

## CHEMICAL TRANSFORMATIONS OF POLYMERS. X.\*

POLY(TRIMETHYL-4-METHACRYLOYLOXYBUTYLAMMONIUM  
CHLORIDE-co-DIVINYLBENZENE)

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Quaternary ammonium hydroxides of the general formula  $RN(CH_3)_3OH$ , where R is methyl, propyl, isobutyl, or even ethyl, split according to Hofmann in concentrated solutions of strong bases at temperatures around 100°C much less than commercially available strong basic anion exchangers, based on poly(vinylbenzyl-trimethyl-ammonium hydroxide)<sup>1</sup>. A similar behaviour can also be expected with polymers of the general formula  $[R'N(CH_3)_3OH]_n$ , where R' is analogous to R. Anion exchangers having an aliphatic structure which corresponds to this condition should have, apart from a higher thermal stability in the  $OH^-$  form, also a weaker tendency toward irreversible sorption of organic compounds than anion exchangers with an aromatic structure<sup>2</sup>.

In the literature, anion exchangers have been described based on the aminoesters of both acrylic and methacrylic acids, and also crosslinked poly(trimethyl-3-acrylamidopropylammonium chloride)<sup>3-8</sup>. The present paper refers to the synthesis of poly(trimethyl-4-methacryloyloxybutylammonium chloride-co-divinylbenzene)<sup>9</sup>. The preparation of 4-chlorobutyl methacrylate, its polymerization and copolymerization with divinylbenzene, polymeranalogous transformation of the copolymer and the ion exchange properties of the product have been outlined. The choice of the structure of the anion exchanger was based on the previously established high hydrolytic stability of polymethacrylates<sup>10</sup>, and also on the assumption that a separation of the nitrogen atom from electronegative atoms with a longer alkyl group would affect favourably the stability of the quaternary ammonium hydroxyl group.

## EXPERIMENTAL

## Materials

4-Chlorobutyl methacrylate was obtained from methacryloyl chloride<sup>11</sup> and tetrahydrofuran according to<sup>12,13</sup> in a yield 70% (related to methacryloyl chloride),  $n_D$  1.4570. Divinylbenzene (technical purity grade) contained 41.3% *m*- and 16.6% *p*-isomer, 29.0% *m*-ethylvinylbenzene, 11.2% *p*-ethylvinylbenzene, 0.3% *o*-ethylvinylbenzene, 0.3% *m*-diethylbenzene, 0.3% *p*-diethylbenzene, 0.1% *o*-diethylbenzene and 0.9% naphthalene, according to gas chromatographic data. It was freed from inhibitor prior to polymerization by extraction with 5% NaOH and water and dried with anhydrous sodium sulphate.

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## Preparation of High-Molecular Weight Compounds

An ampoule containing 2 g of a mixture of monomers and benzoyl peroxide (5%) was five times alternatively evacuated (10–15 Torr) at room temperature and flushed with nitrogen (chemical purity grade), sealed and heated to 70°C for 24 h. The polymerization mixture solidified within approximately ten minutes. The polymer was crushed, extracted with benzene (analytical purity grade) in a Soxhlet apparatus on the G 3 fritted disc for eight hours and dried at 105° to constant weight. 4-Chlorobutyl methacrylate was polymerized under identical conditions. The homopolymer thus obtained was dissolved in benzene and precipitated into methanol. The osmotically determined molecular weight (Automatic Osmometer, Shell – Hallikainen Instr.; toluene, 40°C) was  $3 \times 10^5$ .

During suspension polymerization, 60 g of an oxygen-free monomer mixture (benzoyl peroxide content 5%) and 300 ml of a 0.5% aqueous gelatin solution ( $[\eta] = 2.0 \text{ dl g}^{-1}$  at 20°C) were stirred at 70°C for six hours with a propeller stirrer in a sulphonation flask provided with a thermometer. The copolymer was washed on the G 3 fritted disc with distilled water (2 l) at 90°C, dried to constant weight at 105°C and extracted with benzene under conditions described above.

To the copolymer (0.7 g), swollen in the ampoule with benzene (3 ml, 16 h), a 20% aqueous solution of trimethyl amine (3 ml) was added, the ampoule was sealed and heated for a certain time. The product was filtered and washed (0.5 ml/min) with methanol (50 ml; analytical purity grade) and distilled water (250 ml).

