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## REACTIVE POLYMERS

### XVI\*. SURFACE-MODIFIED POLYMERIC SORBENTS BASED ON GLYCIDYL ESTERS

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#### SUMMARY

Copolymers based on glycidyl methacrylate-co-ethylenedimethacrylate were modified by reaction with a number of amines, and by acid hydrolysis followed by cyanoethylation. The physical and chromatographic properties of the modified copolymers suggest that a single copolymer with reactive functional groups can yield a number of sorbents possessing various polarities and various sorption properties.

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#### INTRODUCTION

Surface treatment of polymeric sorbents influences the retention characteristics of individual sorbates. One procedure used in such treatment is the introduction of a stationary phase<sup>1-4</sup>, so that absorption becomes the dominant separation process. Use of a variety of polymer sorbents and stationary phases showed that in most cases, the highest separation efficiencies could be obtained with a 2–7% coating<sup>5,6</sup>.

The other modification procedure alters the chemical character of the sorbent by a chemical reaction on its surface. The most frequently used treatment of this type is silanization. Silanized copolymers<sup>7</sup> exhibit a higher separation efficiency and considerably smaller tailing of peaks. Polymeric sorbents with reactive functional groups can be modified by polymer-analogous reactions to yield sorbents with completely different separation properties. This procedure was used in the modification of Spheron<sup>8</sup>, the free hydroxy groups of which were used in polymer-analogous transformations with stearoyl chloride and acrylonitrile.

This paper reports the investigation of the surface properties of macroporous polymeric sorbents based on glycidyl methacrylate-co-ethylenedimethacrylate (GMA-co-EDMA), modified by polymer-analogous reactions of the epoxy groups of glycidyl methacrylate units.

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\* For Part XV, see ref. 9.

## EXPERIMENTAL

*Modification of copolymers by polymer-analogous reactions*

*Reactions with amines.* The starting copolymer in reactions with amines was sample 1, containing 55% (w/w) of GMA. Ammonia, methylamine, dimethylamine, ethanolamine and ethylenediamine were used as reagents. The reaction with ammonia was carried out in a stainless steel autoclave, whereas reactions with volatile amines (methylamine, dimethylamine) were performed in ampoules placed in a thermostat. Reactions with less volatile amines (ethanolamine, ethylenediamine) were carried out in a flask under reflux, heated on a water bath. The reaction conditions, the conversion of GMA and the basic physical characteristics of copolymers modified with the amines are given in Table I.

*Hydrolysis of the copolymer GMA-co-EDMA.* The epoxide ring was opened by means of the acid hydrolysis of sample 7 with a 0.1 *N* sulphuric acid solution. The reaction was carried out at 90° for 3 h. The product was decanted with water to neutral reaction and dried. Vicinal hydroxy groups were formed, and no epoxy groups were detected in the copolymer after such hydrolysis.

*Cyanoethylation of the hydrolysed copolymer.* The hydrolysed sample was cyanoethylated after being swollen in a 9 *M* NaOH solution. The reaction with acrylonitrile (AN) was carried out at 25°, with the molar ratio of reagent to the reactive hydroxy unit being 3.2:1. As the copolymer was in the swollen state, the reaction proceeded not only on the surface but also in the bulk.

*Chromatographic and other measurements*

The chromatographic measurements required for calculation of the specific retention volumes, the Kováts retention indices and the modified Rohrschneider constants were carried out in the same way and under the same conditions as described in the previous paper<sup>9</sup>. The 150–200  $\mu\text{m}$  fraction was used in all cases.

The measurement of specific surface areas and thermal stabilities and the determination of the epoxy groups were also carried out in the same way as in the previous paper<sup>9</sup>. The nitrogen content of the copolymers was determined by the method of Kjeldahl<sup>10</sup>.

## RESULTS AND DISCUSSION

The starting copolymer used in the polymer-analogous reactions with ammonia and with a number of amines was sample 1, obtained by the copolymerization of 60% (w/w) of GMA and 40% (w/w) of EDMA. This proportion of the cross-linking EDMA ensures the required mechanical strength, small volume contractions due to the temperature and medium, and a sufficiently large surface area of the resulting copolymer. GMA introduces into the copolymer the required concentration of reactive epoxide groups.

