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## REACTIVE POLYMERS

### XXXI\*. THERMALLY TREATED POLYMERIC SORBENTS BASED ON GLYCIDYLMETHACRYLATE COPOLYMERS

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#### SUMMARY

Heating of polymeric sorbents based on glycidylmethacrylate-ethylenedimethacrylate copolymers to 250–280 °C for short periods in an inert nitrogen atmosphere leads to pronounced morphological changes. The chromatographic properties of sorbents thus treated are mainly characterized by a considerable shortening of the retention times of sorbates. This makes possible rapid chromatographic analyses of mixtures at low working temperatures (as much as 60 °C lower than with Porapak T), which is advantageous for the separation of thermally less stable compounds. The selectivity of separation of polar compounds is also higher for thermally treated copolymers.

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#### INTRODUCTION

The physical and chemical properties of copolymers of the methacrylate type prepared by suspension radical copolymerization under conditions of formation of macroporous structure offer good prospects for their utilization as polymeric sorbents in gas chromatography<sup>1-4</sup>. Especially good results were obtained with copolymers based on glycidylmethacrylate-ethylenedimethacrylate<sup>2-4</sup>. The retention times of sorbates on these copolymers are much shorter than on copolymers of the styrene-divinylbenzene type, so that the chromatographic separation of compounds at lower working temperatures becomes feasible. These copolymers are also characterized by a higher polarity and thus selectivity in the separation of polar compounds having various functional groups<sup>3</sup>.

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\* Part XXX: F. Švec, J. Labský, L. Lányová, J. Hadril, S. Pokorný and J. Kálal, *Angew. Makromol. Chem.*, in press.

The separation of non-polar compounds on copolymers of the methacrylate type is based on their morphology, and predominantly on the specific surface area and porosity (specific pore volume and pore size distribution). These quantities are determined by the magnitude and aggregation of submicroscopic particles, globules and nodules<sup>5,6</sup>, and they may be affected by the conditions of preparation. In the separation of polar compounds, in addition to the above factors, which are attributes of the non-specific interactions between sorbate and polymeric sorbent, some rôle is also played by the chemical composition of copolymers which affects the extent of specific interactions<sup>5</sup>.

Analogous reactions on glycidylmethacrylate copolymers allow us to extend the basic series by including other sorbents having various polarities and specific sorbent properties<sup>4,7</sup>. The polarity of polymeric sorbents of the glycidylmethacrylate type was expressed using modified Rohrschneider constants<sup>3,7</sup> which may be correlated with thermodynamic functions<sup>8</sup>.

In this paper we describe changes in the physical and chromatographic properties of glycidylmethacrylate copolymers caused by heating for short periods of time.

## EXPERIMENTAL

The initial copolymers, grain size 150–180  $\mu\text{m}$ , were treated in a stream of nitrogen (100 ml/min) in a glass column (1.2 cm I.D.) placed in an oven. The temperature range of the experiments was 250–280 °C. Volatile products were condensed at –78 °C. The thermally treated specimens were extracted with benzene and ethanol before further use.

Chromatographic analyses for the determination of the separation efficiency and of the Kováts indices were performed with a Perkin-Elmer F-11 apparatus on glass columns (100  $\times$  0.3 cm I.D.) at 150 °C and at a nitrogen flow-rate of 25 ml/min. The volatile products were analyzed in stainless-steel columns (180  $\times$  0.2 cm I.D.) packed with 15% GE-XE 60 on Chromosorb W at 130 °C, using a nitrogen (carrier gas) flow-rate of 30 ml/min.

The specific surface area of the individual copolymer samples was determined by the method of thermal desorption of nitrogen using the B.E.T. equation.

The thermal stability of the samples was determined with a DuPont 950 apparatus at a heating rate 10 °C/min and a nitrogen flow-rate of 200 ml/min. It was defined as the temperature at which a decrease in weight sets in, as demonstrated by a discontinuity in the thermogravimetric curve.

The content of glycidylmethacrylate in the copolymer was determined by titration<sup>3</sup>.

## RESULTS AND DISCUSSION

A short period of heating in an inert atmosphere to a temperature at which copolymers based on glycidylmethacrylate–ethylenedimethacrylate are already partly thermally degraded leads to morphological changes in these copolymers, which markedly affects their chromatographic properties. Table I shows changes of two samples of glycidylmethacrylate copolymers 1 and 7.

