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## *Reactions*

# Reactive Polymers
## 54. Synthesis of Methacrylate Copolymers with Tributylammonium Groups

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### Summary

Two methods of the synthesis of tributyl ammonium derivatives of glycidyl methacrylate - ethylene dimethacrylate copolymers with various contents of the crosslinking agent were examined. While the two-step process which consists in a reaction with dibutyl amine followed by alkylation with butyl bromide gives products with up to 1.5 mmol/g of required groups, in the case of the single-step reaction of the epoxide group with tributyl amine the content does not exceed 0.4 mmol/g. The use of diamines for increasing the distance between the quaternary group and the polymer backbone does not yield a readily definable product, and cannot therefore become the method of choice.

### Introduction

Polymeric materials containing strongly basic ammonium groups are produced on a large scale by the modification of copolymers of styrene and divinylbenzene and are used as anion exchange resins (1). The ammonium group is usually substituted in these materials with three methyl groups, or with two methyl groups and the 2-hydroxyethyl group. Their synthesis proceeds via the chloromethylated copolymer prepared by a reaction with cancerogenic chloromethylmethyl ether. The synthesis of polymers bearing quaternary ammonium or phosphonium groups with higher substituents ($C_4$ and more) has been particularly developed in connection with polymer-supported phase-trasfer catalysts (2,3). In this case too the predominant position is occupied by the styrene-divinylbenzene matrix; copolymers of 4-vinylpyridine are used only exceptionally.

Methylacrylate polymers as carriers of ammonium groups have been described only in those cases where at least one alkyl group is the methyl group (4,5), and in the patent literature (6,7).

### Experimental

*Preparation of the copolymer with dibutyl amino groups*

10 g of the copolymer glycidyl methacrylate - ethylene dimethacrylate (5) prepared with 2.5 (G-97.5), 30 (G-70) and 40 wt.% of the crosslinking agent (G-60) was swollen in 20 ml of dioxan, and after the addition of 20 ml of dibutyl amine the

mixture was heated with occasional stirring to 80°C for 8 h. The polymer was washed with water and ethyl alcohol and dried at 78°C and 1.3 kPa. The individual polymers contained 4.99, 2.27 and 2.22 % N respectively, which corresponds to the respective contents 3.56, 1.62 and 1.90 mmol of dibutyl amino groups/g.

### *Alkylation of the polymer with dibutyl amino groups*

1 g of the polymer was swollen in an ampoule containing 2.5 ml of nitromethane and 2.5 ml of butyl bromide, the ampoule was sealed and heated to 100 or 120°C for 4 to 336 h. Some polymers were alkylated at 45°C without solvent.

### *Reaction of glycidyl methacrylate copolymers with tributyl amine*

1.5 g of the copolymer glycidyl methacrylate-ethylene dimethacrylate (with 2.5 or 40 wt.% of the crosslinking agent) was swollen in 1 ml of dimethylformamide (or with 0.2 ml water added, respectively) and after the addition of 2 ml of tributyl amine (or in a solution of 2 g of tributyl amine hydrochloride in 3 ml of dimethylformamide, respectively) was heated to 80°C for 48 h.

### *Preparation of copolymers with spaced tributyl ammonium groups*

1 g of the copolymer glycidyl methacrylate - ethylene dimethacrylate (with 2.5 or 40 wt.% of the crosslinking agent) was swollen in 5 ml of dioxan, 3 ml of ethylenediamine (or 2 g of hexamethylenediamine, respectively) was added, and the mixture was heated to 80°C for 8 h; after that it was washed with water and ethyl alcohol, and finally dried at 78°C and a pressure of 1.3 kPa. The intermediate thus prepared was repeatedly alkylated three times with 2 ml of butyl bromide in 2 ml of nitromethane at 120°C for 48 h. After each alkylation (with the exception of the last) the intermediate was transformed into the OH form by means of 1 mol/l NaOH, and washed with water, ethyl alcohol, acetone, and nitromethane.

