 against the values of a reference state (a physicochemical property[1]) chosen for consecutive n-alkanes a straight line is obtained. The polar testing probes [Lewis acids and bases, e.g. chloroform ($CHCl_3$) and tetrahydrofuran (THF)] interacting specifically with the polymer have their corresponding ΔG^0 values above the reference line. The vertical distance between the n-alkane plot and the data for the polar probe of interest gives a ΔG^s value:

$$-\Delta G^s = -(\Delta G^0 - \Delta G^d) = RT \times \ln(V_N / V_{N,ref}) \qquad (9)$$

where V_N denotes the net retention volume of the polar probe and $V_{N,ref}$ is the net retention volume of a hypothetical reference n-alkane having the same V_N value as the polar probe.

Examination of the temperature dependence of ΔG^s gives the possibility of determination of the enthalpy of specific interactions ΔH^s [12]:

$$\Delta H^s = \frac{\delta(\Delta G^s / T)}{\delta(1/T)} \qquad (10)$$

Enthalpy of specific interactions between the examined surface and the test solute may be correlated with acid–base properties of both species by using Drago's equation or, in our opinion better, through the following equation[12]:

$$-\Delta H^s = K_D \times AN + K_A \times DN \qquad (11)$$

where AN and DN are acceptor and donor number of test solute, respectively; parameters K_A and K_D reflect the ability of the examined surface to act as electron acceptor and donor, respectively, and AN denotes acceptor number in Gutman[10] or Riddle–Fowkes scale[11]. The ratio K_D/K_A describes the character of the surface (acidic or basic).

The procedure described above was used in the characterization of silicas, modified silicas, oxides and minerals[12–16]. Chehimi and Pigois-Landureau[17,18] and Panzer and Schreiber[19] used this method for characterization of solid polymers, i.e. conducting polypyrroles and polycarbonates, respectively. Other works were directed to the simplification of the procedure for determination of parameters reflecting acceptor and donor properties of surfaces. For instance, several authors used equation (11) in another form introducing on the left hand side ΔG^s instead of ΔH^s. Such an approach cannot be correct because it combines ΔG^s and Gutman's/Riddle–Fowkes' values derived from ΔH^s terms. Moreover, such treatment leads to the limitation of applicability and comparability of K_A and K_D to only one temperature. It means that K_A and K_D values will change with changing temperature of a measurement.

Osmont and Schreiber introduced an interaction parameter Ω as a measure of acidity and basicity of glass fibres[20]. This parameter was calculated by using specific retention volumes of the injected probes, i.e. n-butanol and butylamine. For acidic surfaces, where the specific retention volume for the base exceeds that for the acidic alcohol:

$$\Omega = 1 - (V_g^0)_b/(V_g^0)_a < 0 \qquad (12)$$

where $(V_g^0)_b$ and $(V_g^0)_a$ denote specific retention volumes of the base and the acid, respectively.

For basic stationary phases the specific retention volume exceeds that for the butylamine and

$$\Omega = (V_g^0)_a/(V_g^0)_b - 1 > 0 \qquad (13)$$

Schreiber *et al.*[21] proposed also another definition of acceptor and donor numbers (assigned here as AN_{Sch} and DN_{Sch}, respectively) not related to Gutman's scale and defined as follows:

$$AN_{Sch} = V_{N,THF}/V_{N,ref} \qquad (14)$$

$$DN_{Sch} = V_{N,CHCl_3}/V_{N,ref} \qquad (15)$$

where $V_{N,THF}$ and $V_{N,CHCl_3}$ denote the net retention volume of test probes—tetrahydrofuran and chloroform, respectively, while $V_{N,ref}$ has the same meaning as defined by equation (9), i.e. the net retention volume of the hypothetical n-alkane having the same vapour pressure as the polar test probe. Acceptor and donor numbers defined by equations (14) and (15) are directly related to the specific component of free energy of adsorption.

Schreiber used such defined AN_{Sch} and DN_{Sch} values to calculate a new index of acid–base properties—K. It is defined as the difference between DN_{Sch} and AN_{Sch} numbers: $K > 0$ for basic surfaces and $K < 0$ for acidic ones; K near zero determines the neutral and amphoteric surface.

Chehimi *et al.*[22] followed Schreiber's idea and suggested the new index of acidity:

$$\Omega_A = V_N^{AB}(\text{base})/V_N^{AB}(\text{acid}) \qquad (16)$$

and the new index of basicity:

$$\Omega_B = \Omega_A^{-1} = V_N^{AB}(\text{acid})/V_N^{AB}(\text{base}) \qquad (17)$$

where V_N^{AB} denotes the acid–base contribution to the net retention volume of the polar probe. They proposed also two dimensionless (H) and soft (S) indices of basicity:

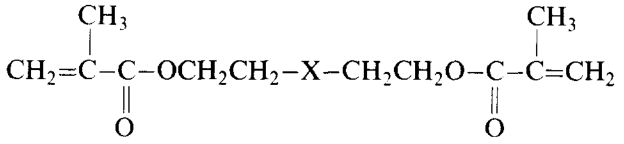
$$\Omega_{HB} = V_N^{AB}(\text{CHCl}_3)/V_N^{AB}(\text{DXN}) \qquad (18)$$

$$\Omega_{SB} = V_N^{AB}(\text{t-BuOH})/V_N^{AB}(\text{THF}) \qquad (19)$$

where $CHCl_3$, DXN, t-BuOH and THF refer to chloroform, 1,4-dioxane, tert-butyl alcohol and tetrahydrofuran, respectively.

Here again the applicability of the above described indices is limited to only one temperature, which strongly reduces their universality.