## Analytical Methods

Chlorine in poly(4-chlorobutyl methacrylate-co-divinylbenzene) was determined titrimetrically after combustion in oxygen<sup>14</sup>. The weight swelling and ion-exchange capacities were determined by usual procedures<sup>15</sup>; the samples were dried to constant weight at 30°C over phosphorus pentoxide. The infrared spectra of the copolymers were measured using KBr tablets with a Perkin-

TABLE I

Copolymers of 4-Chlorobutyl Methacrylate (*I*) with Divinylbenzene (*II*)

$C_{II}$  is the content of *II* in % (calculated with respect to the technical mixture of monomers),  $Q$  is the weight swelling capacity in g benzene/g dry matter,  $(c_{Cl})_A$  is the chlorine content (%) according to analysis,  $N_I^a$  and  $N_I^b$  are molar fractions of *I* in the monomeric mixture or in the copolymer.

$C_{II}$	$Q$	$(c_{Cl})_A$	$N_I^a$	$N_I^b$
2.2	1.82	19.2	0.95	0.94
3.6	1.30	18.8	0.92	0.92
6.4	0.70	17.9	0.86	0.86
9.7	0.39	16.8	0.79	0.79
11.5	0.34	16.2	0.75	0.76

<sup>a</sup> Content of *I* in the mixture with divinyl- and ethylvinylbenzene, calculated from the weighed amounts. <sup>b</sup> Content of the structural units of *I*, calculated from the chlorine content, for a copolymer consisting of *I* + *II* + ethylvinylbenzene.

TABLE II

Weight and Volume Swelling Values ( $Q$ ,  $V_g$ ) of the Poly-98 : 2 (4-chlorobutyl methacrylate-co-divinylbenzene)

Swelling agent	$Q^a$	$V_g^b$
Hexane	0.06	1.8
Methanol	0.08	1.9
Acetone	0.73	2.9
Benzene	1.02	3.4
Tetrahydrofuran	1.15	3.5
Dioxan	1.21	3.2
1,2-Dichloroethane	1.64	3.8

<sup>a</sup> Determined by centrifugation method, expressed in grams of the swelling agent per one gram of the dry matter. <sup>b</sup> Volume of the swollen copolymer column in  $\text{cm}^3$ , corresponding to one gram of the dry matter.

TABLE III

Poly(trimethyl-4-methacryloyloxybutylammonium Chloride-co-divinylbenzene)

$C_{II}$  is the content of divinylbenzene in % (cf. Table I),  $d_{20}^{20}$  is the density in  $\text{g cm}^{-3}$ ,  $Q$  is the weight swelling capacity in water in  $\text{g H}_2\text{O/g}$  dry matter,  $C$  is the total weight capacity in  $\text{mval/g}$  of the dry matter,  $(c_N)_A$  and  $(c_N)_C$  is the nitrogen content (%) according to analysis or from the capacity measurements,  $K$  is molar conversion in %. The molar ratio of trimethyl amine to the main copolymerization component in the individual experiment was as follows (in a descending order): 2.54, 2.59, 2.72, 2.90 and 3.01.

$C_{II}$	$d_{20}^{20a}$	$Q$	$C$	$(c_N)_A$	$(c_N)_C$	$K^b$
2.2	1.040	1.94	4.10	5.6	5.7	96.7
3.6	1.095	1.18	3.72	5.5	5.2	96.4
6.4	1.140	0.85	3.69	5.2	5.2	94.2
9.7	1.170	0.61	3.58	5.0	5.0	95.5
11.5	1.190	0.45	5.55	4.8	4.9	94.0

<sup>a</sup> Swollen copolymer in water. <sup>b</sup>  $K = 354600 (c_N)_A / [c_{Cl} (1401 - 59.11 (c_N)_A)]$ .

Elmer 457 spectrometer; the NMR spectra of poly(4-chlorobutyl methacrylate) were recorded with a JEOL-JNM-3-60 apparatus at 60 Mcps. The pH titration curve of the anion exchanger<sup>15</sup> was recorded with an automatic titration Radiometer, Copenhagen, TTT 1c/SBR 2c/ABU 1c.