The conditions for the polymer-analogous reactions and the basic characteristics of modified copolymers with chemically bonded primary, secondary, and tertiary amines are given in Table I. Although the reactions were carried out in a multiple excess of amines, the conversion of GMA with ammonia and amines containing one nitrogen atom varied from 64 to 79 mole%. In the case of sample 6, when the

TABLE I  
REACTION CONDITIONS AND BASIC CHARACTERISTICS OF SAMPLES MODIFIED WITH AMINES

Sample number	Modified	Mol. ratio (amine/GMA)	Reaction time (h)	Temp. (°C)	N content in sorbent (% w/w)	Conversion of GMA (mole%)	Thermal stability (°C)	Specific surface area (m <sup>2</sup> /g)	Mean pore diameter (nm)
1*	—	—	—	—	—	—	213	69	9.9
2	NH <sub>2</sub>	16.7	5.0	80	3.36	64.7	210	79**	10.8**
3	CH <sub>3</sub> NH <sub>2</sub>	28	4.0	80	3.08	61.0	200	75***	10.4***
4	(CH <sub>3</sub> ) <sub>2</sub> NH	37	1.5	80	3.78	79.4	undetermined	68***	12.1***
5	HOCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	6	6	95	3.50	76.2	206	59**	11.0**
6	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	31	4	80	5.18	53.7†	205	61***	11.9***
								70***	9.8***

\* GMA content = 55% (w/w).

\*\* Measured before conditioning.

\*\*\* Measured after conditioning.

† Assuming that only one amino group of ethylenediamine reacts.

reagent contained two nitrogen atoms, the conversion (assuming that only one amino group of ethylenediamine reacts) was only 53.7 mole%. This result may be distorted by the fact that under appropriate steric conditions ethylenediamine could react with both groups. In addition to amino groups and hydroxy groups introduced by ethanolamine in sample 5, the surface of copolymers thus modified also contains epoxy groups of unreacted GMA. Because the specific surface areas of samples of the modified copolymers vary within a small range about the value of the starting sample 1, it is impossible to follow exactly the effect of polymer-analogous reactions on the change in the surface area. The experimental error in the specific surface area can be considerable ( $\pm 5\%$ ). It may be asserted, however, that polymer-analogous reactions lead to an increase in the mean pore diameter; sample 6 is the only exception to this finding.

Compared with the starting sample 1, the thermal stability of this series of modified copolymers tends to decrease somewhat. The lowest thermal stability was observed with sample 4, the thermogravimetric record of which continued to decrease in the linear region, so that at the characteristic breaking point (onset of decomposition) the weight loss amounted to 7.4%.

Subsequent modifications (Table II) were carried out using sample 7 as the starting copolymer. Its acid hydrolysis yielded a macroporous copolymer with free hydroxy groups on the surface (sample 8). Reaction of AN with the hydroxy groups of the hydrolysed copolymer yielded sample 9, which contained strongly polar nitrile groups. The last in the series is sample 10: a terpolymer, GMA-co-AN-co-EDMA. The latter two samples were compared in order to examine how the properties of the copolymer, with the substrate (AN) attached to the surface, differed from those of the terpolymer, into which the substrate had been incorporated as the monomer.

TABLE II

BASIC CHARACTERISTICS OF THE STARTING COPOLYMER GMA-CO-EDMA AND OF SAMPLES MODIFIED BY HYDROLYSIS FOLLOWED BY CYANOETHYLATION

Sample number	Modified	Content in copolymer		Thermal stability ( $^{\circ}\text{C}$ )	Specific surface area ( $\text{m}^2/\text{g}$ )	Mean pore size ( $\mu\text{m}$ )
		GMA (% w/w)	AN (% w/w)			
7	—	53.5*	—	216	60	11.4
8	by hydrolysis with $\text{H}_2\text{SO}_4$	—	—	207	62	12.0
9	by hydrolysis and cyanoethylation	—	18.9	216	51	20.5
10	—	36.9**	14.8	272	59	17.1

\* GMA-EDMA (60:40, w/w) in the polymerization mixture.

\*\* GMA-AN-EDMA (40:20:40, w/w) in the polymerization mixture.