In our work we decided to describe the acid–base properties of the polymers with the use of K_D and K_A parameters calculated on the basis of ΔH^s determination. For calculation two reference states were chosen: saturated vapour pressure[23] and molecular polarizability[24]. The subject of the investigation was the series of poly(dimethacrylate)s differing only by the presence or type of the heteroatom introduced into the ester group. The following polymers were studied: poly(2,2′-thiobisethanol dimethacrylate), PTEDM; poly(2,2′-oxybisethanol dimethacrylate), POEDM; poly(N-methyldiethanolamine dimethacrylate), PNDM; poly(pentane-1,5-diol dimethacrylate), PPDM; and poly(butane-1,4-diol dimethacrylate), PBDM. The general formulae of the corresponding monomers is given below:



$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OCH_2CH_2{-}X{-}CH_2CH_2O{-}\underset{\underset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2$$

X = S : TEDM; X = O : OEDM;
X = N(CH_3) : NDM; X = CH_2 : PDM;
X = – : BDM.

As reference materials the following polymers were investigated: poly(methyl methacrylate) (PMMA) as the linear polymer and the copolymer of BDM and methacrylic acid [P(BDM-*co*-MA)] as polymer with the acidic surface.

The aim of the work was: (i) to determine the surface properties of the examined polymers in terms of acid–base interactions, (ii) to describe the influence of the heat treatment at various temperatures and atmosphere conditions upon surface properties, and (iii) to discuss the relation between the acid–base and dispersive properties presented previously[1].

EXPERIMENTAL

The preparation of polymers as well as the experiment description were given in Part 1[1]. The i.g.c. measurements were performed at infinite dilution of the test probe. The chromatographic data were collected at three different temperatures: 50, 60 and 70°C.

Two series of experiments were carried out to check the influence of the heat treatment on the surface properties of the polymers: under helium and air. The basic experiment (for initial polymers) was performed after the short conditioning of the polymer probe under helium. The next stop was the heating of the polymer (in the column) in the chosen atmosphere at elevated temperature, first at 80°C for 3 h followed by measurements of solute retention times. Subsequently, the same polymer probe was heated in the chosen atmosphere at 160°C for 3 h and retention times were recorded. For more detailed description see ref. 1.

RESULTS AND DISCUSSION

The specific component of free energy of adsorption. The influence of the reference state upon the numerical values of the parameter

The specific component of free energy of adsorption was evaluated by using two reference states, i.e. the retention data were related to the saturated vapour pressure P^0 (ΔG^0 vs. $\log P^0$) or to molecular polarizability P_D (ΔG^0 vs. P_D). Due to the use of two reference states two different values of ΔG^s were available at each temperature of the experiment. Exemplary values collected for the initial polymers are presented in *Table 1*.

The values of $-\Delta G^s$ depend on the chosen reference state. Those determined by using P^0 as the reference state ($-\Delta G^{s(P)}$) are lower than those found by using P_D as the reference state ($-\Delta G^{s(D)}$). In each case $-\Delta G^s$ decreases with the increasing temperature of the i.g.c. experiments. The lowest $-\Delta G^s$ values (the weakest specific interactions) were found for ether and benzene test probes.

The annealing of the polymer leads to a decrease of $-\Delta G^s$, which is especially large after heating at 160°C. *Figures 1* and *2* present the changes of the specific increment of the free energy of adsorption for several test solutes. The drop in $-\Delta G^s$ depends on the test solute and polymer type and is greater after annealing in air than in helium.

Acceptor and donor properties of the surface. Influence of the reference state and of the solute characteristics (AN or AN) upon the values of* K_D *and* K_A *parameters*

The specific component of enthalpy of adsorption was calculated from $\Delta G^{s(P)}$ and $\Delta G^{s(D)}$ values according to equation (10). Acid–base characteristics were evaluated from equation (11) with the use of two sets of acceptor number (AN—Gutman[10] and AN*—Riddle–Fowkes[11]) and donor number DN given by Gutman[10]. This leads to four series of numerical values:

method A—the use of $-\Delta G^{s(P)}$ and Riddle/Fowkes AN* values in equation (11);
method A′—the use of $-\Delta G^{s(P)}$ and Gutman's AN values in equation (11);
method B—the use of $-\Delta G^{s(D)}$ and Riddle/Fowkes AN* values in equation (11);
method B′—the use of $-\Delta G^{s(D)}$ and Gutman's AN values in equation (11).

The values of acid–base characteristics, i.e. K_D, K_A and S_C (equal to K_D/K_A) are collected in *Tables 2–8*. K_D and K_A determined according to the methods A′ and B′ are expressed in different units, i.e. to obtain both sides of equation (11) in the same units K_D must be in kJ mol^{-1} while K_A has to be unitless. Therefore, evaluation of conclusions from their ratio must be treated with caution since the sense of K_D/K_A is vague. Despite this, S_C values obtained from methods A′ and B′ in all the cases properly reflect the surface character of the investigated polymers and are in fair agreement with S_C values obtained from methods A and B, the only exception being PMMA. Further discussion will be based only on K_D, K_A and S_C values determined according to methods A and B.

Electron donor properties of the surfaces of poly(dimethacrylate)s are much higher than electron acceptor ones (*Figure 3*). The introduction of the amino, ether or sulfide group into the ester group causes a significant increase of the surface affinity to nucleophilic interactions. The highest nucleophilic properties were found for PTEDM, which results from the high polarizability of the sulfur atom. This is in agreement with the definitions of AN* and DN, which lead, in fact, to determination of the electron donor and acceptor surface properties and not to acid–base ones interpreted as the ability to donate or accept a proton (the basicity of the amino group is higher than that of the sulfide group). Although the ability of the surface to nucleophlic and electrophilic interactions may be high or low, the resulting character of the surface (nucleophilic or electrophilic) is determined by the K_D/K_A ratio. For the investigated polymers [except for P(BDM-*co*-MA)] this ratio is dominated by the relatively high K_D values, which cause the determined character of the surface to be explicitly nucleophilic.

