Polymer Vol. 39 No. 15, pp. 3499–3506, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10061-1

Examination of surfaces of solid polymers by inverse gas chromatography. 3. The influence of the annealing time

Ewa Andrzejewska*, Adam Voelkel, Rajab Maga and Maciej Andrzejewski
Poznań University of Technology, Institute of Chemical Technology and Engineering, Pl. M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland
(Accepted 11 July 1997)

Inverse gas chromatography (IGC) has become the most easily accessible and widely used method for characterization of solid materials. The changes in surface properties of a series of poly(dimethacrylates): poly(butane-1,4-diol dimethacrylate) (PBDM), poly(pentane1,5-diol dimethacrylate) (PPDM), poly(2,2′-thiobisethanol dimethacrylate) (PTEDM) and poly(2,2′-oxybisethanol dimethacrylate) (POEDM) were monitored for a long annealing time under helium atmosphere at 80°C. The surface properties were quantified by the dispersive component of surface free energy, as well as by K_D and K_A parameters which reflect the ability of the surface to act as an electron donor and electron acceptor, respectively. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: inverse gas chromatography; poly(dimethacrylates); annealing)

INTRODUCTION

Inverse gas chromatography (IGC) may be successfully applied in the examination of the surface properties of solid polymers (Refs [1,2] and papers cited therein). The surface may be characterized by: (i) its ability to undergo dispersive interactions, i.e., dispersive component of surface free energy γ_s^d and $C'P_{DS}$ parameter [1,3]; (ii) its ability to act as an electron donor or acceptor which is described by parameters K_D and K_A, respectively, as well as by the $S_C = K_D/K_A$ parameter describing the surface character. The evaluation of these parameters is described shortly below.

The specific component of free energy of adsorption may be evaluated by using two reference states, i.e., the retention data are related to the saturated vapour pressure P^o (ΔG^o *versus* log P^o) or to molecular polarizability P_D (ΔG^o *versus* P_D).

The vertical distance between the *n*-alkane plot and the data for the polar probe of interest gives a ΔG^s value:

$$-\Delta G^s = -(\Delta G^o - \Delta G^d) = RT \times \ln(V_N/V_{N,ref}) \qquad (1)$$

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 provides the possibility of determining the enthalpy of specific interactions ΔH^s[5]:

$$\Delta H^s = \frac{\delta(\Delta G^s/T)}{\delta(1/T)} \qquad (2)$$

Enthalpies of specific interactions between the examined surface and the test solute may be correlated to acid–base properties through the following equation[5]:

$$-\Delta H^s = K_D \times AN^* + K_A \times DN \qquad (3)$$

where AN^* and DN are the acceptor and donor number of the test solute on the Riddle–Fowkes[6] or Gutman[7] scale, respectively; parameters K_A and K_D reflect the ability of the examined surface to act as an electron acceptor and electron donor, respectively.

In our earlier papers[1,2] we presented the surface characteristics for a series of polymers differing only in the presence and type of heteroatom in the ester group. A further two reference polymers were characterized by means of this method. The changes in surface properties caused by structural changes and/or annealing of polymers were reflected by: (i) dispersive parameters γ_s^d and $C'P_{DS}$ (introduced by Dong and Donnet [1,3]); (ii) the specific component of free energy of adsorption determined according to Papirer's, $-\Delta G^{s(P)}$[4], and Dong-Donnet's, $-\Delta G^{s(D)}$[3] approach (methods A and B, respectively—for details see Experimental); (iii) acid–base properties, i.e., parameters K_D and K_A and their ratio $S_C = K_D/K_A$.

Owing to the use of two reference states (P^o and P_D), two different values of ΔG^s were available at each experimental temperature. The values of $-\Delta G^s$ depend on the chosen reference state. Those determined by using P^o as the reference state ($-\Delta G^{s(P)}$—method A) were lower than those found by using P_D as the reference state ($-\Delta G^{s(D)}$—method B)[2].

The specific component of enthalpy of adsorption was calculated from $-\Delta G^{s(P)}$ and $-\Delta G^{s(D)}$ values according to equation (2). This led to two series of numerical values of the specific component of enthalpy of adsorption and resulted in two series of surface parameters K_D, K_A and their ratio $S_C = K_D/K_A$.

In Refs [1,2] the examined polymers were characterized before and after annealing at a fixed time (3 h) at elevated temperatures (80 and 160°C) under air and helium atmospheres. It was found that chemically similar polymers may be differentiated in terms of their dispersive parameter[1]. The values of γ_s^d and $C'P_{DS}$ depend on the temperature of IGC experiment, which is determined by the relative temperature gradient. During annealing at

---

* To whom correspondence should be addressed

elevated temperatures the surfaces of the polymers undergo significant modification. The magnitude and direction of the changes observed depend on the polymer and the type of annealing atmosphere. Linear relationships were found between γ_s^d and $C'P_{DS}$. K_D and K_A parameters were calculated using various reference states for -ΔG^s determination[2].