TABLE I

## EFFECT OF THERMAL TREATMENT ON THE PROPERTIES OF GLYCIDYLMETHACRYLATE (GMA)-ETHYLENEDIMETHACRYLATE (EDMA) COPOLYMERS

Copolymer No.	Modification conditions		GMA content in copolymer (% w/w)	Mass loss (%)	Volatile products (%)		Specific surface area		Thermal stability (°C)
	t (°C)	Time (h)			GMA	EDMA	m <sup>2</sup> /g	%	
1*	—	—	31.4	—	—	—	109	100	217
2	250	1	30.7	0.75	50.0	48.4	75	68.8	215
3	250	2	30.2	1.25	49.6	48.8	68	62.4	213
4	250	4	30.2	2.60	49.5	49.1	59	54.1	212
5	260	2	31.1	18.43	49.7	48.4	81	74.3	217
6	280	1	30.9	45.00	52.2	46.2	34	31.2	208
7**	—	—	46.1	—	—	—	64	100	207
8	250	1	41.2	12.12	81.0	17.5	37	57.8	200
9	250	2	40.1	36.55	71.5	27.0	27	42.2	198
10	260	2	38.2	44.30	48.5	50.2	29	45.3	200

\* GMA:EDMA ratio in the polymerization mixture, 45:50 (w/w).

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

Major mass losses observed with samples 8–10 indicate that the degradation process sets in more quickly in the case of copolymers with a higher content of glycidylmethacrylate. The chromatographic analysis of frozen-out volatile products has revealed that the latter contain mainly initial monomers and trace impurities accompanying monomers in the copolymerization. It may be concluded, therefore, that such a treatment does not cause chemical changes in the copolymers, only changes of structural character. Analyses of frozen-out volatile products obtained in several experiments also demonstrate that a higher percentage of glycidylmethacrylate is released by thermal degradation than of ethylenedimethacrylate. Glycidylmethacrylate is more volatile, mainly in the initial stage of heating and also at lower temperatures. The content of impurities which appear in the monomers in trace concentrations increased in volatile products up to 2%.

Exposure of copolymers to 250–280 °C resulted in a marked decrease in the specific surface area. From Table I it can be seen that, under the same conditions of temperature and time, sample 7 having the highest content of glycidyl methacrylate also exhibits the largest contraction of the specific surface area. The heat stability of thermally modified samples slightly decreases, but this decrease does not exceed 10 °C.

Morphological changes due to the heat treatment of the initial copolymers described above also result in large changes in chromatographic properties, graphically illustrated by Figs. 1–5. For instance, using a heat-treated copolymer (sample 6), it is possible to fractionate a mixture of C<sub>6</sub>–C<sub>11</sub> hydrocarbons (Fig. 1) at a working temperature as much as 30 °C lower than for the initial sample 1. In the separation of a mixture of cycloparaffins and of the corresponding aromatics (Fig. 2), in addition to the lower working temperature, a relative delay in the retention of the aromatics on the heat-treated sample 6 is observed, which may be attributed to the higher selectivity or to the larger specific interactions between molecules with free  $\pi$ -electrons

and the surface of the heat-treated copolymer. Figs. 3–5 show that the heat-treated glycidylmethacrylate copolymers allow separations of mixtures of compounds at working temperatures 50–60 °C lower than with Porapak T. The selectivity of the separation of mixtures of polar compounds having various functional groups can be distinctly seen in Fig. 5. Whereas in the separation of 1-chlorobutane (b.p. 77.9 °C),

