

## ACIDOLYSIS OF POLY[(2-TRIPHENYLMETHOXYETHYL) METHACRYLATE]

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The paper reports on the preparation and fractionation of poly[(2-triphenylmethoxyethyl) methacrylate], determination of its molecular characteristics (molecular weight and intrinsic viscosity) and acidolytic transformation (by hydrogen chloride) into poly(2-hydroxyethyl methacrylate). The branching of the molecules of poly[(2-triphenylmethoxyethyl) methacrylate] due to the reaction chain transfer has been proved; however, linear poly(2-hydroxyethyl methacrylate) has been found to be the resulting product of the acidolytic cleavage.

It has been shown in a preliminary communication<sup>1</sup> on the polymeranalogous transformation of poly[(2-triphenylmethoxyethyl) methacrylate] into poly(2-hydroxyethyl methacrylate) that monomeric 2-triphenylmethoxyethyl methacrylate can be obtained in the crystalline state in a high degree of purity, that it can be polymerized radically, that the splitting-off of the trityl group from the polymer can be carried out by hydrogenation or by the acidolytic effect of hydrogen chloride, and that the second reaction is more advantageous. In this paper acidolysis has been investigated in more detail in order to find out whether it is suited for the preparation of linear poly(2-hydroxyethyl methacrylates).

### EXPERIMENTAL

#### Preparation and Acidolysis of Poly[(2-Triphenylmethoxyethyl) Methacrylate] (I)

The polymerization of 2-triphenylmethoxyethyl methacrylate (monomer twice recrystallized from a 60% aqueous alcohol, m.p. 53°) initiated with diisopropyl peroxycarbonate (0.1–0.2% per monomer) was carried out in solution (60% solution in toluene) in nitrogen-free oxygen (sealed ampoules) at 60°C during 3 h. On cooling to room temperature the solution was diluted with toluene to a 5% solution and the polymer was precipitated by pouring it into a tenfold excess of methanol. The polymer was reprecipitated from a 5% benzene solution into a tenfold excess of methanol, filtered off and dried *in vacuo* over phosphorus pentoxide. On drying the polymers became white and powderlike, readily soluble in aromatic hydrocarbons, chloroform, dioxan, and tetrahydrofuran. Dissolution in tetrahydrofurfuryl alcohol, cyclohexanone, cyclopentanone and dimethylformamide required a mild heating-up. The polymers did not dissolve in acetone, methyl ethyl ketone, and esters of the aliphatic alcohols even if heated to boil. Frac-

tionation of *I* was carried out by gradual precipitation of the benzene solutions with methanol at 25°C. The fractions that separated out as viscous solutions were reprecipitated twice from 2% benzene solutions by pouring them into a fivefold excess of methanol; after filtration and a thorough washing with methanol they were dried *in vacuo* at 50°C over phosphorus pentoxide. The results of fractionation are shown in Fig. 1 and Table I in the form of integral distribution curves and the index of polydispersity, respectively. The fractions were characterized by the weight average molecular weight ( $M_w$ ) determined by the light scattering method or read off from the correlation  $[\eta]$  vs  $M_w$  (Fig. 2).

*Acidolysis I.* An approximately 4% suspension of the polymer in methanolic hydrogen chloride (20%) was stirred at room temperature for 10 min. The trityl chloride thus obtained was removed by filtration, and the solution of poly(2-hydroxyethyl methacrylate) (*II*) was precipitated by pouring it slowly into a tenfold excess of distilled water while at the same time neutralizing the mixture with sodium hydroxide to pH 7; the precipitate formed in this process was thoroughly washed by decanting with distilled water. Polymer *II* was reprecipitated from 50 ml of the methanolic solution into 500 ml of ether, filtered and dried *in vacuo* over phosphorus pentoxide. The content of the hydroxylic groups in the reaction products determined by acetylation varied from 12.76 to 13.06%, which corresponds to a transformation from 97.6 to 99.9%. The carbon content varied between 55.28 and 55.67% (55.39% theoretical); the hydrogen content varied between 7.78 and 7.83% (7.69% theoretical).