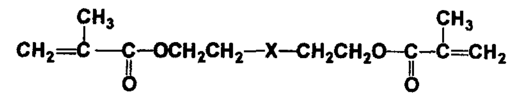
It was found that the introduction of the sulfide, ether or amino functions into the polymer ester group causes both an increase in the nucleophilicity (K_D/K_A) and in the total ability of the surface to undergo acid–base interactions ($K_D + K_A$). The greatest influence is exerted by the sulfide group. The increase in the ($K_D + K_A$) parameter (method A) is associated with a decrease in the ability to undergo dispersive interactions. The annealing of the polymers leads to irreversible changes of their surfaces. During heating in an inert atmosphere (He), surface deactivation resulting from the decay or modification of active centres associated with functional groups usually occurs. This is manifested by a decrease in ($K_D + K_A$) values and an increase in the ability of the surface to undergo dispersive interactions, e.g., γ_s^d values [2].

In the present paper we continued our investigations, taking into account the influence of the annealing time upon the surface properties of polymers. The changes occurring during annealing were characterized by changes in dispersive properties, specific component of free energy of adsorption and the acid–base properties of the surfaces of polymers.

EXPERIMENTAL

The polymers were obtained and purified as described previously[1]. The following polymers were studied: poly(2,2′-thiobisethanol dimethacrylate), PTEDM; poly(2,2′-oxybisethanol dimethacrylate), POEDM; 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:



$CH_2{=}C(CH_3){-}C({=}O){-}OCH_2CH_2{-}X{-}CH_2CH_2O{-}C({=}O){-}C(CH_3){=}CH_2$

X= S : TEDM; X= O : OEDM;

X= CH₂ : PDM; X= - : BDM.

The investigated polymers were crushed, sieved and sized. The GC column used was stainless steel tubing, 1 m length, 3 mm (I.D.). Before the experiment the column was washed with a suitable solvent and packed with a known amount of the polymer. The flow rate of the carrier gas was established at 30 ml/min. The filled column was conditioned at 50°C for 3 h and the column temperature was increased to 80°C. The retention data of the test solutes were collected (at 50–70°C) after 1, 2, 3, 6, 12 and 24 h of annealing at 80°C under helium. The test solutes were the same as previously used[1,2].

The specific component of free energy of adsorption was evaluated via two methods of reference states, i.e,. the retention data were related to the saturated vapour pressure P^o (method A) (G^o *versus* log P^o)[2,4] or to molecular polarization P_D (G^o *versus* P_D) (method B)[2,5]. Owing to the use of two reference states two different values of ΔG^s were available at each experimental temperature. The surface parameters were calculated with the use of equation (3).

Table 1 The influence of annealing time on dispersive properties of the polymers studied {[γ_s^d in mJ/m^2] and [$C'P_{DS}$ in kJ/cm^3]}

	Parameter measured at [°C]		Initial polymer	After annealing time 1 h	2 h	3 h	6 h	12 h	24 h
PPDM		50°C	30.1	30.1	30.2	30.4	30.8	30.9	31.1
	γ_s^d	60°C	29.6	29.7	29.9	30.1	30.3	30.4	30.6
		70°C	28.9	28.9	29.3	29.9	30.1	30.1	30.1
		50°C	1.13	1.14	1.16	1.18	1.26	1.32	1.34
	$C'P_{DS}$	60°C	1.04	1.09	1.12	1.16	1.18	1.20	1.22
		70°C	0.92	0.95	0.98	1.07	1.08	1.10	1.12
PBDM		50°C	27.0	27.2	27.5	27.9	28.0	28.1	28.2
	γ_s^d	60°C	26.8	26.9	26.9	26.9	27.1	27.2	27.3
		70°C	26.4	26.4	26.5	26.6	26.9	27.1	27.1
		50°C	1.00	1.07	1.13	1.17	1.18	1.19	1.19
	$C'P_{DS}$	60°C	0.96	0.97	0.98	0.99	1.03	1.06	1.07
		70°C	0.88	0.90	0.91	0.92	0.95	0.97	1.03
PTEDM		50°C	25.3	25.9	26.7	27.1	28.3	29.6	31.9
	γ_s^d	60°C	24.6	24.8	24.9	24.9	26.2	27.5	31.1
		70°C	24.1	24.1	24.2	24.3	25.1	26.3	30.3
		50°C	0.63	0.77	0.89	1.01	1.25	1.44	1.53
	$C'P_{DS}$	60°C	0.55	0.63	0.74	0.83	0.91	0.99	1.47
		70°C	0.44	0.51	0.59	0.61	0.77	0.85	1.35
POEDM		50°C	26.7	26.3	25.9	25.6	25.2	25.0	24.9
	γ_s^d	60°C	25.8	25.4	25.1	24.9	24.8	24.4	24.3
		70°C	25.1	24.7	24.3	24.1	24.0	24.0	23.9
		50°C	0.92	0.86	0.80	0.76	0.64	0.62	0.59
	$C'P_{DS}$	60°C	0.73	0.69	0.64	0.58	0.55	0.52	0.47
		70°C	0.62	0.53	0.49	0.43	0.41	0.40	0.38

