

## PREPARATION AND CHARACTERISTICS OF 2,2,2-TRICHLOROETHYL METHACRYLATE, 2,2,2-TRICHLOROETHYL ACRYLATE AND THEIR POLYMERS

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Methacryloylation and acryloylation of 2,2,2-trichloroethanol yielded 2,2,2-trichloroethyl methacrylate and 2,2,2-trichloroethyl acrylate, respectively. Free radical polymers of 2,2,2-trichloroethyl methacrylate are found to be predominantly syndiotactic, whereas free radical polymers of 2,2,2-trichloroethyl acrylate are found to be more or less atactic.

Polymers of 2,2,2-trichloroethyl methacrylate and 2,2,2-trichloroethyl acrylate can be expected to have specific properties ensuing from their high chlorine content. Only brief data were found in the literature on the preparation and properties of 2,2,2-trichloroethyl methacrylate and its polymer<sup>1-3</sup>; for the monomer (obtained from methacrylic acid anhydride and 2,2,2-trichloroethanol), m.p. 55°C/1 Torr,  $d_4^{20}$  1.3264,  $n_D^{20}$  1.4718; for the polymer,  $d_4^{10}$  1.15,  $n_D^{20}$  1.52. No data could be found on the properties of 2,2,2-trichloroethyl acrylate and its polymer. This paper reports the preparation of both monomers from 2,2,2-trichloroethanol and acid chlorides and of their polymers, as well as the determination of their basic physical characteristic.

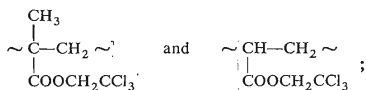
2,2,2-Trichloroethyl methacrylate (*I*) and 2,2,2-trichloroethyl acrylate (*II*) are clear colourless liquids with an agreeable smell. They dissolve in common organic solvents including aliphatic hydrocarbons, but are insoluble in water. The relative stability of the monomers is demonstrated by the fact that the chromatograms of their samples irradiated 4 h with UV radiation in glass ampoules (transmitting light, a wavelength above 2700 Å) and heated 3 h in an inert atmosphere or 1 h with triethylamine (1 : 1 by volume) to 50°C were the same as those of pure compounds. If no inhibitor of radical polymerization is added, the viscosity of both compounds increases after staying several days at room temperature.

Poly(2,2,2-trichloroethyl methacrylate) (*III*) and poly(2,2,2-trichloroethyl acrylate) (*IV*) obtained at 60°C were soluble in hexane, alcohol and water. The block polymer of 2,2,2-trichloroethyl acrylate obtained at temperatures above 60°C was swelling in benzene and in chloroform but did not dissolve.

According to the densities of monomers and polymers at 20°C the volume of polymer *III* represents 90.4% of the volume of the initial monomer *I*, and the volume of polymer *IV* represents 88% of the volume of the initial monomer *II*. The volume contraction during the polymerization of *I* and *II* is lower than during the polymerization of methyl methacrylate, when the volume of the

polymer represents 78% of the volume of the initial monomer<sup>4</sup>. The blocks of polymers *III* and *IV* become coated with black when put into the dark flame of the gas burner, soften and smoke; however, outside the flame they neither burn nor smoulder. The copolymers of *I* with methyl methacrylate burn outside the flame even if the content of *I* is 80%.

The structure of the above compounds can be characterized by means of the parameters obtained from the analysis of NMR spectra. Parameters estimated from experimental spectra were used to calculate the theoretical spectra of compounds *I* and *II* on a Minsk 22 computer; the parameters were adjusted by an iteration procedure so as to give the best agreement between the experimental and theoretical spectra. From the viewpoint of proton NMR, compound *I* can be regarded as a seven-spin system, with only two geminal protons in the group  $C=CH_2$  in strong interaction. The parameters obtained from an analysis of the spectrum of compound *I* are given in Table I and agree well with those obtained from an analysis of the NMR spectra of similar compounds<sup>5</sup>. Compound *II* contains five protons; of these it is sufficient to consider in the analysis only the three-spin system of the group  $CH=CH_2$  (Table I). The NMR spectra of polymers *III* and *IV* have broad bands characteristic of polymers (Fig. 1), so that a full analysis of the spectra is not feasible. From a comparison of the NMR spectra of polymers *III* and *IV* with the NMR spectra of poly(methyl methacrylate)<sup>6</sup> and poly(methyl acrylate)<sup>7</sup> it follows, however, that polymers *III* and *IV* can be assigned structural units



*III* is predominantly syndiotactic and *IV* is more or less atactic.