*Viscosity measurements* and determination of the molecular weight of polymers. The viscosity of the toluene solutions was measured at 25°C in capillary viscometers of the Ubbelohde type; intrinsic viscosities were evaluated by graphic extrapolation<sup>2</sup>. Molecular weights were determined by the light scattering method with a Photo-Gonio-Diffusiomètre Sofica apparatus; for polymers *I*, dioxan ( $dn/dc = 0.180$ ) was used as solvent, with toluene for a check-up ( $dn/dc = 0.114$ ), while for polymers *II* the solvent was dimethylformamide or the mixture propanol-25 vol-% water<sup>3</sup>. The measurements of 4–5 concentrations for each sample were made in unpolarized monochromatic light ( $\lambda$  546 nm) over a range of angles from 30° to 150°. Molecular weights  $M_w$  were evaluated by the Zimm extrapolation method; the results were reproducible, and both solvents gave the same value of  $M_w$ .

TABLE I  
Characteristics of Unfractionated Poly[(2-Triphenylmethoxyethyl) Methacrylates]

Polymer	$C_i, \%$ <sup>a</sup>	$M_w \cdot 10^{-3}$	$M_n \cdot 10^{-3}$	$M_w/M_n$	$[\eta]$ cm <sup>3</sup> g <sup>-1</sup>	
1	0.2 <sup>b</sup>	1 000 <sup>c</sup> , 1 130 <sup>d</sup>	210 <sup>d</sup>	5.35	37.1	37.1 <sup>d</sup>
2	0.10	690 <sup>d</sup>	220 <sup>d</sup>	3.14	33.0	33.4 <sup>d</sup>
3	0.17	320 <sup>d</sup>	108 <sup>d</sup>	2.93	—	18.0 <sup>d</sup>
4	0.01	1 400 <sup>c</sup>	—	—	—	—
5	0.16	1 100 <sup>c</sup>	—	—	—	42.7
6	0.20	480 <sup>c</sup>	—	—	—	23.8
7	0.20	350 <sup>c</sup>	—	—	21.7	—

<sup>a</sup> Addition of initiator referred to monomer; <sup>b</sup> Polymerization without solvent; <sup>c</sup> Determined by light-scattering method; <sup>d</sup> Determined by summation from results of fractionation.

## RESULTS AND DISCUSSION

If the acidolytic cleavage of poly[(2-triphenylmethoxyethyl methacrylate) (*I*)] proceeded quantitatively, the molecular weights ratio of the reaction products ( $M_{\text{exp}}$ ) and of the original polymer ( $M_{\text{in}}$ ) should be equal to the molecular weights ratio of the monomers (i.e. 0.350). However, the results of the cleavage summarized in Table II and shown graphically in Fig. 3 indicate that this ratio or the ratio  $p$  defined as  $p = M_{\text{exp}}/M_{\text{th}}$  and equivalent to it decreases with increasing  $M_{\text{in}}$ : at low  $M_{\text{in}}$ ,  $p > 1$ , and inversely, at  $M_{\text{in}} > 1 \cdot 10^6$   $p$  is distinctly lower than unity. The deviations in the upwards direction could mean that the reaction did not proceed quantitatively. The fact that the situation is more complex than it seems at the first glance is corroborated not only by the contents of the hydroxyl groups determined here, but also by the finding that  $p$  is higher than unity only at low values of  $M_{\text{in}}$ , while at high  $M_{\text{in}}$  (where an incomplete reaction could rather be expected) we obtain  $p < 1$ .

The yields of the isolated polymer attain 70–90% at the utmost and decrease slightly with decreasing molecular weight of the initial polymer. The lower yields are very likely to be due to the incomplete isolation of the product from the reaction mixture. Owing to the hydrophilic character of the polymer and to the character of the solutions, the latter contain about 1–2% of the polymer after the completion of acidolysis. The precipitation of such diluted solution is connected with large losses, especially for polymers having a lower molecular weight. Since the initial fractions used in the acidolysis were not monodisperse, lower polymer homologs

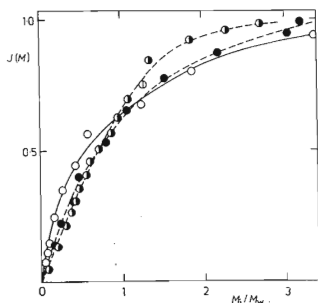


FIG. 1

Integral Distribution Curves of Molecular Weights of Poly[(2-Triphenylmethoxyethyl) Methacrylate] (*I*)

Fractions: ○ 1, ● 2, ● 3.