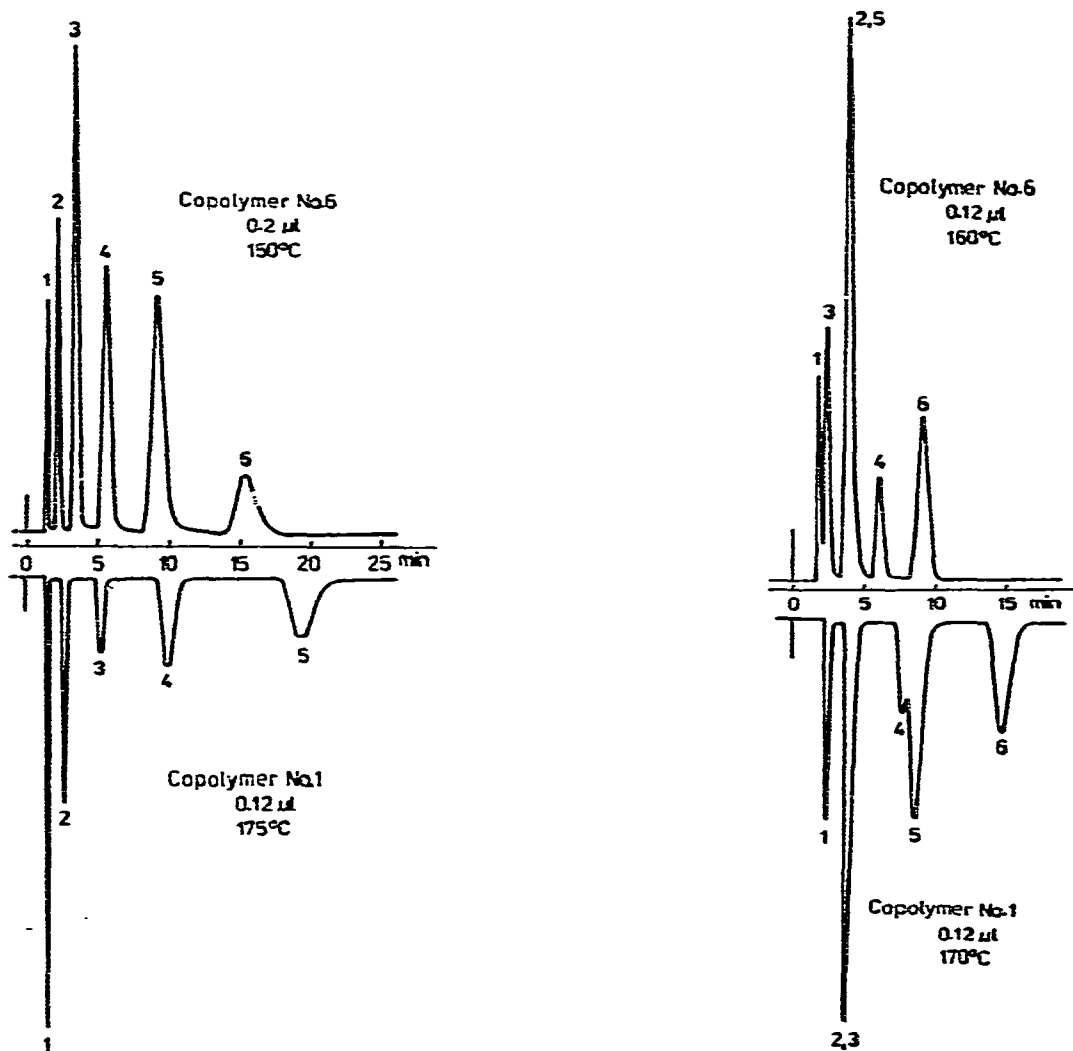


Fig. 1. Separation of a hydrocarbon mixture on modified copolymer 6 and on the initial copolymer 1. Glass columns (100 × 0.3 cm I.D.); nitrogen flow-rate of 25 ml/min. Peaks: 1 = hexane; 2 = heptane; 3 = octane; 4 = nonane; 5 = decane; 6 = undecane. Separation conditions as given on figures.

Fig. 2. Separation of a mixture of cycloparaffins and of the corresponding aromatics on modified copolymer 6 and on the initial copolymer 1. Columns and flow-rate as in Fig. 1. Peaks: 1 = cyclohexane; 2 = benzene; 3 = methycyclohexane; 4 = toluene; 5 = ethylcyclohexane; 6 = ethylbenzene.

ethyl acetate (77.1 °C) and methyl ethyl ketone (79.6 °C) one peak is obtained with Porapak T<sup>3</sup> (components 3–5), the separation factor of copolymer 7 in the separation of components 3 and 4 is  $\theta = 0.80$  and of components 4 and 5 it is  $\theta = 0.65$ , with the heat-treated copolymer 10 all the three components are completely separated.

The modified Rohrschneider constants<sup>3,7</sup> were chosen as a measure of the polarity of glycidylmethacrylate copolymers, *i.e.*, of their ability to interact specifically with molecules of polar sorbates. It also follows from Table II that the thermal treat-

