letters

Comments on 'Characterization of dispersive and acid–base properties of crosslinked polymers by inverse gas chromatography' by A. Voelkel *et al.*

(Received 30 September 1993)

Dear Sir

In a recent *Polymer Communication* Voelkel *et al.*[1] showed that the above technique enables the changes occurring at the surface during thermal treatment of photopolymerized 2,2'-oxybisethanol dimethacrylate (polyOEDM) and 2,2'-thiobisethanol dimethacrylate (polyTEDM) to be described. The authors showed that such changes were reflected in the retention of n-alkanes, Lewis acids and Lewis bases. Following the approach of Saint Flour and Papirer[2] for the characterization of solids by inverse gas chromatography (i.g.c.), Voelkel *et al.* produced physico-chemical constants describing the surface thermodynamics of polyOEDM and polyTEDM. Dispersive properties were evaluated by γ_s^D, the dispersive contribution to the surface energy of the solids, and acid–base properties were described by K_A and K_D. These constants measure the ability of the surface to accept (A) or to donate (D) electrons. In other words, K_A and K_D describe the Lewis acidity and basicity of the solid surface, respectively.

Whilst the results and discussion of K_A and K_D are plausible, the authors produced very low values of γ_s^D in the range of 0.36–2.66 mJ m^{-2} for polyOEDM and 0.61–3.66 mJ m^{-2} for polyTEDM. The authors were indeed surprised to obtain such low values. In our opinion, these γ_s^D values are not reliable because generally the methacrylates have γ_s^D values[3] in the range of 35–40 mJ m^{-2}. In our own i.g.c. studies of poly(methyl methacrylate) (PMMA)[4] and Luxtrak (photocured aromatic methacrylate resin based on diphenyl oxide)[5] we determined the γ_s^D values shown in *Table 1*. Note that for Luxtrak, the surface energy gradient $d\gamma_s^D/dT$ is -0.062 mJ m^{-2} °C^{-1} and comparable to that of a methacrylate polymer[3].

Added to the disagreement on the absolute values of γ_s^D, one has to keep in mind that the very low values obtained by Voelkel *et al.* lie in the range of accuracy and reproducibility of the γ_s^D as determined by means of i.g.c. Even the 'non-stick' poly(tetrafluoroethylene) has γ_s^D values of ~22 and 14 mJ m^{-2} at 20 and 140°C[3], respectively, much greater than 0.36–3.66 mJ m^{-2}.

In practical situations, knowledge of the γ_s^D values of two interacting materials enables the evaluation of W^D, the dispersive component of the work of adhesion[6]:

$$W^D = 2(\gamma_{s1}^D \gamma_{s2}^D)^{0.5}$$

where subscripts 1 and 2 refer to the interacting species.

For this reason an accurate evaluation of γ_s^D is of great importance.

EXPERIMENTAL

The general experimental details have been described elsewhere[7]. In the case of the data reported here, the stainless steel columns used had an outer diameter of ~0.6 cm and were ~1 m long. The columns were packed with 9 and 10 g of Luxtrak powder and PMMA beads, respectively (without the use of any chromatographic support) and conditioned at 100°C for 15 h. Luxtrak was crushed and sieved (100–250 μm) prior to packing.

PMMA and Luxtrak were purchased from Aldrich and Zeneca Ltd, respectively.

Table 1 γ_s^D values of PMMA and Luxtrak

	Temperature (°C)	
Polymer	25	47.7
PMMA	38.8	–
Luxtrak	42.0	40.6

Marie-Laure Abel and Mohamed M. Chehimi
Institut de Topologie et de Dynamique des Systèmes
de l'Université Paris 7 Denis Diderot,
associé au CNRS URA 34,
1 rue Guy de la Brosse,
75005 Paris, France

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Reply to comments and corrections

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We read with necessary attention the comments on our paper[1] written by Abel and Chehimi[2] and we have to state that, regretfully, the authors of the comments are right. We checked our results again and found an important error in our computer program which influenced the values of all the examined parameters, both of dispersive and specific interactions. *Tables 1* and *2* contain the recalculated values of the parameters presented in our earlier paper[1] and, additionally, values of γ_s^D at 60 and 70°C.

The corrected values of γ_s^D lie in the range of 24.8–31.7 mJ m^{-2}. However, they are still lower than the γ_s^D obtained by us for poly(methyl methacrylate) (Zakłady Chemiczne, Oświęcim, Poland) at 50°C (36.1 mJ m^{-2}). Please note that our results were obtained at 50°C and not at 25°C as reported by Abel and Chehimi[2]. The temperature gradient $d\gamma_s^D/dT$ varies from -0.05 to -0.085 mJ m^{-2} °C^{-1}.

We assume that the comment on the surface energy temperature gradient is as a result of a misunderstanding. In the tables we indicated the temperatures under which the polymers were conditioned, e.g. under He at 80°C for 3 h. The retention data were then collected at 50, 60 and 70°C.

The corrected K_A and K_D values for both polymers may be discussed as follows:

1. K_A values are very similar for both polymers; K_D values are markedly higher for the sulfur-containing polymer;
2. the ratio K_D/K_A reflecting the surface character indicates that the two polymers are nucleophilic but the surface nucleophilicity of polyTEDM is ~21% higher;
3. annealing under He leads to deactivation of the surfaces of both polymers, as demonstrated by the lower values of K_A

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Table 1 Dispersive and acid–base characteristics for poly(2,2′-oxybisethanol dimethacrylate) (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	26.5	25.7	24.8	26.5	25.6	25.0
at 60°C	25.7	24.8	24.2	25.7	24.8	24.5
at 70°C	25.0	24.0	23.7	25.0	23.9	24.0
K_A	0.139	0.092	0.082	0.139	0.131	0.088
K_D	0.575	0.449	0.451	0.575	0.533	0.646
K_D/K_A	4.148	4.86	5.492	4.148	4.078	6.596

Table 2 Dispersive and acid–base characteristics of poly(2,2′-thiobisethanol dimethacrylate) (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	25.1	26.9	31.7	25.1	26.8	31.1
at 60°C	24.7	26.0	31.0	24.7	26.1	30.4
at 70°C	24.1	25.3	30.4	24.1	25.4	29.9
K_A	0.133	0.107	0.092	0.133	0.093	0.106
K_D	0.668	0.680	0.480	0.668	0.709	0.745
K_D/K_A	5.023	6.371	4.937	5.023	7.626	7.264

and K_D. However, the ratio K_D/K_A changes which may suggest the appearance of new functional groups;

4. the results of annealing in air are not unequivocal. Generally, the acidity of both polymers decreases whereas the basicity increases, but to a higher degree for polyTEDM. As a result, the increase in surface nucleophilicity occurs which is probably caused by the appearance of oxide groups of various types.

We would like to apologize for the errors in our earlier published data[1] and to express our gratitude to Abel and Chehimi for their constructive criticism.

A. Voelkel, E. Andrzejewska, R. Maga
and M. Andrzejewski
Poznań Technical University,
Institute of Chemical Technology and Engineering,
P1.M.Skłodowskiej-Curie 2,
60-965 Poznań, Poland

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