As we can see from *Figure 3* and *Tables 2–8*, the large increase in the ability of the surface to nucleophilic interactions by introduction of the heteroatom goes, in general, hand in hand with a smaller increase in the

Table 1 Specific component of the free energy of adsorption $-\Delta G^s$ determined with the use of two different reference states ($-\Delta G^{s(P)}$ and $-\Delta G^{s(D)}$)

		$-\Delta G^{s(P)}$ (J mol^{-1})			$-\Delta G^{s(D)}$ (J mol^{-1})		
Polymer	Solute	50°C	60°C	70°C	50°C	60°C	70°C
PNDM	Benzene	1557	1488	1367	2665	2668	2546
	Acetone	3082	1694	1656	3735	3689	3202
	Ether	1280	996	676	1791	1564	1157
	Chloroform	3172	3021	2772	4463	4208	3754
	Methylene chloride	3790	3622	3198	5395	5092	4362
	Dioxane	3046	2986	2766	5318	5111	4600
	Ethanol	3194	2988	2749	6708	6159	5218
	Propanol	3624	3486	3082	7097	6602	5577
PPDM	Benzene	2423	2338	2240	3328	3133	3003
	Acetone	2560	2461	2390	3714	3627	3397
	Ether	1889	1725	1631	2112	2032	1875
	Chloroform	3940	3765	3646	4018	3812	3693
	Methylene chloride	4570	4483	4391	4773	4422	4113
	Dioxane	3637	3556	3450	4394	4176	3984
	Ethanol	3484	3356	3267	4228	4133	4022

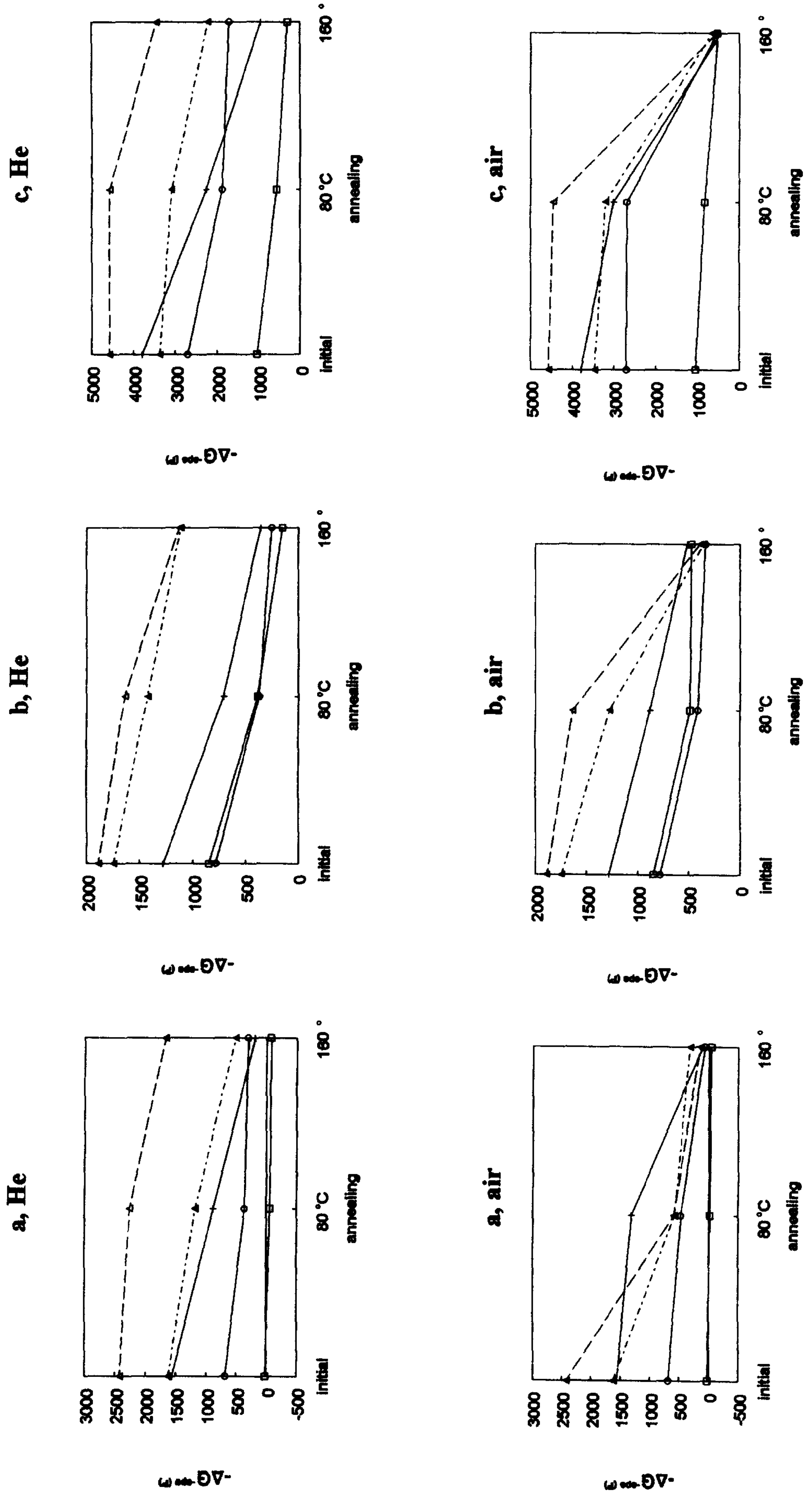


Figure 1 The influence of annealing under helium (He) and air (air) upon the specific component of the free energy of adsorption (reference state P^0) $\Delta G^{\mathrm{spe}(P)}$ at 50°C: (a) benzene; (b) ether; (c) methylene chloride. (+) PNDM; (△) PPDM; (○) P(BDM-*co*-MA) denoted as COP; (▲) PTEDM; (□) PMMA