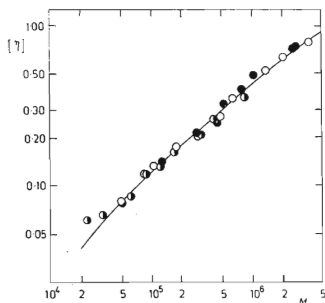


FIG. 2

Correlation of Intrinsic Viscosity and Molecular Weight of Polymer *I*

Fractions: ○ 1, ● 2, ● 3.

escaped during the isolation of the products. As a consequence, the ratio  $p$  must increase above the theoretical value.

A semiquantitative idea of what the consequences of these losses for the molecular weight of the product are has been formed by a model calculation based on mathematical fractionation. By using a procedure described in detail earlier<sup>4</sup>, we were trying to find out how the relative degree of polymerization of the fraction  $P_{w,1}/P_{w,0}$  depends on its magnitude expressed by its weight fraction  $w_1$ , assuming that the molecular weight distribution of the initial polymer is given by the Schulz-Zimm distribution function, that the index of polydispersity of the initial polymer,  $P_{w,0}/P_{n,0}$  is 2 or 1.5, and that the Flory-Huggins theory of phase equilibria can be applied to the system (the symbols  $P_{w,1}$  and  $P_{w,0}$  designate the weight average degree of polymerization of the fraction and of the initial polymer respectively, the symbol  $P_{n,0}$  designates the number average degree of polymerization of the initial polymer). Although the conditions under which the products were isolated certainly did not fulfil the assumptions of the calculation, the results can nevertheless be used for semiquantitative purposes. They show that for  $w_1 = 0.5$  (i.e. if only 50% of the polymer were obtained by isolation) the ratio  $P_{w,1}/P_{w,0}$  would be 1.4–1.5 (for  $P_{w,0}/P_{n,0} = 2$ ) and 1.3–1.4 (for  $P_{w,0}/P_{n,0} = 1.5$ ). If  $w_1 = 0.80$  (i.e. if the loss during the isolation was 20%), the ratio  $P_{w,1}/P_{w,0} = 1.20$  or 1.15. The ratio  $p$  in our experiments does not exceed 1.6, and the differences against  $p = 1$  lie mostly within the limits of values ensuing from the model calculation.

The incomplete isolation and its consequences must be taken into consideration even if the ratio  $p$  becomes close to unity, where the fit between the theoretical and

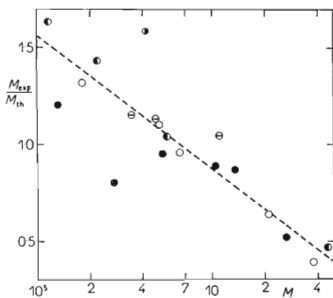


FIG. 3

Correlation of the Ratio  $p$  with Molecular Weight of Initial Polymer

Fractions: ○ 1, ● 2, ◐ 3, ◑ 4, ⊙ unfractionated samples.

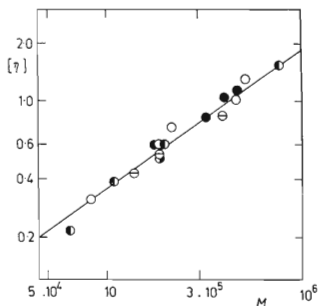


FIG. 4

Correlation Between Intrinsic Viscosity and Molecular Weight of Products of Acidolyses

Solvent: dimethylformamide (25°C). Straight line calculated according to relationship<sup>3</sup>  $[\eta] = 8.90 \cdot 10^{-5} M^{0.72}$ . Fractions of polymer I: ○ 1, ● 2, ◐ 3, ◑ 4, ⊙ unfractionated polymers.

experimental values of the molecular weight seems to suggest a perfect transformation. With respect to the losses during isolation, it must be borne in mind that in these cases too the actual value of  $p$  is larger than unity. If, moreover, we take into account that at  $M_{in} > 1 \cdot 10^6$  substantially lower  $p$  values are found also experimentally

TABLE II

Results of Acidolysis of Poly[(2-Triphenylmethoxyethyl) Methacrylates]

$M_{in}$  initial molecular weight,  $M_{th}$  or  $M_{exp}$  respectively theoretical or determined molecular weight of products of acidolyses (weight average values).

