Characterization of dispersive and acid–base properties of crosslinked polymers by inverse gas chromatography

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The dispersive and acid–base properties of the surfaces of two poly(dimethacrylate)s were examined by inverse gas chromatography in terms of parameters expressing the ability of the surface to accept or donate electrons. These parameters appeared to be sufficiently sensitive to describe the changes occurring on the surface during thermal treatment and to describe variations in the ester group structure.

(Keywords: inverse gas chromatography; acid–base properties; crosslinked polymers; poly(dimethacrylate)s)

Introduction

The surface properties of solid organic polymers significantly influence their adhesive properties, wettability, friction, coating ability, permeability, corrosion and biocompatibility. The presence of acidic and basic centres on the polymer surface increases specific intermolecular interactions with solvents, plasticizers, other polymers and fillers. The susceptibility of the surface to changes in its acid–base characteristic determines the practical applications of polymers.

The surface properties of any solid, e.g. a polymer, may be examined by inverse gas chromatography (i.g.c.). The material of interest is placed into the chromatographic column and carefully selected volatile probes are injected at infinite dilution. The retention parameters of testing probes depend on the nature and the magnitude of solute–polymer intermolecular interactions[1–14]. Both dispersive and acid–base interactions contributing to the work of adhesion may be determined by i.g.c.

Dispersive properties may be successfully quantified by the dispersive component of surface free energy γ_s^D calculated according to Dorris and Gray[15]:

$$\gamma_s^D = \frac{(\Delta G_{CH_2})^2}{4N^2 a_{CH_2}^2 \gamma_{CH_2}} \qquad (1)$$

where N is the Avogadro number, a_{CH_2} the cross-sectional area of an adsorbed methylene group (0.06 nm^2), γ_{CH_2} the surface free energy of polyethylene surface and ΔG_{CH_2} the free energy of adsorption increment for a methylene group.

Until now only the dispersive properties of organic polymers with high molecular weight have been studied extensively. Most work concerning specific (polar) interactions has been limited to determination of the sum of dispersive and specific components of the free energy of adsorption and has been unable to characterize acidic and basic properties separately.

Vidal *et al.*[10] in work concerning modified silicas, defined the surface free energy of specific interactions ΔG_{sp} as the difference in energy of interaction between a polar testing probe and a hypothetical reference *n*-alkane having the same vapour pressure as the polar probe. The enthalpy of specific interactions ΔH_{sp} may be determined from the temperature dependence of ΔG_{sp}. Papirer and co-workers[4,6] correlated this value with the so-called acceptor number (*AN*, non-dimensional units) and donor number (*DN*, in kcal mol^{-1}) of testing solutes as expressed in the semi-empirical Gutman scale[16]:

$$-\Delta H_{sp} = K_A DN + K_D AN \qquad (2)$$

where K_A and K_D represent the ability of a given surface to interact as, respectively, electron acceptor or electron donor.

The literature contains much more data on the *AN* and *DN* of solutes than is available for Drago's system based on an analogous relation but with different parameters. It is therefore possible to use a set of testing solutes representing acidic, basic and amphoteric character.

Papirer's method for determination of ΔG_{sp} has been used by several authors to characterize mineral solids, carbon fibres and carbon fibres treated with epoxy resin[14]. Some recent work concerning conductive polymers (polypyrroles) has appeared[12,13,17], but those authors prefer to describe the polymer surface properties in terms of Drago's parameters[17].

Very recently Panzer and Schreiber[18] reported on the acid–base characteristic of a polycarbonate determined by i.g.c. according to Papirer's method but using acceptor number (*AN**) values modified for dispersive contribution and expressed in kcal mol^{-1} (ref. 19). The polycarbonate examined was coated onto a support.

In our work we decided to test Papirer's method for determining ΔG_{sp} as well as K_D and K_A by using Gutman's *DN* values[16] and *AN** modified according to Riddle and Fowkes[19] for characterization of the surface properties of insoluble or crosslinked organic polymers. In this case the crushed polymers were placed into the column directly without any support. As the first subject of investigation we chose highly crosslinked dimethacrylates obtained by photopolymerization, since this group of polymers and this method of their preparation have found practical applications in the production of protective layers, for which surface properties are of special importance. The polymers selected were two analogous poly(dimethacrylate)s

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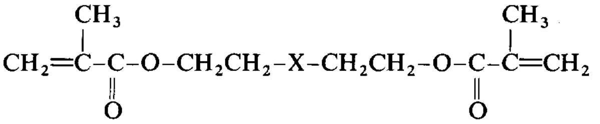
differing only in the heteroatom introduced to their ester groups.

The aim of the work was to determine and compare dispersive and acid–base properties of the polymers and to check the thermal dependence of their surface properties. This paper presents preliminary results of our investigation.

Experimental

The polymers were obtained by photopolymerization of 2,2′-oxybisethanol dimethacrylate (OEDM) and 2,2′-thiobisethanol dimethacrylate (TEDM) in the presence of 0.01 M α,α-dimethoxy-α-phenylacetophenone (Irgacure 651 from Ciba-Geigy) in argon atmosphere. The monomers were synthesized as described elsewhere[20].



$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_2CH_2-X-CH_2CH_2-O-\underset{\underset{O}{\|}}{C}-\overset{CH_3}{\overset{|}{C}}{=}CH_2$$

X=O: OEDM
X=S: TEDM

The polymers were crushed, sieved and placed into the chromatographic columns. The conditions for the i.g.c. experiment were as follows: gas chromatograph, Jeol JGC 1100; detector, f.i.d.; columns, stainless steel, 1 m long, 3 mm i.d.; oven temperature, 50, 60 and 70°C; injector, detector, 150°C; carrier gas, helium, 30 cm^3 min^{-1}; conditioning time, overnight under helium.