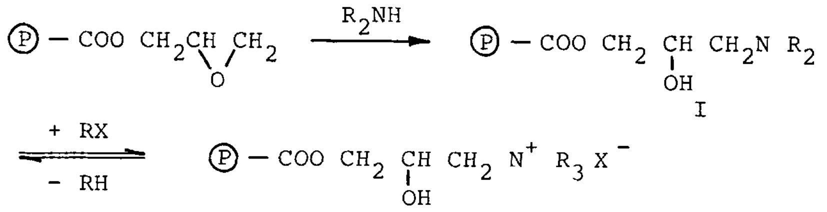
The nitrogen content in the product was determined by elemental analysis. The content of quarternary groups was ascertained by potentiometric titration in 1 mol/l NaCl using an automatic apparatus Mettler by 0.1 mol/l HCl after the groups had been transformed into the $OH^-$ form by washing with 50 ml of 1 mol/l NaOH and water.

Water regain ($V_g$) was determined by the centrifugation technique, and the porosity (p) was calculated therefrom.

The infrared spectra were measured by the KBr technique using a Grating Infrared Perkin-Elmer Spectrophotometer, model 577. The presence of a band near 2640 $cm^{-1}$ indicated tributyl ammonium groups.

## Results and Discussion

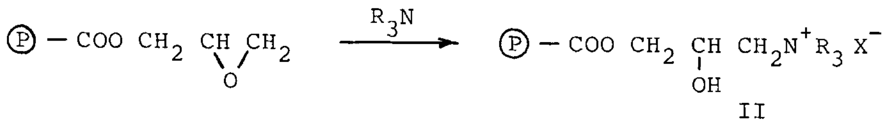
The quarternary ammonium derivative can be prepared from glycidyl methacrylate - ethylene dimethacrylate copolymers by two procedures. The first, a two-step one, consists in the modification of the epoxide group with dialkyl amine (e.g., dibutyl amine) followed by an alkylation of the polymer tertiary amine with alkyl halide:



(A)

I

The second procedure consists of a single-step reaction and the required product is obtained by reacting the epoxide group of the polymer with trialkyl amine:



(B)

II

The reaction with dialkyl amines proceeds quite readily, with relatively high conversions also under mild conditions (5). The product is easily definable, and the whole amount of nitrogen determined by elemental analysis is present in groups characterized by formula I.

The subsequent alkylation requires harder conditions. As evidenced by samples 11 and 12 (Table 1), at 45°C and within 72 h less than 20% of the nitrogen atoms present become alkylated. Only when the temperature has been raised to 100° the

Table 1 Alkylation of methacrylate copolymers containing di(n-butyl)amino groups with n-butyl bromide
(Conditions: 1 g of polymer, 2.5 ml of nitromethane and 2.5 ml of n-butyl bromide)

| Number | Polymer | Temperature °C | Time h | Content of $Bu_3N$ groups mmol/g | Fraction of the total content % | %N | $V_g$ ml/g | P % |
|---|---|---|---|---|---|---|---|---|
| 1 | G-60[a] | 100 | 23 | 0.844 | 47.5 | 2.27 | 2.015 | 72.4 |
| 2 | | | 47.5 | 0.849 | 47.8 | 2.30 | 1.686 | 68.7 |
| 3 | | | 336 | 0.967 | 54.4 | 2.40 | 1.598 | 67.5 |
| 4 | | 120 | 4 | 0.215 | 12.1 | 2.40 | 0.972 | 55.8 |
| 5 | | | 8 | 0.606 | 34.1 | 2.07 | 0.669 | 46.5 |
| 6 | | | 18 | 0.793 | 44.6 | 2.97 | 0.538 | 41.1 |
| 7 | | | 68 | 0.829 | 46.6 | - | - | - |
| 8 | | | 168 | 0.569 | 32.0 | 2.14 | - | - |
| 9 | G-97.5[b] | 120 | 48 | 1.516 | 42.5 | 4.99 | 3.539 | 82.1 |
| 10 | G-97.5[c] | 120 | 48 | 1.625 | 45.6 | 4.96 | 2.226 | 74.3 |
| 11 | G-60[d] | 45 | 72 | 0.199 | 11.2 | 0.98 | - | - |
| 12 | G-60 | 45 | 72 | 0.304 | 17.1 | 2.26 | - | - |
| 13 | G-70[a] | 120 | 48 | 0.744 | 45.9 | 2.27 | 1.594 | 67.4 |