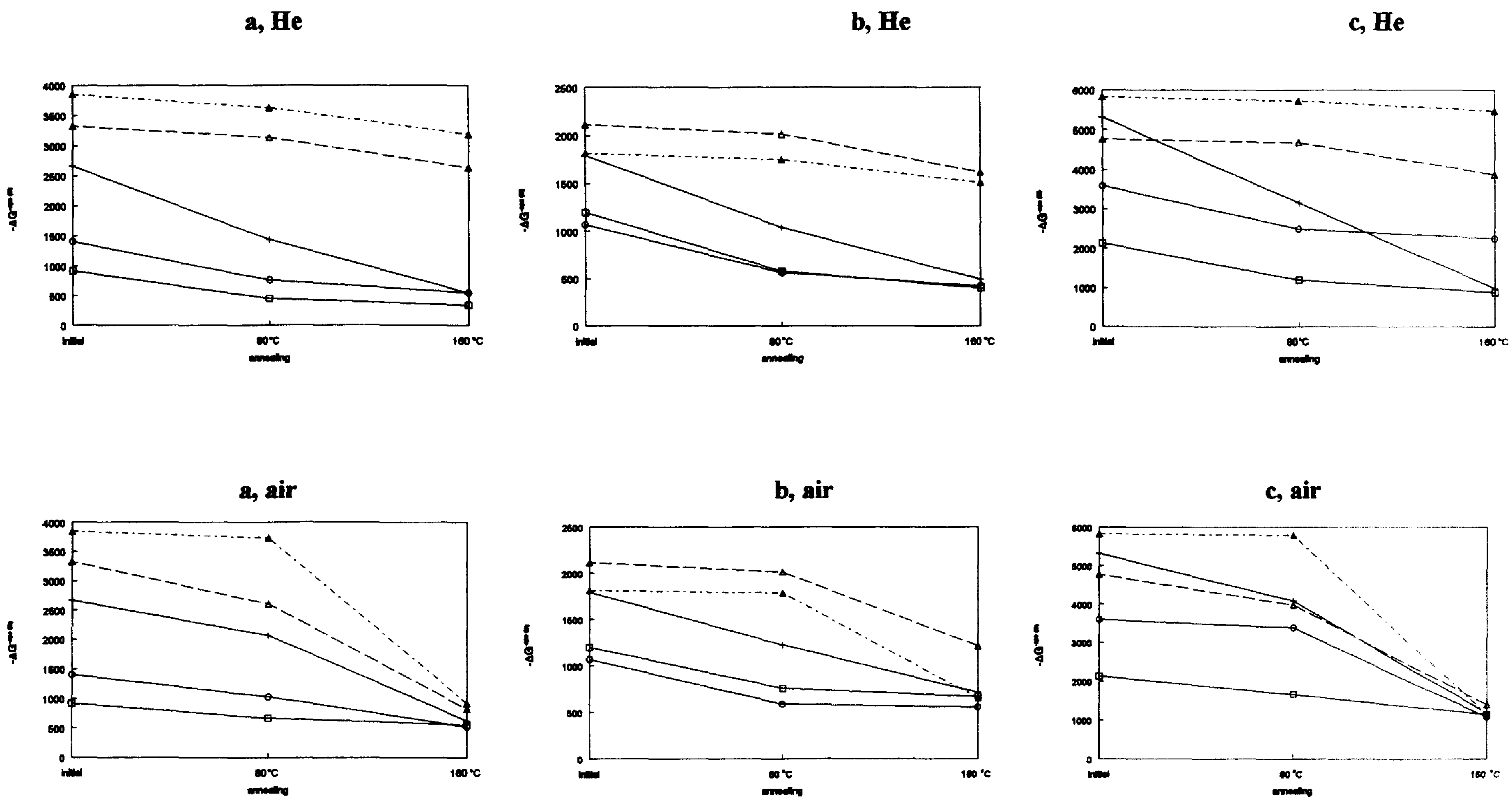


Figure 2 The influence of annealing under helium (He) and air (air) upon the specific component of the free energy of adsorption (reference state P_D) $\Delta G^{\mathrm{spe}(P)}$ at 50°C. (a) benzene; (b) ether; (c) methylene chloride (symbols as in *Figure 1*)

Table 2 Acid–base characteristics for PBDM

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.400	0.287	0.153	0.400	0.444	0.236
	K_A	0.177	0.092	0.066	0.117	0.069	0.035
	S_C	3.418	3.134	2.317	3.418	6.389	6.777
A′	K_D	0.453	0.388	0.337	0.453	0.423	0.159
	K_A	0.115	0.099	0.096	0.115	0.104	0.043
	S_C	3.929	3.900	3.510	3.929	4.082	3.717
B	K_D	0.891	0.422	0.225	0.891	0.885	0.378
	K_A	0.233	0.136	0.076	0.233	0.112	0.055
	S_C	3.824	3.103	2.960	3.824	7.902	6.873
B′	K_D	0.925	0.631	0.311	0.925	0.905	0.511
	K_A	0.212	0.148	0.083	0.212	0.123	0.074
	S_C	4.363	4.263	3.745	4.363	7.358	6.905

Table 3 Acid–base characteristics for PPDM

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.402	0.394	0.375	0.402	0.515	0.282
	K_A	0.106	0.070	0.073	0.106	0.077	0.041
	S_C	3.778	5.596	5.167	3.778	6.670	6.895
A′	K_D	0.409	0.431	0.298	0.409	0.332	0.262
	K_A	0.128	0.110	0.073	0.128	0.075	0.052
	S_C	3.181	3.912	4.063	3.181	4.441	5.062
B	K_D	0.980	0.622	0.511	0.980	0.647	0.588
	K_A	0.254	0.145	0.115	0.254	0.138	0.093
	S_C	3.858	4.280	4.443	3.858	4.686	6.322
B′	K_D	0.925	0.822	0.495	0.952	0.621	0.525
	K_A	0.273	0.188	0.113	0.273	0.129	0.088
	S_C	3.487	4.372	4.381	3.487	4.814	5.965

Table 4 Acid–base characteristics for POEDM

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.575	0.449	0.451	0.575	0.533	0.646
	K_A	0.139	0.092	0.082	0.139	0.131	0.088
	S_C	4.148	4.860	5.492	4.148	4.078	6.596
A′	K_D	0.630	0.382	0.348	0.660	0.557	0.801
	K_A	0.135	0.125	0.045	0.135	0.121	0.152
	S_C	4.671	3.048	7.774	4.671	4.591	5.270
B	K_D	1.268	1.111	0.847	1.268	1.042	0.877
	K_A	0.263	0.218	0.173	0.263	0.204	0.152
	S_C	4.821	5.096	4.896	4.821	5.108	5.770
B′	K_D	1.237	1.125	0.845	1.237	1.012	0.833
	K_A	0.221	0.200	0.166	0.221	0.183	0.134
	S_C	5.597	5.625	5.090	5.597	5.530	6.216

