

CHROM. 14,530

REACTIVE POLYMERS

XLI. EFFECT OF THE CONTENT AND DISTRIBUTION OF POLAR GROUPS ON THE POLARITY OF GLYCIDYLMETHACRYLATE POLYMERIC SORBENTS

J. LUKÁŠ*, F. ŠVEC and J. KÁLAL

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

and

B. JEŽEK

The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 118 40 Prague 1 (Czechoslovakia)

(Received November 9th, 1981)

SUMMARY

Photoelectron spectroscopy has revealed that the distribution of polar groups (carboxylic and epoxy groups) in macroporous copolymers based on glycidylmethacrylate (GMA)–ethylene dimethacrylate (EDMA) is not uniform, but that their concentration increases starting from the surface towards the centre of the globules. Heat treatment of these copolymers gives rise to conformational changes, which in turn cause an increase in the concentration of polar groups on the surface of the globules, and thus also a rise in polarity.

Differences between the modified Rohrschneider constants on the copolymers GMA–EDMA and methyl methacrylate (MMA)–EDMA were used in order to evaluate the participation of epoxy groups in the overall polarity of glycidylmethacrylate polymeric sorbents.

INTRODUCTION

Sorbents based on macroporous copolymers GMA–EDMA are polymeric beads which consist of more or less regular agglomerates of so-called globules¹. Their physical and specific chromatographic properties² which can be modified by polymer-analogous reactions³ or heat treatment⁴ have been reported in the literature.

The polarity of GMA sorbents has been expressed using the modified Rohrschneider method²⁻⁵. The modification consists in the replacement of a standard stationary phase (squalane) with a non-polar adsorbent Carboxpack B, the porosity and specific surface of which are close to the values of these copolymers. A similar

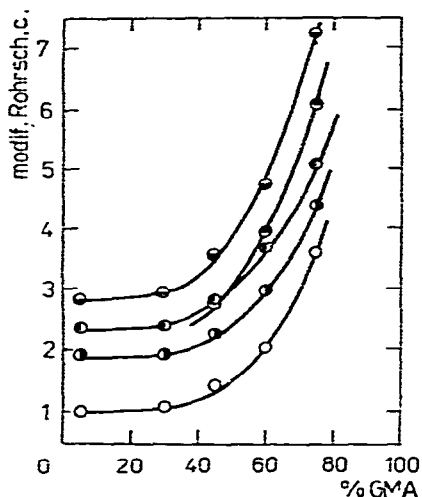


Fig. 1. Effect of GMA content on the polarity of GMA-EDMA copolymers expressed through the modified Rohrschneider constants. O, x' values (benzene); ●, y' values (ethanol); ○, z' values (methyl ethyl ketone); ●, u' values (nitromethane); ●, s' values (pyridine).

procedure was employed by Lindsay Smith *et al.*⁹ in order to modify the McReynolds constants in the characterization of the selectivity of aromatic copolymers.

In this paper, the relationships existing between the concentration of polar groups, their distribution in the surface layer of the globules and the polarity of sorbents are elucidated using photoelectron spectroscopy (XPS).

EXPERIMENTAL

Photoelectron spectroscopy

Measurements were performed with an ESCA 3 Mark II photoelectron spectrometer (VG Scientific, Great Britain) using $Al-K_{\alpha}$ (1486.6 eV) radiation. Copolymer samples were ground in an agate dish and deposited in thin layers on double-sided Scotch tape on a holder. The signal intensities of electrons, from levels C_{1s} , O_{1s} , O_{2s} , were determined at $1 \cdot 10^{-6}$ Pa and at angles between the planes of the samples surface and the electron escape into the inlet slit of the analyser (θ) 20, 40, 60 and 80°.

Gas chromatography

The values of the modified Rohrschneider constants for the basic series of copolymers GMA-EDMA (Fig. 1) were taken from an earlier paper²; the same procedure was also employed in the determination of these constants for the samples of the MMA-EDMA copolymers.

RESULTS AND DISCUSSION

In an earlier paper² we determined the polarity of the basic series of the polymeric sorbents GMA-EDMA. Fig. 1 shows that the GMA content has a decisive influence on the polarity of the copolymers. Up to a GMA content of *ca.* 40% the

TABLE I

O/C MOLAR RATIO IN GMA-EDMA COPOLYMERS DETERMINED AT VARIOUS ANGLES OF ELECTRON ESCAPE (Θ)

Θ ($^\circ$)	Composition of GMA-EDMA copolymers (% _w , w/w)				
	5:95	30:70	45:55	60:40	75:25
20	0.354	0.364	0.359	0.369	0.368
40	0.377	0.373	0.370	0.382	0.384
60	0.379	0.376	0.380	0.385	0.388
80	0.382	0.373	0.381	0.390	0.383
Theoretical*	0.401	0.408	0.413	0.417	0.421