Particle size (µm): [a]150-250, [b]<300, [c]300-500, [d]25-32(without solvent), [e]150-250(without solvent).

fraction of alkylated groups increases above 50%. The effect of the polar solvent also seems to be favourable. A further rise in temperature to 120°C, though it further accelerates the alkylation reaction, but at the same time increases the rate of undesired side reactions which degrade the ammonium group by eliminating butylene via Hofmann's mechanism back to the dibutyl amino derivative. This becomes particularly apparent at a longer reaction time, as shown in Fig.1. At 100°C, the rate of alkylation exceeds that of elimination, and the content of quaternary groups does not decrease even after 14 days of continuous reaction. However, even within such a long reaction time the conversion does not exceed 50 % theoretical to any important degree, and the maximum attainable capacity in the case of a macroporous copolymer with 40% of the crosslinking agent is about 1 mmol/g.

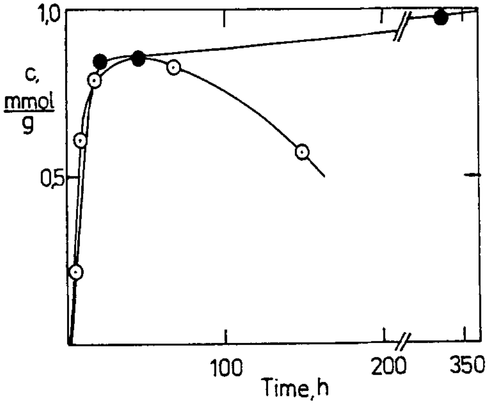


Fig. 1 Time dependence of alkylation of methacrylate copolymers containing di(n-butyl)amino groups with n-butyl bromide at 100°C (●) and 120°C (⊙).

However, maintaining the polymer at an elevated temperature brings about a change also in the inner structure of the macroporous particle, and water regain decreases in spite of the increasing content of hydrophilic groups.

Higher capacities (up to 1.6 mmol/g) can be reached using low-crosslinked gel materials containing 2.5 % of the crosslinking agent. When one compares the conversion of dibutyl amine groups to tributyl ammonium ones, it can be perceived that irrespective of the type of the initial polymer the conversion value varies in the range between 41 and 54 % ; the lower value is not optimized, and it may be assumed that it could even be somewhat raised. Nevertheless, no essential increase above 50% can be reached in any case.

Compared with the two-step procedure, the direct reaction of the epoxide group with trialkyl amine (B) is less advantageous. On the one hand, it gives rise to products with a considerably lower content of the required groups (Table 2); on the other, and contrary to expectations, it does not give a product in which quaternary groups would be the only nitrogen-containing ones bound to the polymer. On the contrary, they are minority groups, and the reason can again be seen in the elimination which takes place simultaneously, not leading, how-

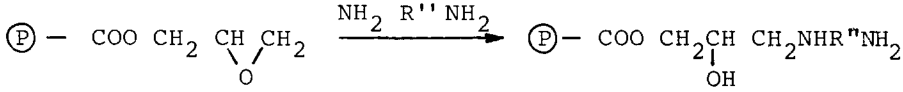
Table 2 Reaction of glycidyl methacrylate copolymers with tri(n-butyl)amine
(Conditions: 1 g of polymer, 1 ml of dimethylformamide, 2 ml of tri(n-butyl)amine (or 3 ml of dimethylformamide and 2 g of tri(n-butyl amine hydrochloride, 80°C, 48 h)

| Number | Polymer | Reagent | Content of $Bu_3N$ groups mmol/g | Fraction of the total content % | %N | $V_g$ ml/g | P % |
|---|---|---|---|---|---|---|---|
| 18 | G-60 | $Bu_3N.HCl$ | 0.037 | 23.8 | 0.22 | 1.057 | 57.9 |
| 19 | G-97.5 | $Bu_3N$ | 0.081 | 11.2 | 1.01 | 0.918 | 54.4 |
| 20 |  | $Bu_3N^a$ | 0.229 | 27.9 | 1.15 | 2.226 | 73.3 |
| 21 |  | $Bu_3N.HCl$ | 0.384 | 45.9 | 1.17 | 0.586 | 43.2 |