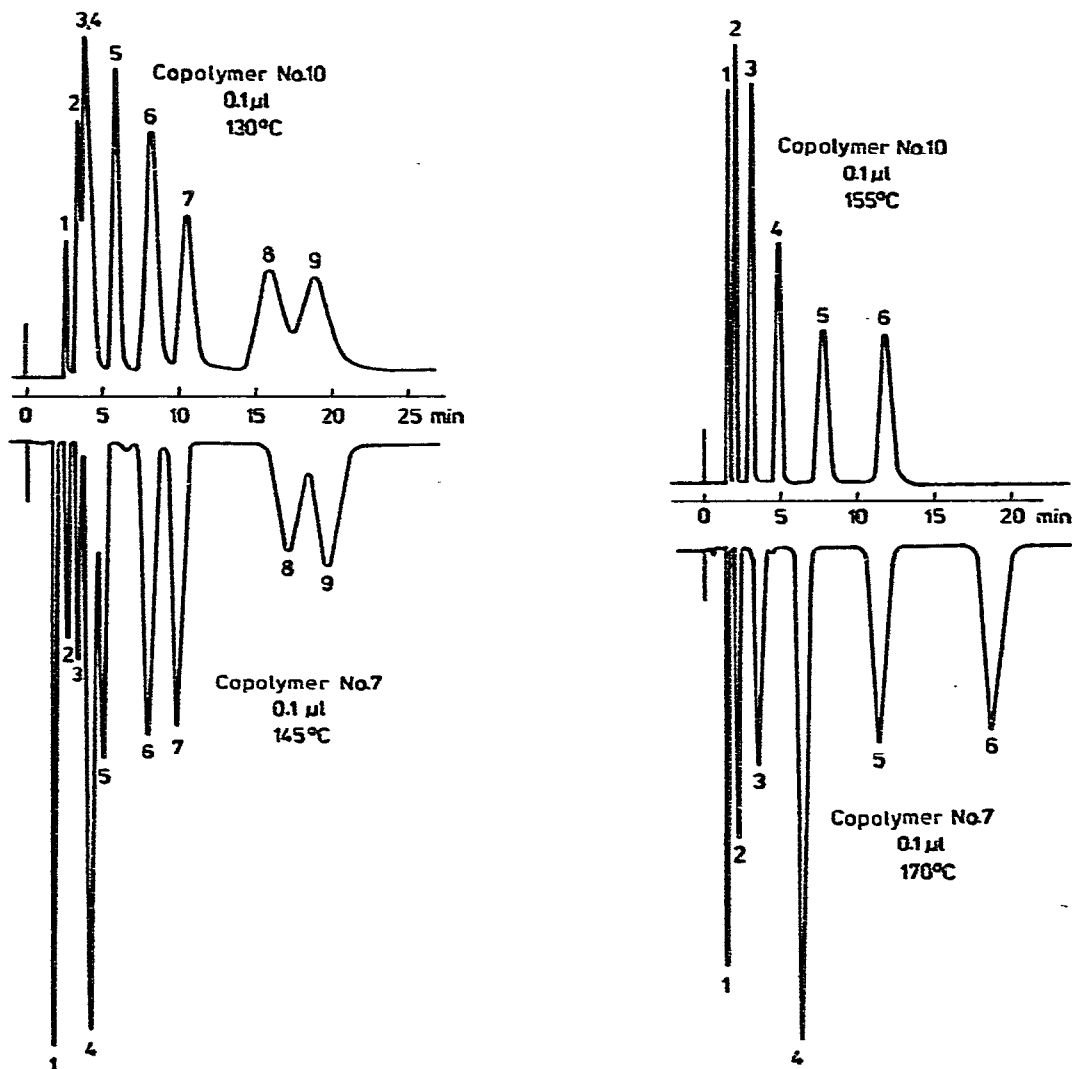


Fig. 3. Separation of a mixture of alcohols on modified copolymer 10 and on initial copolymer 7. Columns and flow-rate as in Fig. 1. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *tert.*-butanol; 5 = propanol; 6 = isobutanol; 7 = butanol; 8 = 3-methylbutanol; 9 = pentanol.

Fig. 4. Separation of acetic acid esters on modified copolymer 10 and on initial copolymer 7. Columns and flow-rate as in Fig. 1. Peaks: 1 = methyl acetate; 2 = ethyl acetate; 3 = propyl acetate; 4 = butyl acetate; 5 = pentyl acetate; 6 = hexyl acetate.