As with copolymers modified with amines, in this case too the changes in the specific surface areas are comparatively small, and one can also observe an increase in the mean pore diameter (with sample 9, this change is conspicuously large) in relation to the starting copolymer. Comparison of the thermal stabilities of modified

copolymers and the starting sample 7 shows that the stability of the hydrolysed sample has decreased by *ca.*  $10^\circ$ . The reason is the lower stability of the vicinal hydroxy groups. Subsequent cyanoethylation of the hydrolysed copolymer caused an increase in thermal stability to that of the starting sample 7. A considerably higher stability was observed with the terpolymer. A possible cause of the difference in the thermal stabilities of samples 9 and 10 is the ether bond formed in the reaction of AN with the hydroxy groups of the hydrolysed copolymer.

It follows from the specific retention volumes in Table III that modified sorbents have quite different sorption properties. Although the specific surface areas of modified samples do not differ much from those of the original copolymers, the differences in the retention values of compounds on the individual samples are considerable. With the majority of samples (2-6 and 8) the retention values of not only polar, but also non-polar compounds are increased compared with the starting copolymers (1 and 7). Thus important changes in the pore distribution probably occur in the polymer-analogous reactions. Of the modified copolymers, only sample 9 containing AN is an exception: as with the terpolymer 10, the retention values on sample 9 are shorter than those on sample 7.

TABLE III  
SPECIFIC RETENTION VOLUMES OF SORBATES ON COPOLYMER SAMPLES  
Column temperature  $150^\circ$ , flow-rate of argon 25 ml/min; injected amount 0.1  $\mu$ l.

Sorbate	Sample number									
	1	2	3	4	5	6	7	8	9	10
Pentane	2.8	5.4	4.4	3.2	1.6	1.6	3.0	6.1	0.9	1.7
Hexane	5.8	9.7	8.9	6.4	2.5	2.9	4.3	11.3	1.6	3.2
Heptane	11.4	18.0	16.5	11.6	4.0	5.0	8.1	19.4	3.3	5.8
Octane	22.1	—	32.8	21.2	7.4	9.2	15.0	—	5.2	9.3
Nonane	44.2	—	65.8	38.6	13.0	17.0	26.7	—	7.8	13.4
Methanol	5.3	18.8	13.7	10.9	10.2	16.4	6.2	18.8	4.8	5.7
Ethanol	8.8	32.3	25.6	15.8	13.7	21.5	7.6	37.3	5.5	7.6
Propanol	17.1	68.2	42.6	29.4	22.9	37.3	14.4	86.3	8.4	13.3
Butanol	34.3	147.2	93.4	56.7	41.2	65.9	27.5	—	13.7	23.4
Benzene	17.3	40.0	27.4	20.3	11.9	12.3	15.5	44.9	6.0	12.6
Methyl ethyl ketone	18.4	—	40.1	24.1	17.2	—	14.7	71.5	8.1	14.4
Nitromethane	27.8	61.6	44.2	36.3	28.8	43.8	26.2	60.9	18.9	27.9
Pyridine	57.1	266.9	159.7	92.9	70.2	107.0	45.4	—	25.4	41.8

The dynamic conditions in columns packed with modified copolymers based on glycidyl esters are analogous to the starting copolymers<sup>9</sup>; the separation efficiency is somewhat reduced only in the series modified with amines. This finding is confirmed by the fact that the structure of porous particles is essentially unchanged during the modification.

The polar character of the sorbent, which is the cause of major or minor specific interactions with the sorbate molecules, is reflected in the basic chromatographic data, retention times, or volumes. This is also why the Kováts retention indices, which are interpolated logarithms of the retention of compounds related to the homologous series of alkanes, express the chromatographic properties of the separation materials.

TABLE IV

MODIFIED ROHRSCHEIDER CONSTANTS<sup>9</sup> OF THE COPOLYMER SAMPLES

Related to Kováts indices determined at 150° on Carbo-pack B:  $I_{\text{benzene}} = 561$ ,  $I_{\text{ethanol}} = 296$ ;  $I_{\text{methyl ethyl ketone}} = 476$ ,  $I_{\text{nitromethane}} = 358$ ,  $I_{\text{pyridine}} = 547$ .