RESULTS AND DISCUSSION

The dependence of dispersive properties of polymers on the annealing time

The influence of the annealing time on dispersive properties of the polymers is given in *Table 1*. Elongation of the annealing time causes most often an increase in the ability to undergo dispersive interactions of the polymer surface. The dispersive component of surface free energy γ_s^d measured at 50°C for PPDM increased from 30.1 to 30.4 mJ/m^2 after 3 h of annealing and further to 31.1 mJ/m^2 after 24 h. The corresponding values obtained previously[1] for annealing at 80°C (3 h) and 160°C (3 h) were equal to 30.3 and 31.5 mJ/m^2, respectively. That means that prolonged annealing at an elevated temperature leads to similar changes in the dispersive properties of the surface as heating for shorter times at a much higher temperature. For

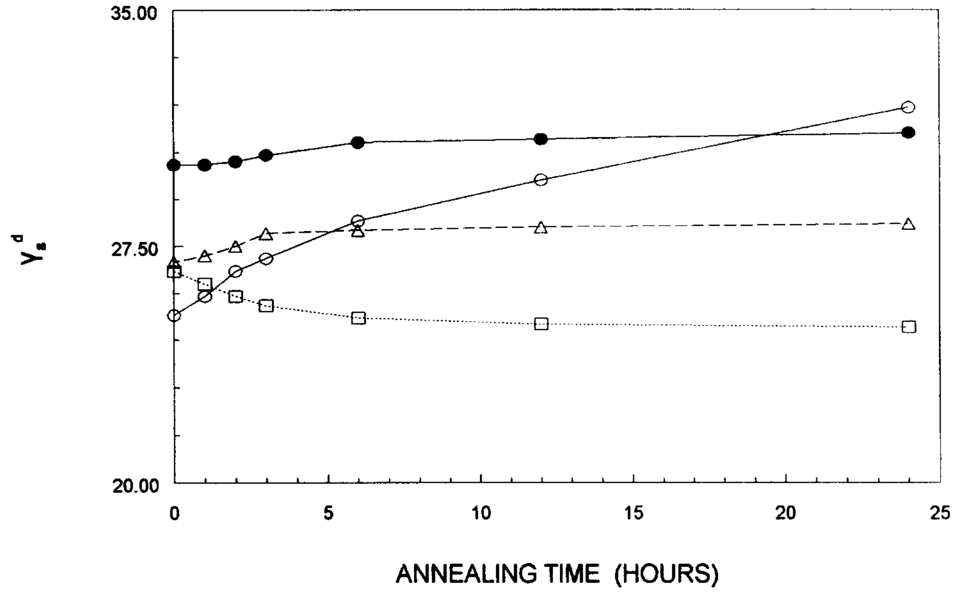


Figure 1 The influence of the annealing time on the dispersive component of surface free energy γ_s^d [mJ/m^2] at 50°C of the polymers studied (●, PPDM; △, PBDM; ○, PTEDM; □, POEDM)

Table 2 The influence of the annealing time on $-\Delta G^{s(P)}$ [J/mol] values for PBDM (method A) Part 1

Solute	$-\Delta G^s$ values after given annealing time at 80°C											
	Initial			1 h			2 h			3 h		
	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C
Benzene	1625	1587	1582	1284	1135	1065	785	699	574	185	169	144
Acetone	2302	2247	2172	2121	2073	1932	1532	1325	1116	532	335	216
Ether	2060	1887	1784	1836	1645	1562	1325	1221	1033	345	221	114
$CHCl_3$	3080	2873	2823	2812	2674	2546	1623	1544	1385	584	439	337
CH_2Cl_2	4285	4030	3965	4066	3829	3753	1796	1567	1396	752	513	347
Dioxane	2488	2350	2191	2211	2122	1915	1700	1576	1431	658	521	341
EtOH	2048	1685	1338	1925	1586	1298	1743	1502	1226	732	496	228

Table 3 The influence of the annealing time on $-\Delta G^{s(P)}$ [J/mol] values for PBDM (method A) Part 2

Solute	$-\Delta G^s$ values after given annealing time at 80°C								
	6 h			12 h			24 h		
	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C
Benzene	173	149	134	161	141	129	153	138	125
Acetone	525	315	199	516	306	189	492	297	183
Ether	330	218	106	328	207	102	307	199	99
$CHCl_3$	226	402	335	529	399	328	501	388	317
CH_2Cl_2	711	501	347	690	496	337	613	476	328
Dioxane	651	525	367	601	514	326	570	493	319
EtOH	729	491	217	711	482	203	692	471	194

Table 4 The influence of the annealing time on $-\Delta G^{s(D)}$ [J/mol] values for PBDM (method B) Part 1