Table 5 Acid–base characteristics for PTEDM

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.668	0.680	0.480	0.668	0.709	0.745
	K_A	0.133	0.107	0.092	0.133	0.093	0.106
	S_C	5.023	6.371	4.937	5.023	7.626	7.264
A′	K_D	1.033	0.868	0.427	1.033	0.807	0.646
	K_A	0.352	0.272	0.176	0.352	0.248	0.193
	S_C	2.935	3.193	2.425	2.935	3.250	3.560
B	K_D	1.412	1.422	1.028	1.412	1.446	1.477
	K_A	0.282	0.233	0.193	0.282	0.198	0.190
	S_C	5.007	6.103	5.330	5.007	7.303	7.774
B′	K_D	1.402	1.266	0.938	1.402	1.043	0.887
	K_A	0.246	0.211	0.182	0.246	0.194	0.154
	S_C	5.699	6.000	5.154	5.699	5.531	5.760

Table 6 Acid–base characteristics for PNDM

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.551	0.738	0.754	0.551	0.942	0.962
	K_A	0.122	0.152	0.136	1.122	0.133	0.119
	S_C	4.515	4.859	5.548	4.515	7.090	8.090
A′	K_D	0.521	0.676	0.600	0.521	0.716	0.868
	K_A	0.129	0.169	0.126	0.129	0.146	0.182
	S_C	4.047	4.002	4.760	4.047	4.907	4.772
B	K_D	0.904	0.676	0.731	0.904	0.905	0.749
	K_A	0.272	0.169	0.163	0.272	0.167	0.151
	S_C	3.331	4.002	4.485	3.310	5.422	4.963
B′	K_D	0.856	0.751	0.585	0.856	0.775	0.620
	K_A	0.113	0.159	0.132	0.113	0.126	0.144
	S_C	7.579	4.725	4.431	7.579	7.160	4.311

Table 7 Acid–base characteristics for P(BDM-*co*-MA)

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.172	0.049	0.019	0.182	0.058	0.046
	K_A	0.700	0.263	0.241	0.735	0.196	0.114
	S_C	0.245	0.188	0.077	0.247	0.298	0.406
A′	K_D	0.088	0.047	0.033	0.116	0.040	0.046
	K_A	0.649	0.260	0.251	0.696	0.204	0.110
	S_C	0.136	0.182	0.130	0.167	0.196	0.416
B	K_D	0.294	0.050	0.060	0.303	0.073	0.141
	K_A	0.968	0.337	0.294	0.926	0.344	0.309
	S_C	0.304	0.147	0.203	0.327	0.213	0.458
B′	K_D	0.245	0.039	0.036	0.319	0.066	0.128
	K_A	0.902	0.342	0.376	1.095	0.344	0.293
	S_C	0.271	0.114	0.095	0.291	0.191	0.436

Table 8 Acid–base characteristics for PMMA

			Annealing (He)			Annealing (air)	
Method	Parameter	Initial polymer	80°C	160°C	Initial polymer	80°C	160°C
A	K_D	0.290	0.265	0.165	0.290	0.168	0.131
	K_A	0.151	0.086	0.054	0.151	0.088	0.048
	S_C	1.920	3.064	3.055	1.920	1.919	2.735
A′	K_D	0.288	0.252	0.160	0.288	0.163	0.133
	K_A	0.137	0.089	0.060	0.137	0.076	0.055
	S_C	2.108	2.837	2.667	2.108	2.140	2.409
B	K_D	0.790	0.550	0.422	0.790	0.407	0.393
	K_A	0.405	0.229	0.175	0.405	0.255	0.180
	S_C	1.953	2.398	2.411	1.953	1.989	2.184
B′	K_D	0.760	0.521	0.403	0.760	0.483	0.381
	K_A	0.139	0.090	0.070	0.134	0.110	0.087
	S_C	5.474	5.797	5.757	5.474	4.384	4.388

ability to electrophilic interactions. This leads to substantial enhancement of the S_C ratio, i.e. enhancement of the nucleophilic character of the surface. This ratio, as in the case of the K_D parameter, is the highest for the sulfur-containing polymer. Moreover, the total ability of the surface to acid–base interactions, which may be expressed by the sum $K_D + K_A$, increases. According to method A this sum is the highest for P(BDM-*co*-MA), which is in agreement with intuitive expectations; the second position is taken by PTEDM. In contrast, method B shows PTEDM as having the greatest ability to acid–base interactions while P(BDM-*co*-MA) takes the next position. The arrangement of polymers according to decreasing $K_D + K_A$ values is as follows:

method A: P(BDM-*co*-MA) > PTEDM > POEDM > PNDM > PBDM ≈ PPDM > PMMA
method B: PTEDM > POEDM > P(BDM-*co*-MA) > PMMA > PNDM > PPDM > PBDM

The higher ability to polar interactions should be associated with the lower ability to dispersive interactions expressed by the dispersive component of surface free energy γ_s^d (ref. 1). Indeed, the order of polymers with increasing γ_s^d values:

$$\mathrm{P(BDM\text{-}\mathit{co}\text{-}MA)} < \mathrm{PTEDM} < \mathrm{POEDM} < \mathrm{PBDM} < \mathrm{PPDM} < \mathrm{PMMA} < \mathrm{PNDM}$$