Sample number	$x'$	$y'$	$z'$	$u'$	$s'$
1	2.02	3.65	2.96	4.75	3.93
2	2.69	5.02	—	5.43	5.92
3	2.13	4.67	3.52	4.84	4.80
4	2.32	4.58	3.47	5.33	5.04
5	3.23	6.12	4.74	6.83	6.53
6	2.89	6.40	—	6.98	6.54
7	2.45	3.88	3.22	5.39	4.37
8	2.93	5.24	4.64	5.52	—
9	2.71	5.14	4.29	7.13	5.81
10	3.26	4.64	4.43	7.00	5.97

The polarity of the samples of sorbents under investigation was expressed using the modified Rohrschneider constants<sup>9</sup>, the calculations of which are based on the Kováts retention indices of the Rohrschneider standards (benzene, ethanol, methyl ethyl ketone, nitromethane, pyridine) on the given sorbent and on non-polar Carbo-pack B. Table IV shows that all polymer-analogous reactions lead to an increase in the polarity of modified copolymers. The highest polarity was obtained with samples prepared by reaction with ethanolamine (5), ethylenediamine (6), and by hydrolysis (8) followed by cyanoethylation (10). Compared with sample 9, the specific interactions of terpolymer 10 are stronger in the separation of aromatic ( $x'$ ), weaker in the separation of alcohols ( $y'$ ), and approximately the same in the separation of the other types of sorbate ( $z'$ ,  $u'$ ,  $s'$ ).

Because the retention values are smallest on samples 9 and 10, these samples are the most suitable for application. Moreover, the separation efficiency, thermal

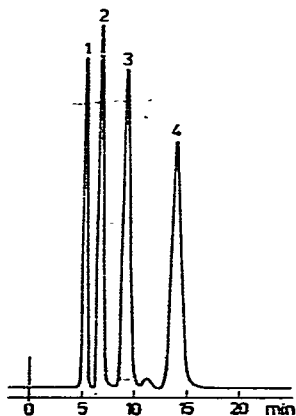


Fig. 1. Separation of carboxylic acids  $C_2$ - $C_4$  on sample 9. Glass column ( $100 \times 0.3$  cm I.D.); injection,  $0.15 \mu\text{l}$ ; column temperature,  $165^\circ$ ; flow-rate of nitrogen, 30 ml/min. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = butyric acid; 4 = valeric acid.

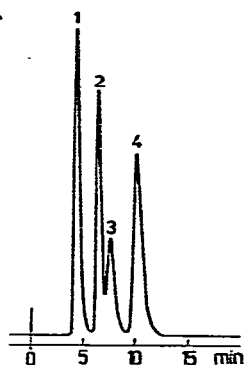


Fig. 2. Separation of mixture of polar compounds with close boiling points on sorbent 9. Glass column ( $100 \times 0.3$  cm I.D.); injection,  $0.1 \mu\text{l}$ ; column temperature,  $90^\circ$ ; flow-rate of nitrogen, 30 ml/min. Peaks: 1 = 1-chlorobutane; 2 = ethanol; 3 = butyraldehyde; 4 = methyl ethyl ketone.

stability and lifetime of these packings in the chromatographic column are the highest. The reactivity of the epoxy groups in the copolymer GMA-co-EDMA rules out the separation of carboxylic acids and amines. On the other hand, on copolymers subjected to surface modification with AN the separation of carboxylic acids proceeds without problems (Fig. 1), as is the case with the terpolymer GMA-co-AN-co-EDMA. The separation of mixtures of polar compounds with close boiling points on sample 9 is shown in Fig. 2. This modified copolymer exhibits inversion in the separation of 1-chlorobutane and ethanol compared with the starting copolymer<sup>9</sup>. The separation of chlorinated hydrocarbons on this sorbent is highly selective, and the peaks obtained are highly symmetrical. This is illustrated by the separation of isomers of trichlorobenzene (Fig. 3).

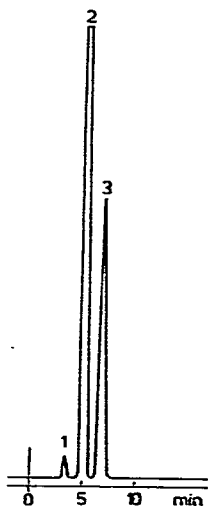


Fig. 3. Separation of trichlorobenzene isomers on sorbent 9. Glass column ( $100 \times 0.3$  cm I.D.); injection,  $0.1 \mu\text{l}$ ; column temperature,  $190^\circ$ ; flow-rate of nitrogen, 30 ml/min. Peaks: 1 = 1,3,5-trichlorobenzene; 2 = 1,2,4-trichlorobenzene; 3 = 1,2,3-trichlorobenzene.

The results described in this paper show that by modifying polar polymeric sorbents based on glycidyl esters by means of polymer-analogous reactions, one can obtain a great number of sorbents possessing various polarities and various sorption properties.

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