	$-\Delta G^s$ values after given annealing time at 80°C											
	Initial			1 h			2 h			3 h		
Solute	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C
Benzene	2625	2587	2582	2553	2381	2325	1602	1412	1332	1182	1168	1125
Acetone	3302	3147	3072	3292	3087	3032	2178	1997	1796	1582	1362	1197
Ether	3060	2887	2784	2987	2673	2584	2014	1834	1695	1348	1234	1088
$CHCl_3$	4080	3773	3413	3857	3546	3312	2416	2305	2125	1593	1416	1203
CH_2Cl_2	5285	4730	4199	4621	4451	3976	2845	2387	2147	1725	1489	1225
Dioxane	3488	3035	2611	3245	3046	2712	2214	2036	1785	1673	1412	1235
EtOH	3048	2685	2330	2879	2578	2299	2156	1925	1768	1736	1524	1232

Table 5 The influence of the annealing time on $-\Delta G^{s(D)}$ [J/mol] values for PBDM (method B) Part 2

	$-\Delta G^s$ values after given annealing time at 80°C								
Solute	6 h			12 h			24 h		
	50°C	60°C	70°C	50°C	60°C	70°C	50°C	60°C	70°C
Benzene	1164	1151	1121	1155	1142	1118	1042	987	935
Acetone	1562	1339	1297	1551	1304	1275	1489	1294	1251
Ether	1331	1214	1072	1317	1203	1054	1301	1185	1002
$CHCl_3$	1579	1410	1219	1561	1397	1218	1502	1373	1211
CH_2Cl_2	1695	1451	1228	1646	1432	1227	1518	1371	1224
Dioxane	1615	1401	1202	1561	1388	1175	1462	1373	1152
EtOH	1726	1517	1212	1717	1505	1195	1697	1493	1182

long annealing times a saturation effect in γ_s^d increase is observed. This effect may be the result of a transformation of inactive and/or slightly active centres in dispersive interactions. Owing to thermal reactions their ability to interact by dispersive forces significantly increases (*Figure 1*). Relations similar to those found for PPDM were observed for PBDM and PTEDM. In the latter case the increase in both γ_s^d and $C'P_{DS}$ values with annealing time was significant but this process was not completed after 24 h of heating, which may point to the high sensitivity of the

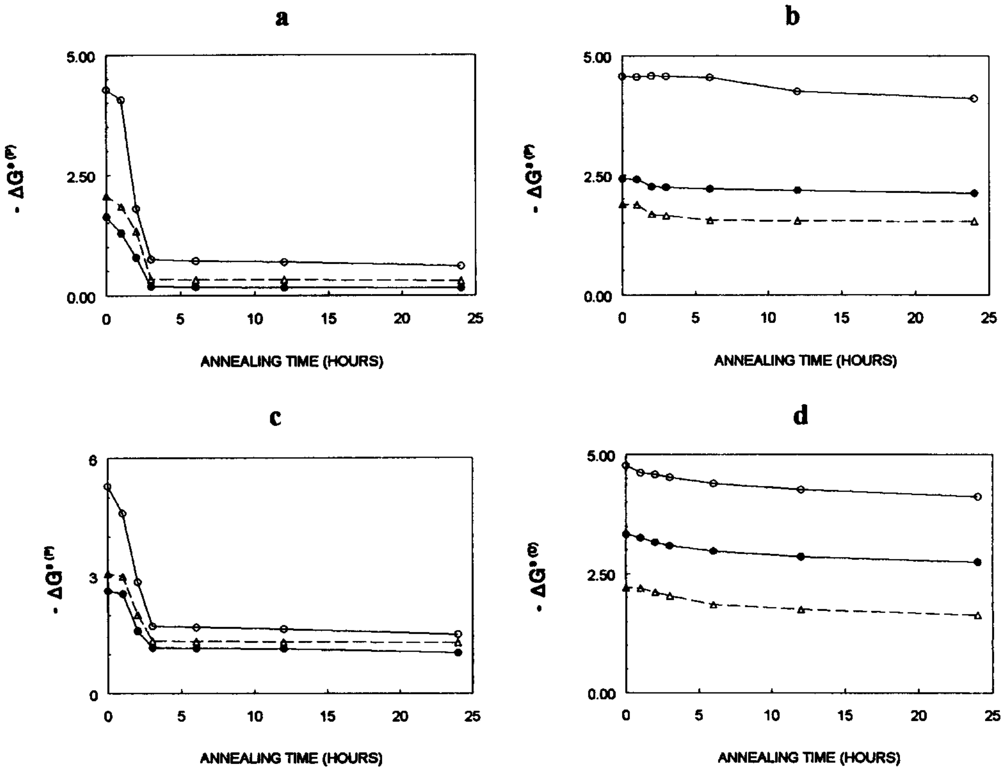


Figure 2 The annealing time impact on the free energy of acid–base interactions $-\Delta G^s$ [kJ/mol] for PBDM (a, c) and PPDM (b, d) determined according to the method A (a, b) and method B (c, d) approach (●, benzene; △, ether; ○, CH_2Cl_2)