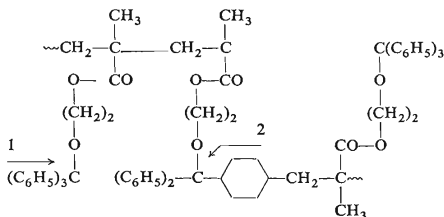
$M_{in} \cdot 10^{-3}$	$M_{th} \cdot 10^{-3}$	$M_{exp} \cdot 10^{-3}$	$M_{exp}/M_{th}$	$[\eta], \text{cm}^3 \text{g}^{-1b}$
Fraction of polymer 1 <sup>a</sup>				
3 800	1 330	525	0.39	133
2 100	735	470	0.64	103
650	227	218	0.96	74.5
490	171	190	1.11	60.5
180	63	83	1.32	31.5
Fraction of polymer 2 <sup>a</sup>				
2 630	919	475	0.52	115
1 350	470	410	0.87	106
1 050	368	328	0.89	83.0
520	182	178	0.95	60.1
286	100	80	0.80	—
130	46	55	1.20	—
Fraction of polymer 3 <sup>a</sup>				
420	120	190	1.58	51.0
Fraction of polymer 4 <sup>a</sup>				
4 600	1 600	776 <sup>c</sup>	0.47	154
550	192	200	1.04	60.5
220	77	110	1.43	38.7
115	40	65	1.63	21.4
Unfractionated polymers 5—7 <sup>a</sup>				
1 100	385	400	1.04	81.6
480	168	190	1.13	52.5
350	122	140	1.15	43.0

<sup>a</sup> Cf. Table I; <sup>b</sup> Intrinsic viscosity of product in dimethylformamide at 25°C; <sup>c</sup> Molecular weight determined from intrinsic viscosity in dimethylformamide.

(that is, for incomplete isolation), we can deduce that in an ideal case (*i.e.* for complete isolation) the ratio  $p$  would be less than unity even if the cleavage were complete. The acidolytic reaction obviously leads not only to a splitting-off of the trityl groups, but also to a degradation of the polymer. An acceptable explanation ensues from the following reasoning.

Unfractionated polymers  $I$  are strongly polydisperse compared to other polymers prepared by radical polymerization; the molecular weight distribution curves are spread in the region of high molecular weights which is typical of branched polymers (Fig. 1, Table I). Also the correlation between intrinsic viscosity and molecular weight (Fig. 2) exhibits deviations usual for branched polymers. Moreover, a more detailed study of the solution properties, particularly under the  $\Theta$  conditions, indicates the same conclusions<sup>5</sup>. Since the monomer after several recrystallization procedures is free even from small traces of the tetrafunctional ethylene-dimethacrylate monomer, it seems that the only reaction which could lead to the branching of the polymer and to an extension of the distribution curve is the transfer of the reaction chain to polymer.

The aromatic compounds are known<sup>6,7</sup> to be able to transfer radical chains. Since in the molecule of  $I$  there are three benzene rings per one monomeric unit, the transfer of the reaction chain in these sites can lead to the formation of branched structures:



If the system is treated with hydrogen chloride, only trityl chloride splits off in the sites designated by arrow 1, while the whole polymer chain separates from the branched units in sites designated by arrow 2; the initial molecule decomposes into  $(m + 1)$  chains ( $m$  being the number of branched units). If the initial polymer were monodisperse and decomposed by hydrogen chloride into chains of the same length, the molecular weight of the product of acidolysis would be  $M_{\text{exp}} = M_{\text{th}}/(m + 1)$ . Since the high-molecular weight fractions of branched polydisperse polymers are more branched, it is easy to understand that the ratio  $p = M_{\text{exp}}/M_{\text{th}}$  decreases with increasing molecular weight  $M_{\text{in}}$ .

The existence of branched sites which undergo decomposition by acidolysis is also corroborated by the correlation of the intrinsic viscosity and molecular weight

of the products of acidolysis. Fig. 4 shows a comparison of this correlation with a "standard" curve obtained earlier<sup>1</sup> for fractions of poly(2-hydroxyethyl methacrylate) (*II*) and confirmed by measurements<sup>8</sup> carried out with the fractions of a polymer prepared from a carefully purified monomer (the content of ethylene dimethacrylate being thousandths of %). The points corresponding to the products of acidolysis lie in a close proximity of the "standard" curve  $[\eta]$  vs  $M$ , and the frequency of deviations is the same in both directions. It can be deduced from the above correlation that the acidolytic cleavage of polymer *I* makes possible the preparation of linear *II*, although the molecules of the initial polymer are branched.

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