is almost identical with the order of polymers with

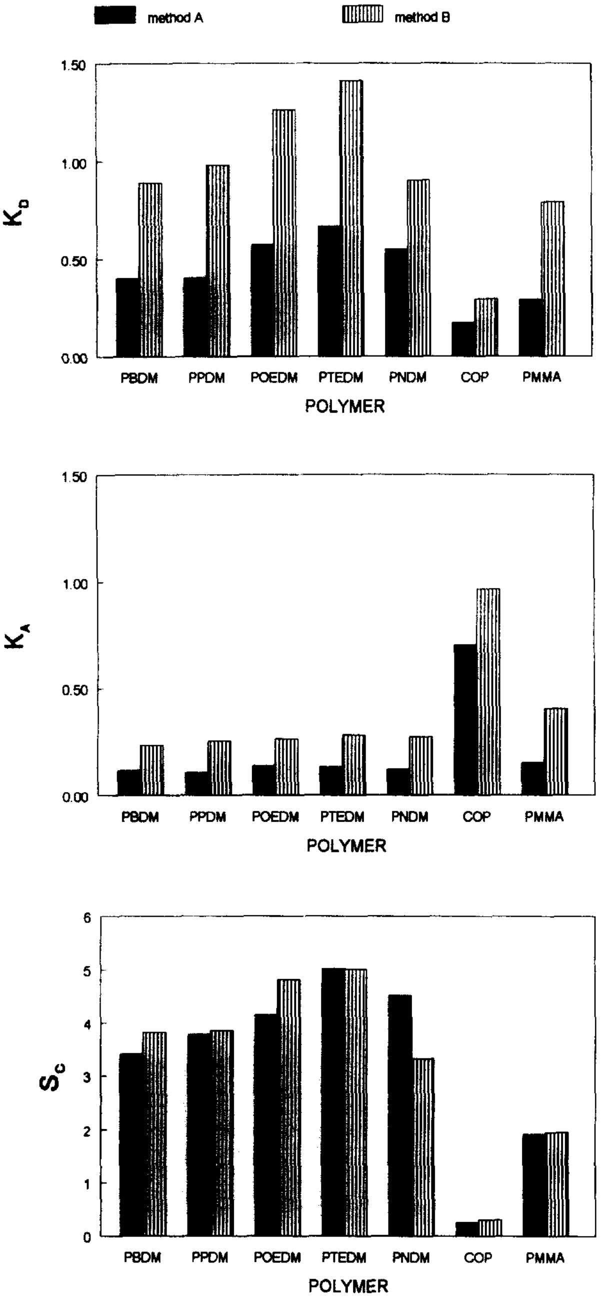


Figure 3 Surface characteristics for initial polymers determined according to methods A and B (see text for details)

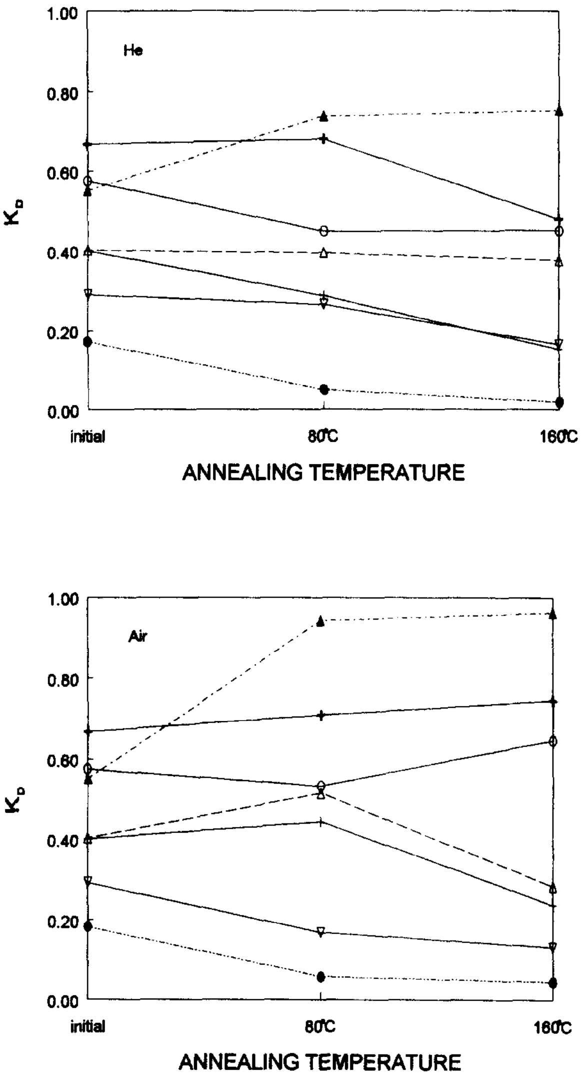


Figure 4 The influence of the annealing under helium and air upon K_D values (method A): (+) PPDM; (△) PBDM; (○) POEDM; (+) PTEDM; (▲) PNDM; (●) P(BDM-*co*-MA); (▽) PMMA

decreasing $K_D + K_A$ values found in method A. The different position of PNDM in these two arrangements may result from some physical factors influencing its position in the order concerning γ_s^d values[1].

Comparing the results obtained by methods A and B it is clearly seen that method B leads to much higher values of K_D and K_A parameters. In several cases K_D and K_A are twice as high as those found in method A (*Tables 2–8*, *Figure 3*). However, the S_C parameter describing the surface character is similar in both methods, with somewhat greater difference only in the case of PNDM.

Influence of polymer annealing upon the acceptor and donor properties of the surface

As we found in the previous part of our investigation[1], the annealing of the polymers at 80 and 160°C irreversibly changes their surfaces, which is revealed in increase of γ_s^d and $C' \times P_{DS}$ values. The variation in the dispersive properties are accompanied by significant changes in the acid–base characteristics of the polymers. The changes in the K_D, K_A and S_C parameters after heating of the polymers at 80 and 160°C under helium and air are presented in *Table 9*. The general trend observed is a substantial decrease of the K_A values even up to 90%, independently of the heating atmosphere (the only exception being PNDM), and somewhat lower in the magnitude drop of the K_D values after annealing in helium (exception PNDM) (*Figure 4*). So, we may conclude that the heat treatment leads to a deactivation of the surface by a modification or decay of active centres. The especially large drop in K_A parameter for P(BDM-*co*-MA) may be ascribed to dehydration of the carboxylic groups with the formation of the anhydride ones. However, after the annealing under air we observe an increase in the K_D values for the polymers containing a heteroatom in the ester group (for PNDM twice as high as under He). The heating of the polymers in the presence of atmospheric oxygen must provoke the formation of oxide groups of various types (e.g. sulfoxide and nitroxide), increasing the surface ability to nucleophilic interactions. The greater drop in K_A than in the K_D