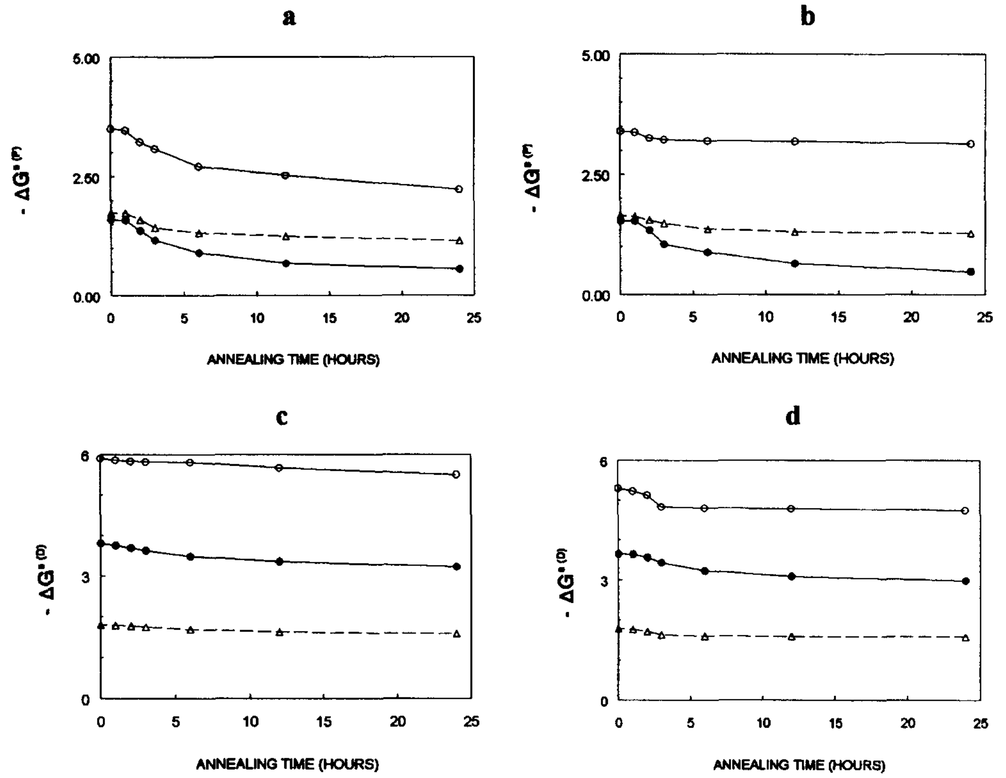


Figure 3 The annealing time impact on the free energy of acid–base interactions $-\Delta G^{\mathrm{S}}$ [kJ/mol] for PTEDM (a, c) and POEDM (b, d) (symbols as in *Figure 2*)

surface of this polymer to thermal treatment. An exceptional behaviour exhibits POEDM. In contrast to its sulfur and carbon analogues its $\gamma_{\mathrm{s}}^{\mathrm{d}}$ and $C'P_{\mathrm{DS}}$ values decrease with the increase in annealing time. Thus, in this case part of the active centres responsible for dispersive interactions undergo a thermal transformation which decreases their activity. In conclusion, we can say, that thermal treatment increases the ability of the surfaces of the polymers studied to dispersive interactions (the only exception being POEDM).