* Calculated stoichiometrically from the composition of copolymers.

polarity does not vary very much, and a steep rise appears only beyond this value. Such a non-linear dependence could be explained by using XPS spectra of these copolymers recorded at various angles between the plane of the sample and the electron escape (Θ) into the slit of the analyser. The copolymer particles were used in the XPS measurements in a pulverized state. It was found microscopically that only the particular agglomerates of the globules can be separated by rubbing, but that no destruction of globules takes place. Because of the small dimensions of the globules (68–80 nm) the deposited layer of the pulverized copolymer can be regarded as sufficiently smooth for the XPS measurements. The spectra provided information on the composition of the surface layer of the globules approximately to a depth of 18 nm⁷. This depth represents roughly 20–25% of the diameter of the globule. Table I shows the theoretical molar oxygen: carbon ratios determined at various Θ angles for copolymers having various GMA-EDMA compositions. The results indicate that the oxygen content on the surface of the globules is always lower compared with the theoretical results obtained from the stoichiometric composition of the copolymers and that it increases with increasing angle Θ (and hence with the depth of the recorded spectrum). This means that there exists a concentration of oxygen in the direction from the surface to the centre of the globules. Some decrease in O/C should be assigned at the expense of the so-called contamination carbon deposited on the sample surface in the course of the measurement. However, the overall effect cannot be attributed merely to the effect of this carbon, as the existence of the concentration gradient of oxygen in the globules can be proved also by determination of the intensities of signals of oxygen electrons from the 1s and 2s levels. For the individual copolymers this ratio varies between 16.8 and 21.4, while theoretically it should correspond to the ratio of the effective cross-sections of the given lines multiplied by factors depending on the kinetic energy of the electrons (mean free path of the electrons, + transmission of the analyser), amounting to 25.9. The determined lower values compared with the theoretical ones indicate a relatively stronger O_{2s} electron signal which, owing to their higher kinetic energy and hence also a longer mean free electron path, comes from a greater depth.

The composition heterogeneity of the individual globules is closely connected with the physicochemical properties of both copolymerizing monomers. It has been

TABLE II

O/C MOLAR RATIO IN THE INITIAL AND THERMALLY TREATED GMA-EDMA COPOLYMERS DETERMINED AT VARIOUS ANGLES OF ELECTRON ESCAPE (θ)

GMA-EDMA (%, w/w)	Heat treatment		θ ($^{\circ}$)			
	($^{\circ}$ C)	(h)	20	40	60	80
45:55*	—	—	0.359	0.370	0.380	0.381
45:55	280	1	0.391	0.395	0.393	0.389
45:55	250	4	0.384	0.392	0.389	0.380
60:40*	—	—	0.369	0.382	0.385	0.390
60:40	250	2	0.387	0.396	0.379	0.379
60:40	260	2	0.398	0.403	0.397	0.393

* Initial copolymers.

demonstrated⁵ that the double bond of GMA is more reactive and thus polymerizes more quickly. Thus, at the very beginning of polymerization at a low GMA concentration in the polymerization mixture the polymer molecules formed are richer in GMA and form a nucleus which later gives rise to a globule. These nuclei continuously increase in volume owing to the proceeding copolymerization in which GMA is more quickly removed from the system and the mixture of monomers becomes richer in EDMA. In the final stage it is mainly EDMA that remains, and the surface layer of the globules consists predominantly of a polymer rich in EDMA. If the GMA content in the mixture is higher than 40% (w/w), no such marked loss of GMA occurs in the mixture, because reactivity parameters of the two monomers do not differ much from each other and the globules become more homogeneous. The higher content of GMA units appears also on the surface, which in the case where the copolymers are utilized in chromatography facilitates interactions between polar groups and molecules of the sorbents. A further rise in the GMA content will be reflected in an essential rise in polarity.

The heat treatment of the GMA-EDMA copolymers in which the basic mono-

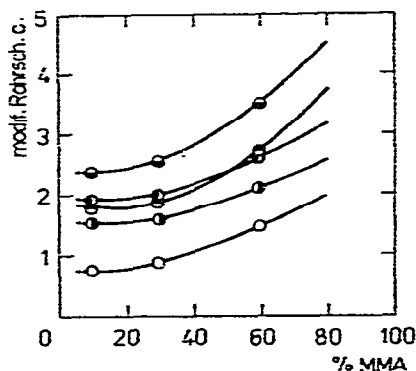


Fig. 2. Effect of MMA content on the polarity of MMA-EDMA copolymers expressed through the modified Rohrschneider constants. Sorbates denoted as in Fig. 1.