The testing probes used were n-alkanes C_6–C_{12}, methanol, ethanol, propanol-1, butanol-1, propanone-2, butanone-2, pentanone-2, benzene, toluene, xylene, ethylbenzene, ether, chloroform, methylene chloride, dioxane-1,4. Probes were injected at infinite dilution by 1 μl Hamilton gas-tight syringe.

Two series of experiments were carried out, under helium and under air, to check the thermal dependence of the surface properties of polymers. The basic experiment was carried out after a short conditioning of the polymer probe under helium. The polymer was then heated (in the column) in the chosen atmosphere at elevated temperature, i.e. 80°C, for 3 h followed by measurement 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 measured. The temperatures of 80 and 160°C were selected after d.t.a.–t.g. analysis of the polymers[21]. Just after 80°C in air, both polymers begin to lose weight and at 160°C the weight loss achieves 3% for polyOEDM and 2% for polyTEDM, whereas the rapid destruction of polymers sets in at about 180 and 240°C, respectively.

Results

The dispersive character of the polymer surface is quantified by the dispersive component of surface free energy. Values of this parameter determined for OEDM and TEDM polymers at 50°C are presented in *Tables 1* and *2* respectively. Values of γ_s^D (both for polyOEDM and polyTEDM) are much lower in comparison to values reported for silicas[10], carbon fibres[6] or conducting polymers[13]. These values decrease with increasing temperature, i.e. values of γ_s^D at 50, 60 and 70°C, respectively, are 2.66, 1.31 and 0.36 mJ m^{-2} for polyOEDM and 0.61, 0.44 and 0.40 mJ m^{-2} for polyTEDM.

Samples of polyOEDM and polyTEDM behave differently when heated. For polyOEDM, γ_s^D decreases after heating at 80 and 160°C whereas for polyTEDM γ_s^D increases significantly from 0.61 and 3.66 mJ m^{-2}. The same γ_s^D values were obtained after heating under helium and air, therefore we can conclude that the heating atmosphere does not influence the changes of dispersive parameter.

A comparison of the acid–base properties represented by K_A and K_D values for the two polymers shows that the surface of polyOEDM possesses much higher activity than that of polyTEDM (it is 15 times more acidic and about 30 times more basic). The surface character of both polymers is amphoteric, although for polyOEDM the basicity and acidity of the surface are almost balanced whereas for polyTEDM the acidity prevails.

Table 1 Dispersive and acid–base characteristics of polyOEDM

	Probe no. 1 heated under He			Probe no. 2 heated under air		
	before heating	at 80°C	at 160°C	before heating	at 80°C	at 160°C
γ_s^D (mJ m^{-2}) at 50°C	2.66	1.31	0.36	2.66	1.31	0.36
K_A	0.653	0.137	0.032	0.653	0.148	0.705
K_D	0.685	0.071	0.016	0.685	0.076	0.363
K_D/K_A	1.049	0.515	0.515	1.049	0.515	0.515

Table 2 Dispersive and acid–base characteristics of polyTEDM

	Probe no. 1 heated under He			Probe no. 2 heated under air		
	before heating	at 80°C	at 160°C	before heating	at 80°C	at 160°C
γ_s^D (mJ m^{-2}) at 50°C	0.61	2.79	3.66	0.62	2.71	3.63
K_A	0.045	0.127	0.662	0.045	0.771	0.552
K_D	0.023	0.066	0.341	0.023	0.397	0.284
K_D/K_A	0.511	0.515	0.515	0.511	0.515	0.515

Annealing of the polymers is accompanied by changes in their acid–base characteristics. Heating polyOEDM both in air and helium at 80°C causes a significant decrease of K_A and K_D, indicating a stepwise decay of functional groups and/or their modification. The K_D/K_A ratio changes, which suggests either a change in the ratio of acidic to basic centres or a change in their activity, which leads to a less basic character than before. The changes of the two parameters are similar at 80°C both in air and helium, which proves that they are not caused by the oxidation process. Further heating at 160°C results in continued deactivation of the surface in helium or a significant increase of activity in air as compared to 80°C, but the ratio of basic to acidic centres on the surface remains the same judging from the constant K_D/K_A value.

The changes occurring on the surface of the sulfur-containing polymer during heating are quite different to those of the oxygen-containing polymer. Under helium, a stepwise increase of surface activity occurs up to values 15 times higher (at 160°C) than before heating. Annealing in air causes a 17-fold increase of both K_A and K_D at 80°C, and these values fall only slightly at 160°C; the K_D/K_A ratio in all cases remains practically the same.

It is interesting that the heat treatment at 80°C leads to such changes on the surface of both polymers that the same K_D/K_A ratios are obtained independently of the heating atmosphere. These ratios remain constant up to 160°C in spite of significant variations in the activity of acidic and basic centres.

Taking into account that the two polymers investigated differ only by the type of heteroatom present in their ester group, we can conclude that all differences in the behaviour of surfaces of annealed polymers are caused by the specific reactions occurring at the ether or thioether bond. To explain the role of –O– and –S– linkages in the surface properties of poly(dimethacrylate)s, our next target is to characterize the dispersive and acid–base interactions of analogous poly(dimethacrylate)s that do not contain heteroatoms in the ester group. A more detailed study of polyOEDM and polyTEDM is now in progress and will be published in the near future.

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