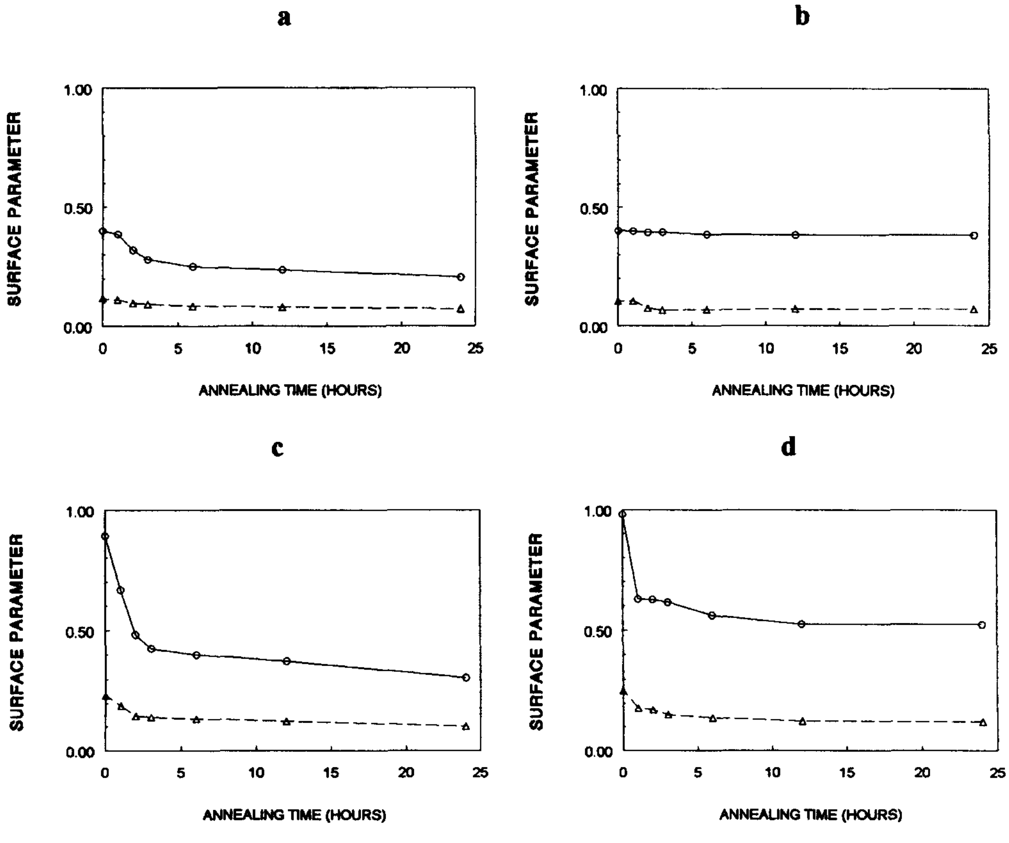


Figure 4 The influence of annealing time on K_{D} and K_{A} values for PBDM (a, c) and PPDM (b, d) evaluated by method A (a, b) or method B (c, d) (○, K_{D}; △, K_{A})

The influence of annealing time on the specific component of free energy of adsorption

The increase in the annealing time causes a significant decrease in the $-\Delta G^s$ values determined according to both methods, A and B. The exemplary data presenting the influence of the annealing time on $-\Delta G^s$ are given in *Table 2* and *Table 3* (method A) and *Table 4* and *Table 5* (method B). The data for the initial polymers were published earlier[2]. According to the results obtained previously[2], method B gives much higher values of $-\Delta G^s$ than method A (*Figures 2 and 3*). The rate of $-\Delta G^s$ decrease is significant during the first 3–6 h of annealing. Further heating causes much smaller changes of the parameters examined. One should note a very sharp decrease of $-\Delta G^s$ observed for PBDM (first 3 h, *Figure 2*) and slight decrease of $-\Delta G^s$ for PTEDM and PPDM. (*Figure 3*). The $-\Delta G^s$ value for methylene chloride on PBDM decreased from 4285 J/mol (initial polymer, 50°C) to 328 J/mol after 24 h of annealing (*Tables 2 and 3*)[2]. For the sake of comparison, the corresponding values found on PTEDM changed only from 3472 to 1795 J/mol.

The decrease of $-\Delta G^s$ values during annealing determined according to method A was more substantial than that found from method B (*Figure 3*). For PPDM the decrease of both $-\Delta G^s$ parameters is almost linear within the whole period considered. Generally, the changes in the acid–base component of the free energy of adsorption indicate an increasing deactivation of the surfaces during annealing at 80°C under helium. Bearing in mind that both $-\Delta G^s$ values depend on the type of the surface and the solute as well as on the selected reference state, it is much better to discuss the influence of the annealing time with the use of surface parameters (*Figures 4–6*).

The annealing time impact on acid–base properties

During the first 3 h of annealing, a significant decrease in the surface ability to undergo electron–donor interactions (K_D) was observed. The rate of the change varied from polymer to polymer and depended also on the method used for the evaluation of surface parameters. The most significant decrease was found again for PBDM (both methods A and B, *Figure 4a* and *c*). A slight difference was observed in PTEDM behaviour: its K_D parameter began to decrease later, between the third and fifth hour of the annealing experiment (*Figure 5*, method A). The longer experiment did not cause any serious variations of K_D. Similar relations between the annealing time and the surface parameter were observed for electron–acceptor ability (K_A).

However, the decrease of this parameter is less substantial than K_D. Only for PBDM was a permanent but small decrease in the K_A parameter found. It was interesting to compare K_D and K_A values found after 3 and 24 h of annealing with those found in previous experiments[2] at 80°C (3 h, He) and at 160°C (3 h, He), respectively. Results of both experiments after 3 h of annealing at 80°C are very close. A comparison of K_D and K_A values leads to the following conclusion: a long (24 h) annealing time did not cause the same deactivation of the polymer's surface as a relatively short conditioning at elevated temperature (160°C) (*Table 6*). All values found after 24 h at 80°C are significantly higher that those reported earlier for annealing at 160°C, which points to a much higher activity of the surface. This seems to indicate that the polymer surface after a relatively long treatment at medium temperature undergoes less deactivation than after a short annealing in extreme conditions.