Table 9 Relative changes (in %) of the polymer surface properties during annealing under helium and air

			Change under He		Change under air	
Polymer	Method	Parameter	80°C	160°C	80°C	160°C
PBDM	A	K_D	−28.2	−61.7	11.0	−41.0
		K_A	−21.4	−43.6	−41.0	−70.1
		S_C	−8.3	−32.2	86.9	98.3
	B	K_D	−52.6	−74.7	−0.7	−57.5
		K_A	−41.6	−67.2	−51.9	−76.4
		S_C	−18.8	−22.5	106.6	79.7
PPDM	A	K_D	−2.0	−6.7	28.1	−29.8
		K_A	−40.0	−31.1	−27.3	−61.3
		S_C	48.1	36.8	76.5	82.5
	B	K_D	−36.5	−47.8	−34.0	−40.0
		K_A	−42.9	−54.7	−45.6	−63.4
		S_C	10.9	15.2	21.5	63.9
POEDM	A	K_D	−21.9	−21.6	−7.3	12.3
		K_A	−33.8	−41.0	−5.8	−36.7
		S_C	17.2	−132.0	−1.7	59.0
	B	K_D	−12.4	−33.2	−17.8	−30.8
		K_A	−17.1	−34.2	−22.4	−42.2
		S_C	5.7	1.6	5.9	19.8
PTEDM	A	K_D	1.8	−28.1	6.1	11.5
		K_A	−19.5	−30.8	−30.0	−20.3
		S_C	26.8	−12.5	51.8	44.6
	B	K_D	0.7	−27.1	2.4	4.6
		K_A	−17.3	−31.5	29.8	−32.6
		S_C	21.9	6.4	45.8	55.3
PNDM	A	K_D	33.9	36.8	71.0	74.6
		K_A	24.6	11.5	9.0	−2.5
		S_C	7.6	22.9	57.0	79.2
	B	K_D	−25.2	−19.1	0.1	−17.1
		K_A	−37.9	−40.1	38.6	−44.5
		S_C	20.1	34.6	63.8	49.9
P(BDM-*co*-MA)	A	K_D	−71.5	−65.6	−68.1	−74.7
		K_A	−62.4	−88.9	−73.7	−84.5
		S_C	−23.2	−68.6	21.6	65.7
	B	K_D	−83.0	−79.6	−75.9	−53.5
		K_A	−65.2	−69.6	−62.8	−66.8
		S_C	−51.6	−33.2	−34.9	40.1
PMMA	A	K_D	−8.6	−43.1	−42.1	−54.8
		K_A	−43.0	−64.2	−41.7	−68.2
		S_C	59.6	59.1	−0.1	42.4
	B	K_D	−30.3	−46.6	−48.5	−50.2
		K_A	−43.4	−56.7	−37.0	−55.5
		S_C	22.8	23.4	1.8	11.8

parameter causes a tendency for the K_D/K_A ratio to increase and, although in most cases the absolute value of the surface ability to nucleophilic interactions substantially decreases, the character of the polymer becomes more nucleophilic. Generally, the drop in acid–base activity of the surface after heat treatment is accompanied by enhancement of its ability to dispersive interactions (cf. ref. 1).

The changes of K_D and K_A parameters during annealing may result not only from chemical processes leading to the modification (or decay) of active centres or appearance of new ones. The increase of temperature mobilizes the polymer chains, allowing the occurrence of various relaxation processes which may lead to changes in chain arrangement on the surface and change in the accessibility of various functional groups.

The relative changes of the examined parameters calculated with the use of methods A and B are most often different, but the tendency of the changes remains the same, i.e. increasing or decreasing. However, in several cases both methods lead to different conclusions (*Figure 5*, *Table 9*).

Taking into account the fact that the method B approach gives higher values of the specific component of the energy of adsorption ΔG^s as well as of K_D and K_A parameters, one may expect that the results will be more precise in comparison with those of method A. However, the results obtained from method A lead to conclusions which are in better agreement with conclusions drawn from the dispersive parameters as well as with the intuitive expectations.

The sensitivity of both methods upon the changes in the ester group are comparable (*Table 10*).