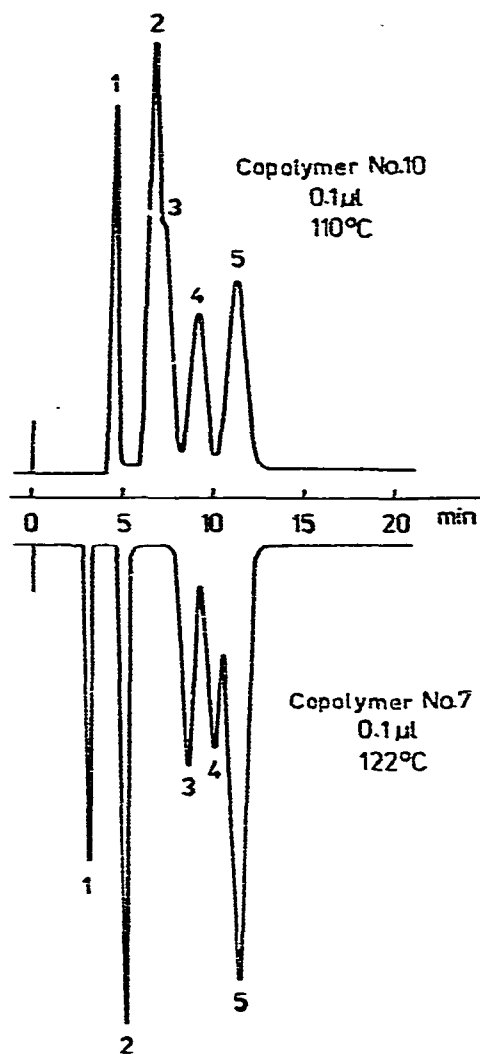


Fig. 5. Separation of compounds with various functional groups and similar boiling points on modified copolymer 10 and on initial copolymer 7. Columns and flow-rate as in Fig. 1. Peaks: 1 = methanol; 2 = ethanol; 3 = 1-chlorobutane; 4 = ethyl acetate; 5 = methyl ethyl ketone.

ment of these materials causes a further considerable rise in polarity, although the content of glycidylmethacrylate, whose epoxy groups are mainly responsible for the polar properties of these sorbents, is somewhat reduced in the partial degradation process (Table I). This finding may be explained by conformational changes in the copolymer chains which may take place under the temperatures of modification. The increased mobility of chains probably results in a rise in the concentration of hydrophilic glycidyl groups on the sorbent surface, so that their interactions with polar sorbates are more pronounced. Interactions with pyridine in the case of thermally modified samples may even assume irreversible character ( $s'$  values).

The HETP values determined at 150 °C for a number of sorbates (Table III)

TABLE II

MODIFIED ROHRSCHEIDER CONSTANTS<sup>3</sup> OF COPOLYMER SAMPLES  
Determined at 150°C.

Copolymer No.	$x'$	$y'$	$z'$	$u'$	$s'$
1	1.44	2.66	2.23	3.48	2.67
2	1.86	2.85	2.67	4.76	—
3	2.49	4.01	3.39	5.47	—
4	2.50	3.97	3.38	5.48	—
5	2.09	3.64	2.87	4.69	—
6	3.15	4.85	4.02	6.55	—
7	2.27	3.86	3.09	4.87	4.02
8	3.03	4.85	3.92	6.40	—
9	3.24	5.09	4.06	6.74	—
10	3.43	5.39	4.26	7.15	—

exhibit a slight decrease for thermally modified copolymers. This is due to the fact that at such a considerable shortening of retention times there is no proportional narrowing of peaks, even though their sharpness remains very good. Some lower HETP values may also be explained by the fact that the temperature, 150 °C, at which they were recorded is not optimal for the chromatographic analysis of these compounds.

The thermally treated glycidylmethacrylate copolymers extended the series of polymeric sorbents and added some strongly polar materials. Their main advantage consists in the possibility of a quick chromatographic analysis at considerably lower working temperatures, which is particularly valuable in the separation of thermally less stable compounds.

TABLE III

SEPARATION EFFICIENCY ON COPOLYMER SAMPLES EXPRESSED AS HETP (cm)  
Measured at 150°C and at a nitrogen flow-rate of 25 ml/min.

Sorbate	Copolymer No.									
	1	2	3	4	5	6	7	8	9	10
Hexane	0.29	0.52	0.57	0.58	0.43	0.59	0.34	0.59	0.60	0.48
Heptane	0.21	0.34	0.37	0.40	0.36	0.41	0.29	0.44	0.41	0.35
Octane	0.18	0.24	0.25	0.31	0.22	0.33	0.24	0.35	0.36	0.25
Benzene	0.13	0.25	0.25	0.27	0.23	0.31	0.13	0.22	0.20	0.15
Methyl ethyl ketone	0.31	0.37	0.30	0.26	0.29	0.30	0.17	0.21	0.20	0.23
Nitromethane	0.11	0.15	0.17	0.29	0.25	0.29	0.17	0.21	0.21	0.20
Methanol	0.38	0.40	0.41	0.48	0.39	0.46	0.43	0.42	0.45	0.41
Ethanol	0.29	0.32	0.34	0.38	0.30	0.38	0.33	0.35	0.36	0.30
1-Propanol	0.19	0.24	0.26	0.31	0.25	0.31	0.19	0.20	0.23	0.20
1-Butanol	0.15	0.17	0.18	0.20	0.19	0.22	0.13	0.17	0.19	0.14

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