## RESULTS AND DISCUSSION

Homogeneous mixtures of 4-chlorobutyl methacrylate and divinylbenzene copolymerized over a sufficiently wide range of mutual ratios with respect to the formation of crosslinked networks, usual for the ion-exchange systems (Table I). The copolymers prepared in substance had a comparatively high benzene extract (about 20%); the composition of copolymers, calculated from the chlorine content, was nevertheless in good agreement with the composition of the monomer mixture (Table I). The suspension copolymer had a considerably lower extract (about 5%) and a lower degree of swelling than the copolymer prepared in substance. Argentometric titration of the disperse medium after suspension copolymerization showed that if chlorides were split from the ester during polymerization, the reaction occurred to an extent less than 2%.

The solvation properties of the poly(4-chlorobutyl methacrylate-*co*-divinylbenzene) network are described by the swelling values in various solvents (Table II). The chemical structure has been confirmed by the IR and NMR spectroscopy. In the infrared spectra, bands were found which corresponded to the characteristic vibrations of the  $\text{CH}_2$  and  $\text{CH}_3$  groups in the region 2800 to 3000  $\text{cm}^{-1}$ , vibration of an esterified carboxyl group (1730  $\text{cm}^{-1}$ ), and valency vibration C—Cl (660  $\text{cm}^{-1}$ ).

In the NMR spectra, bands were determined which corresponded to the groups  $\text{CH}_3^a$  ( $\tau = 8.95$  and 8.84),  $\text{CH}_2^b$  ( $\tau = 8.19$ ) and  $\text{CH}_2^{c,d}$  ( $\tau = 5.98$  and 6.51). The ratios of the common integrated intensities,  $\text{CH}_3^a : \text{CH}_2^b : \text{CH}_2^{c,d} = 3.04 : 6.1 : 4.0$  are in agreement with the structural formula

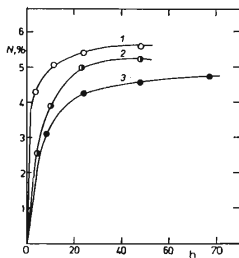
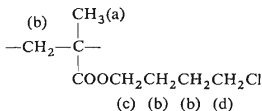


FIG. 1

Conversion of Poly(4-chlorobutyl methacrylate-*co*-divinylbenzene) into Poly(trimethyl-4-methacryloyloxybutyl ammonium chloride-*co*-divinylbenzene)

Content of divinylbenzene, %: ○ 2.2, ○ 6.4, ● 11.5.

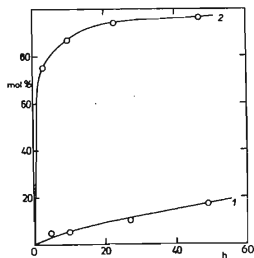


FIG. 2

Course of the Polymeranalogous Reaction of Poly(4-chlorobutyl methacrylate) with Trimethyl Amine  
1 30°C, 2 60°C.

The polymeranalogous transformation of poly(4-chlorobutylmethacrylate-co-divinylbenzene) into poly(trimethyl-4-methacryloyloxybutylammonium chloride-co-divinylbenzene) occurred to high conversions (Table III). The course of the reaction was considerably temperature-dependent (Fig. 1) and almost independent of the degree of crosslinking of the starting copolymer (Fig. 2). It follows from the comparison of these results that the rate of transformation depends more on the reaction kinetics than of the diffusion through the gel phase. An increase in the crosslinking of the starting copolymer did not affect even the final conversion value (Table III), which indicates the accessibility of the majority of the reaction sites also at a high degree of crosslinking. The fact that trimethyl amine reacted with formation of exchange groups is demonstrated by the determined capacity values. The molar conversions, calculated from the nitrogen contents obtained by elemental analysis and from the exchange capacity values, are in good agreement with each other (Table III). The course of the pH titration curve of the anion exchanger corresponds to the titration of a monofunctional strong base. Infrared spectra also correspond to the formation of trimethyl ammonium groups. The polymeranalogous transformation could be accompanied by an alkaline hydrolysis of the ester bonds. However, owing to the well-known high hydrolytic stability of the polymethacrylate structures<sup>10</sup> it is not surprising that the actual weight yields of the copolymers with quaternary ammonium groups, around 98% theoretical calculated with respect to the chlorine content in the starting copolymer, were very high, and the methanolic extract of the final product was only 1 to 2%.

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