$^a$0.2 ml $H_2O$

ever, back to the starting group, but to groups I; as a consequence, the fraction of reactive epoxides systematically decreases not being compensated for by an increase in the quaternary groups content. The results obtained are at variance with those reported in patents (6,7), and the method cannot virtually be applied in the synthesis of the required product II.

In some applications it is advantageous to raise the mobility of the quaternary ammonium group by increasing its distance from the polymer backbone by means of spacers. In the case of modification of glycidyl methacrylate copolymers this may be achieved, e.g., by reacting the epoxide group with diamine, which is followed by alkylation:



$$\textcircled{P} - COO\,CH_2\,\underset{O}{CH\,CH_2} \xrightarrow{NH_2\,R''NH_2} \textcircled{P} - COO\,CH_2\underset{OH}{CH}\,CH_2NHR''NH_2 \quad (C)$$

The reaction B is however only one of the many reactions which may take place between the two components. One cannot rule out the reaction between both amino groups of the diamine, which obviously also occurs here (5). This reverses the requirement of increased mobility. The alkylation reaction with alkyl halide may be carried out both on the primary and on the secondary amino group, which leads to a great variety of alkylated products. In order to reach a reasonable content of quaternary groups in the polymer, the quaternization was performed by repeating several times the reaction with alkyl halide after the product had been previously transformed into the $OH^-$ form (Table 3). However, not even repeating the reaction three times would lead to a content exceeding 0.5 mmol/g. There are probably more reasons than one which impede the obtaining of better results; in addition to the elimination already discussed above, they may also include an increased network density of the polymer. It is evident that the use of the diamine in order to introduce the spacer is not the optimal solution, and other routes are being examined.

Table 3 Alkylation of products of the reaction with diamines (Conditions: 1 g of copolymer, 1 ml of nitromethane, 1 ml of n-butyl bromide, 120°C, 48 h)

| Number | Polymer | Diamine | Content of $Bu_3N$ groups mmol/g | Fraction of the total content % | %N | $V_g$ ml/g | P % |
|---|---|---|---|---|---|---|---|
| 14 | G-60 | Ethylenediamine | 0.169 | 6.3 | 3.75 | 1.590 | 67.4 |
| 15 | | Hexamethylenediamine | 0.496 | 24.4 | 2.93 | 1.567 | 67.1 |
| 16 | G-97.5 | Ethylenediamine | 0.370 | 22.5 | 6.07 | 1.236 | 61.6 |
| 17 | | Hexamethylenediamine | 0.157 | 13.3 | 4.85 | 0.712 | 48.1 |

Quaternary ammonium groups bound to the methacrylate polymer were successfully applied as polymer-supported phase-transfer catalysts (8).

## References

1. M. Marhol, "Ion Exchanges in Analytical Chemistry", Academia, Praha 1982
2. F. Montanari, D. Landini and F. Roua, Phase-Transfer Catalysed Reactions in "Host Guest Complex Chemistry II", F. Vogtle (Ed.) Springer Verlag Berlin, 1982, p.147
3. W.F. Ford and M. Tomoi, Adv.Polym.Sci. 55, 50 (1984)
4. J. Štamberg, S. Ševčík and J. Holata, J.Polym.Sci. 47, 335 (1974)
5. F. Švec, H. Hrudková, D. Horák and J. Kálal, Angew.Makromol.Chem. 63, 23 (1977)
6. J.C.H. Hwa, US pat. 2630 427 (1951)
7. V.J. Webers, US pat. 2676 166 (1954)
8. J. Hradil, F. Švec and J.M.J. Frechet, in preparation

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