TABLE III
 INCREMENTS OF MODIFIED ROHRSCHEIDER CONSTANTS EXPRESSING THE PARTICIPATION OF EPOXY GROUPS OF GLYCIDYL-METHACRYLATE UNITS ($-\dot{\text{C}}\text{H}-\text{C}\text{H}_2\text{O}$) IN THE COPOLYMER IN SPECIFIC INTERACTIONS WITH MOLECULES OF THE SORBATES

GMA content in the copolymer (% w/w)	$\Delta(\Delta I)_x \cdot 10^{-2}$ (%)	$\Delta(\Delta I)_y \cdot 10^{-2}$ (%)	$\Delta(\Delta I)_z \cdot 10^{-2}$ (%)	$\Delta(\Delta I)_w \cdot 10^{-2}$ (%)	$\Delta(\Delta I)_v \cdot 10^{-2}$ (%)
10	0.22 (22.2)	0.42 (18.1)	0.33 (17.7)	0.44 (15.6)	—
20	0.23 (22.5)	0.44 (18.8)	0.33 (17.6)	0.46 (16.0)	—
30	0.22 (21.0)	0.46 (19.3)	0.34 (17.9)	0.47 (16.0)	—
40	0.26 (22.2)	0.46 (17.7)	0.37 (18.0)	0.48 (15.0)	—
50	0.48 (32.7)	0.86 (28.7)	0.71 (29.8)	1.01 (26.2)	0.99 (32.7)
60	0.94 (46.8)	1.47 (40.8)	1.25 (42.7)	1.93 (39.4)	1.80 (46.2)
70	1.73 (59.2)	2.05 (46.1)	1.88 (49.9)	3.07 (48.0)	2.78 (52.5)

mers (GMA in the first place) are split off yielded sorbents which surprisingly possessed a higher polarity⁴. Table II clearly demonstrates that the oxygen concentration in the surface layer of the globules is higher in the thermally treated samples than in the initial ones, and even that it increases towards the surface (lower values at $\Theta = 20^\circ$ are probably affected by the contamination carbon). This means that, during heat treatment, migration of the copolymer chains gives rise to conformational changes leading to a rise in polarity. The results of measurements by the XPS method demonstrate that the polarities of sorbents based on GMA-EDMA are determined not only by the content of carboxylic and epoxy groups, but also by the orientation of these groups inside the globules.

For comparison, we determined the effect of the MMA content in a series of MMA-EDMA copolymers on their polarity. It can be seen from Fig. 2 that with increasing MMA content no pronounced discontinuity appears in the dependence as is the case with GMA. Bearing in mind that the glycidylmethacrylate unit in the copolymer differs from the methyl methacrylate unit only in the epoxy end group ($-\text{CH}-\text{CH}_2\text{O}$), it is obvious that this epoxy group is the cause underlying the much higher polarity of copolymers of the GMA type. From the differences between values of the modified Rohrschneider constants of GMA and MMA copolymers (by using the graphic displays in Figs. 1 and 2), it is possible to obtain increments for the individual contents of monomers which represent the participation of epoxy end-groups in specific interactions with the individual types of molecules of the sorbates (Table III). Also, these results confirm that the effect of epoxy groups on polarity becomes markedly apparent at a GMA content in the copolymer of $>40\%$ (w/w). The participation of epoxy groups in the overall polarity suggests that their interaction is strongest with sorbates containing free π -electrons (benzene- x' , pyridine- s'). On the contrary, in specific interactions of GMA copolymers with nitromethane (u'), which are the strongest (*cf.* Fig. 1), the epoxy groups alone participate to a smaller extent.

REFERENCES

- 1 Z. Pelzbauer, J. Lukáš, F. Švec and J. Kálal, *J. Chromatogr.*, 171 (1979) 101.
- 2 J. Lukáš, F. Švec and J. Kálal, *J. Chromatogr.*, 153 (1978) 15.
- 3 J. Lukáš, F. Švec, E. Votavová and J. Kálal, *J. Chromatogr.*, 153 (1978) 373.
- 4 J. Lukáš, E. Votavová, F. Švec, J. Kálal and M. Popl, *J. Chromatogr.*, 194 (1980) 297.
- 5 J. Lukáš, *J. Chromatogr.*, 190 (1980) 13.
- 6 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 21.
- 7 P. Cadman, G. Gossedge and J. D. Scott, *J. Electron Spectrosc. Relat. Phenom.*, 13 (1978) 1.
- 8 D. Horák, F. Švec, C. M. A. Ribeiro and J. Kálal, *Angew. Makromol. Chem.*, 87 (1980) 127.