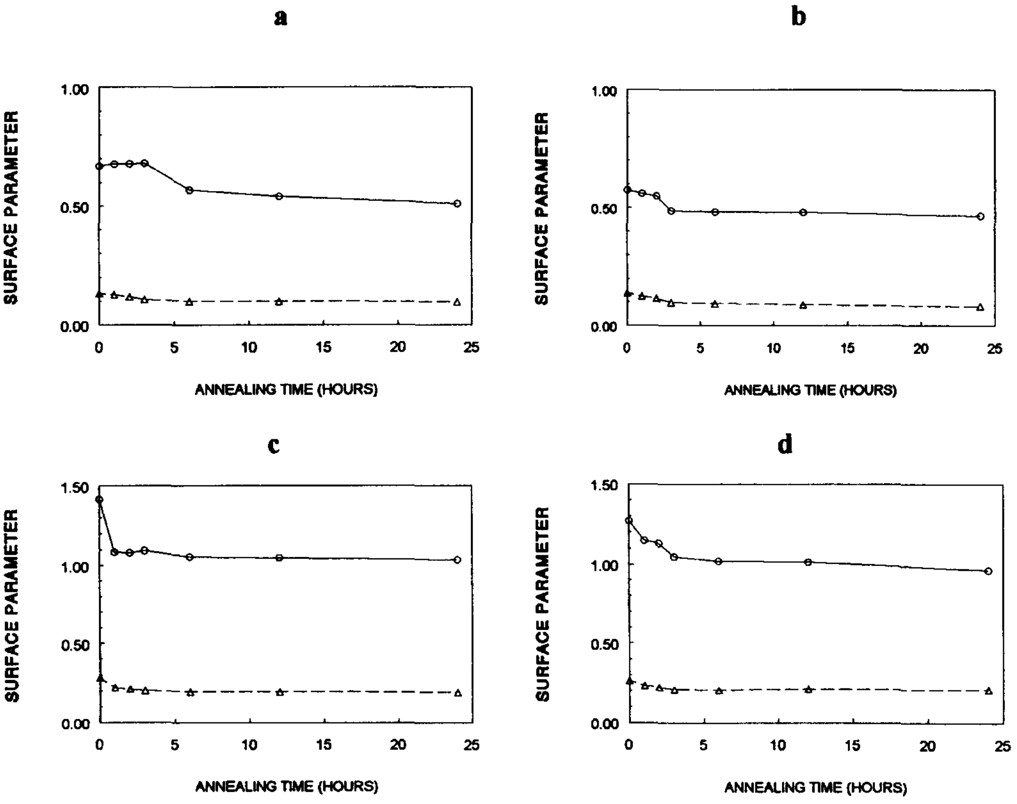


Figure 5 The influence of annealing time on K_D and K_A values for PTEDM (a, c) and POEDM (b, d) evaluated by method A (a, b) method B (c, d) (symbols as *Figure 4*)

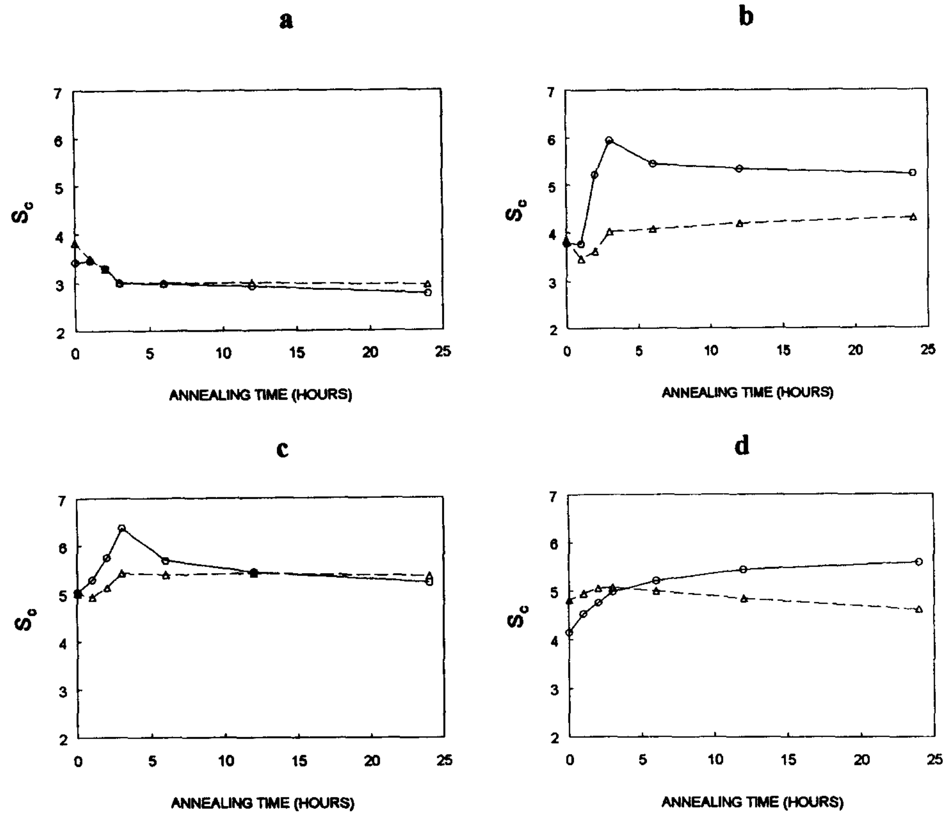


Figure 6 The influence of annealing time on the surface character of the polymers examined: (a) PBDM; (b) PPDM; (c) PTEDM; (d) POEDM (○, method A; △, method B)