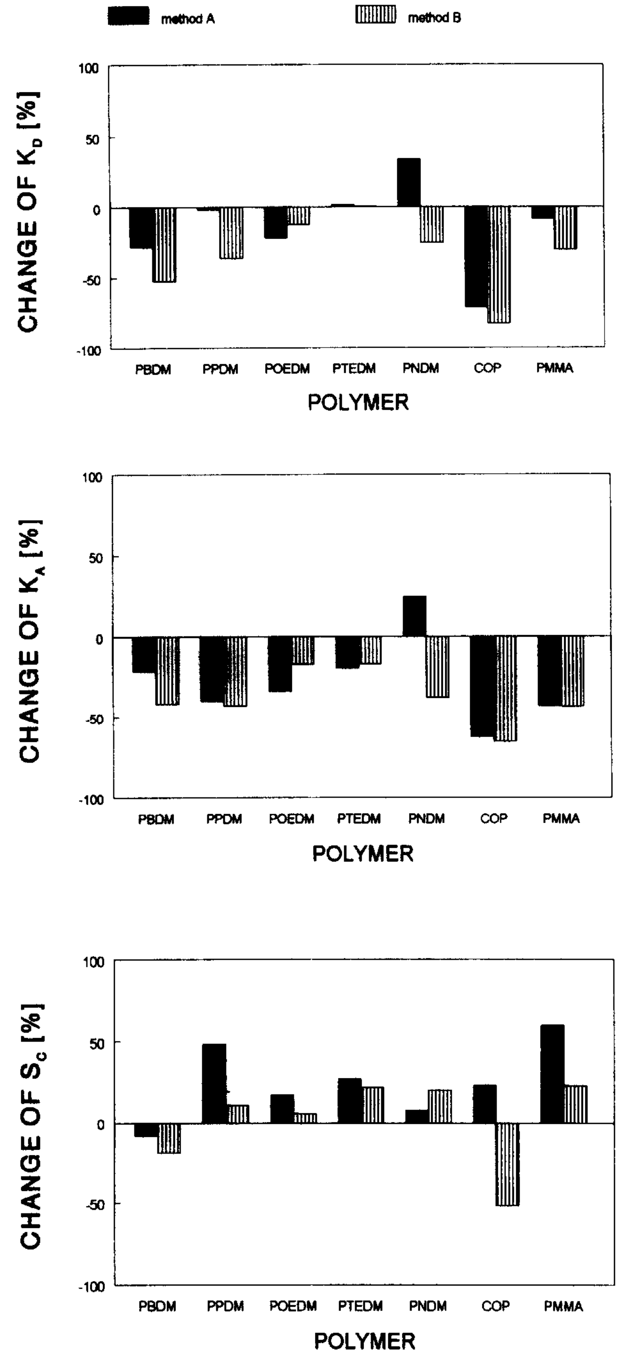


Figure 5 The relative change of the surface characteristics for the examined polymers determined according to methods A and B after the annealing at 80°C under helium

Table 10 Sensitivity of surface characteristics to the presence of heteroatom $[(P_{max} - P_{min})/P_{max}] \times 100\%^a$

Parameter	Method A	Method B
K_D	74.3	79.2
K_A	84.9	75.9
S_C	95.1	93.9

^{a} P denotes K_D, K_A or S_C parameter

CONCLUSIONS

The i.g.c. experiments in conjunction with the calculation methods used allowed us to determine separately the ability of the polymer surfaces to nucleophilic and electrophilic interactions (K_A and K_D parameters). The numerical values of K_A and K_D depend highly on the reference state used for ΔG^s determination, but the general trends of variation of parameters found by methods A and B with temperature or with change in the polymer ester group structure are similar. Generally, the surface character (K_D/K_A) of poly(dimethacrylate)s (except the copolymer with MA) is nucleophilic, and the nucleophilicity as well as the total ability to acid–base interactions ($K_A + K_D$) increase after introduction of the amino, sulfide or ether functions into the polymer ester group. The highest influence is exerted by the sulfide group. The increase in the $K_A + K_D$ parameter (obtained by method A) is associated with the decrease in the ability to dispersive interactions γ_s^d, when the parameters are changed as the result of the polymer ester group modification and/or by heating at elevated temperatures. The annealing of the polymers leads to irreversible changes of their surfaces. During heating in the inert atmosphere (He) usually surface deactivation, connected with an increase of the nucleophilic character K_D/K_A is observed.

ACKNOWLEDGEMENT

This work was supported by KBN Grant 7 S201 003 06, which is gratefully acknowledged.

REFERENCES

1 Voelkel, A., Andrzejewska, E., Maga, R. and Andrzejewski, M. *Polymer* 1996, **37**, 455
2 Fowkes, F. M., Ranay, G. S. and Schrick, M. J. *J. Phys. Chem.* 1959, **63**, 1684
3 Bolger, J. C. and Michaels, A. S. in 'Interface Conversion for Polymer Coatings' (Ed. P. Weiss), Elsevier, New York, 1968
4 Lipatov, Yu. S. and Sergeeva, L. M. 'Adsorption of Polymers', Halsteol, New York, 1974
5 Sprensen, P. *J. Paint Technol.* 1975, **47**, 31
6 Pinentel, G. C. and McClellan, A. L. 'The Hydrogen Bond', Freeman, San Francisco, CA, 1960
7 Jensen, W. B. *J. Adhes. Sci. Technol.* 1991, **5**, 1
8 Drago, R. S. and Wayland, B. *J. Am. Chem. Soc.* 1965, **87**, 3571
9 Drago, R. S., Vogel, G. C. and Needham, T. E. *J. Am. Chem. Soc.* 1971, **93**, 6014
10 Gutman, V. 'The Donor–Acceptor Approach to Molecular Interactions', Plenum Press, New York, 1978
11 Riddle, F. L. and Fowkes, F. M. *J. Am. Chem. Soc.* 1990, **112**, 3259
12 Nardin, M., Balard, H. and Papirer, E. *Carbon* 1990, **28**, 43
13 Balard, H., Sidqi, M., Papirer, E., Donnet, J. B., Tuel, A., Hommel, H. and Legrand, A. P. *Chromatographia* 1988, **25**, 712
14 Papirer, E., Balard, H., Rahmani, Y., Legrand, A. P., Facchini, L. and Hommel, H. *Chromatographia* 1987, **23**, 639
15 Sidqi, M., Balard, H., Papirer, E., Tuel, A., Hommel, H. and Legrand, A. P. *Chromatographia* 1989, **27**, 311
16 Sidqi, M., Ligner, G., Jagiello, J., Balard, H. and Papirer, E. *Chromatographia* 1989, **28**, 588
17 Pigois-Landureau, E. and Chehimi, M. M. *J. Appl. Polym. Sci.* 1993, **49**, 183
18 Chehimi, M. M. and Pigois-Landureau, E. *J. Mater. Chem.* 1994, **4**, 741
19 Panzer, U. and Schreiber, H. P. *Macromolecules* 1992, **25**, 3633
20 Osmont, E. and Schreiber, H. P. in 'Inverse Gas Chromatography. Characterization of Polymers and Other Materials'

(Eds D. R. Lloyd, T. C. Ward and H. P. Schreiber), ACS Symposium Series No. 391, American Chemical Society, Washington, DC, 1989, Ch. 17, p. 230
21 Schreiber, H. P., Viau, J.-M., Fetoui, A. and Zhuo Deng *Polym. Eng. Sci.* 1990, **30**, 263
22 Chehimi, M. M., Abel, M.-L., Pigois-Landureau, E. and Delamar, M. *Synth. Met.* 1993, **60**, 183
23 Saint Flour, C. and Papirer, E. *J. Colloid Interface Sci.* 1983, **91**, 69
24 Dong, S., Brendle, M. and Donnet, J. B. *Chromatographia* 1989, **28**, 469