Table 6 Comparison of surface parameters after 24 h annealing at 80°C and 3 h annealing at 160°C

Polymer	Method	Parameter	Annealing time	
			3 h at 160°C[2]	24 h at 80°C
PBDM	A	K_D	0.153	0.205
		K_A	0.066	0.074
		S_C	2.317	2.764
	B	K_D	0.225	0.306
		K_A	0.076	0.104
		S_C	2.960	2.953
PPDM	A	K_D	0.375	0.383
		K_A	0.073	0.073
		S_C	5.167	5.237
	B	K_D	0.511	0.524
		K_A	0.115	0.122
		S_C	4.443	4.309
PTEDM	A	K_D	0.480	0.509
		K_A	0.092	0.097
		S_C	4.937	5.224
	B	K_D	1.028	1.038
		K_A	0.193	0.193
		S_C	5.330	5.363
POEDM	A	K_D	0.451	0.464
		K_A	0.082	0.083
		S_C	5.492	5.576
	B	K_D	0.847	0.965
		K_A	0.173	0.209
		S_C	4.896	4.613

The influence of annealing time on surface character

The surface character expressed by the $S_C = K_D/K_A$ parameter for all the polymers examined is bigger than 1, which indicates that the nucleophilic character prevails. The S_C parameter changes during the annealing. In the first period of conditioning (< 6 h) the nucleophilic character of the surfaces of PTEDM and POEDM increased (*Figure 6*). A similar variation of the surface character was found for PPDM despite a small decrease of the S_C parameter after the first hour of annealing. Further annealing led to a slow decrease of the basic character of the polymer surfaces. However, one should note the different direction of the changes of the S_C parameter found using methods A and B. A comparison of the surface character after 24 h annealing at 80°C and after 3 h of annealing at 160°C shows that the values of both sets of S_C are very close. However, 24 h of annealing causes most often a smaller decrease in the surface nucleophilicity (K_D) and acidity (K_A) than after a short (3 h) conditioning at 160°C (*Table 6*).

CONCLUSIONS

The influence of annealing time upon surface parameters was found to be significant. During the first 3 h of annealing a large decrease in K_A and K_D parameters was observed. Further annealing did not cause any serious variations of both parameters. A comparison of the results collected after 24 h of annealing at 80°C with those found in earlier experiments after 3 h of annealing at 160°C indicated that the surface exhibited a higher activity (values of K_A and K_D parameters) following prolonged heating under relatively mild conditions than after a short conditioning at high temperature. Despite this, the values of the S_C parameter obtained after annealing according to both procedures were very similar. The difference in the rates of the decrease in K_D and K_A parameters led to the appearance of a maximum on the S_C *versus* annealing time plot. The occurrence of the maximum along with continuous deactivation of the surface (decrease of K_D and K_A) may indicate that: (i) polar active centres of different chemical composition (ester, ether, thioether) undergo thermal reactions; elevated temperatures lead most often to a modification of the surface which lowers its acid–base character; (ii) in the first period of annealing a significant part of active centres undergo thermal consecutive reactions, during which their ability to undergo nucleophilic interactions initially increases; functional groups, being the result of these reactions, are not thermally stable and participate in further transformations to centres having weaker nucleophilic character.

ACKNOWLEDGEMENTS

This work was supported by PUT grants BW 32/237/96 and DS 32/271/96, which are gratefully acknowledged.

REFERENCES

1. Voelkel, A., Andrzejewska, E., Maga, R. and Andrzejewski, M., *Polymer*, 1996, **37**, 455.
2. Andrzejewska, E., Voelkel, A., Andrzejewski, M. and Maga, R., *Polymer*, 1996, **37**, 4333.
3. Dong, S., Brendle, M. and Donnet, J. B., *Chromatographia*, 1989, **28**, 469.
4. Saint Flour, C. and Papirer, E., *J. Colloid Interface Sci.*, 1983, **91**, 69.
5. Nardin, M., Balard, H. and Papirer, E., *Carbon*, 1990, **28**, 43.
6. Riddle, F. L. and Fowkes, F. M., *J. Am. Chem. Soc.*, 1990, **112**, 3259.
7. Gutman, V., *The Donor–Acceptor Approach to Molecular Interactions*. Plenum Press, New York, 1978.