The infrared spectra (Fig. 2) support the assumed structure of compounds *I-IV*. The infrared spectra of compounds *I-IV* confirm the presence of the  $C=O$ ,  $C-Cl$ ,  $C-O$  bonds. In the infra-

TABLE I

Parameters of the NMR Spectra of Compounds  $\begin{array}{c} \text{H}^a \\ | \\ \text{C}=\text{C}(\text{R})\text{COOCH}_2\text{CCl}_3 \\ | \\ \text{H}^b \end{array}$

R	Chemical shifts $\delta, \tau$				Coupling constants $c/s$		
	$H^a$	$H^b$	$H^c$	$CH_2$	$J_{ab}$	$J_{ac}$	$J_{bc}$
$CH_3^c$	4.317	3.766	8.029	5.219	1.5	1.6	1.0
$H^c$	4.033	3.498	3.803	5.204	1.6	10.3	17.4

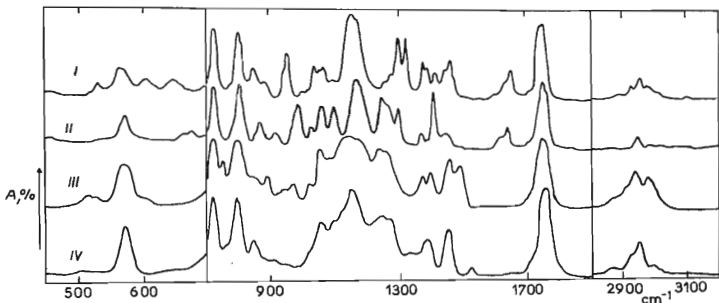


FIG. 1

The IR Spectra of Poly(2,2,2-trichloroethyl methacrylate) (III) and Poly(2,2,2-trichloroethyl acrylate) (IV)

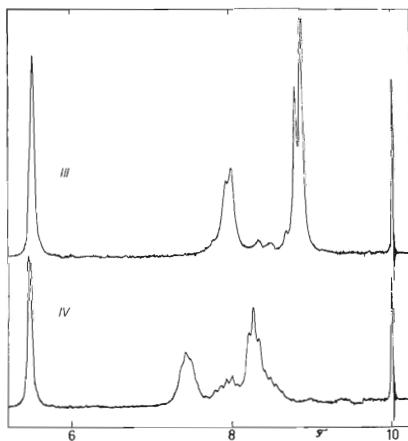


FIG. 2

The IR Spectra of 2,2,2-Trichloroethyl Methacrylate (I), 2,2,2-Trichloroethyl Acrylate (II) and Their Polymers (III, IV)

red spectra of polymers *III* and *IV* there are — besides the absorption bands which are characteristic of the spectra of poly(methyl methacrylate) and poly(methyl acrylate)<sup>8</sup> — also bands in the region 500–850 cm<sup>-1</sup> corresponding to the vibrations of the C=Cl bond. In contrast with the spectra of monomers *I* and *II*, the spectra of polymers *III* and *IV* do not exhibit any absorption bands near to 1650 cm<sup>-1</sup> corresponding to the vibration of the C=C bond.

## EXPERIMENTAL

The density of the monomers and dried polymer blocks was determined pycnometrically. The infrared spectra of the monomers and polymers were recorded on a Zeiss UR 10 spectrometer. The NMR spectra were recorded on a PS-100 (Jeol) spectrometer at 100 Mc/s, using HMDS ( $\tau$  9.95) as the internal standard. The measurements were made with 0.5 molar monomer solutions in CDCl<sub>2</sub> at room temperature and 10% (w/v) polymer solutions in an equimolar mixture of tetrahydroethylene and *o*-dichlorobenzene at 140°C. The number average molecular weight of the polymers was determined in a toluene solution with a Hallikainen Model 1361 DS 4 membrane osmometer.

**Materials.** 2,2,2-Trichloroethanol, b.p. 58–59°C/15 Torr,  $n_D^{20}$  1.4910, chromatographically pure (Apiezon L on Chromoton N). Methacryloyl chloride<sup>10</sup>, b.p. 96–97°C,  $n_D^{20}$  1.4433, acryloyl chloride<sup>11</sup>, b.p. 76–78°C,  $n_D^{20}$  1.4345. Triethylamine was dried with solid potassium hydroxide and distilled, b.p. 89°C. Benzene, pure, was dried with sodium and distilled.

### Preparation of 2,2,2-Trichloroethyl Methacrylate (*I*) and 2,2,2-Trichloroethyl Acrylate (*II*)

Data for the preparation of *II* are given in brackets.

*a*) To a solution of 40 g (78.8 g) of 2,2,2-trichloroethyl alcohol in 50 ml (80 ml) of benzene, a solution of 27 g (53.2 g) triethylamine, 27.9 g methacryloyl chloride (47.6 acryloyl chloride) and 0.1 g 1,4-benzoquinone in 50 ml (100 ml) benzene was added dropwise with stirring and cooling with icy water so that the temperature of the reaction mixture did not exceed 10°C. The mixture was then heated to the reflux and eventually cooled to room temperature. The triethylamino hydrochloride precipitate was filtered off, the benzene filtrate was shaken three times with 30 ml (50 ml) of icy water and dried with anhydrous sodium sulphate. Benzene was removed by distillation from the dried solution under reduced pressure (70 Torr); the residue was rectified in a stream of nitrogen on a column consisting of concentric tubes (25 TP). 35 g of *I* was obtained (50.5 g of *II*), b.p. 36.5°C/0.9 Torr (31.5°C/0.5 Torr),  $d_4^{20}$  1.3211 and  $d_4^{20}$  1.2858 (1.3763 and 1.3366),  $n_D^{20}$  1.4725 (1.4738); the fractions were chromatographically pure (Apiezon L on Chromoton N). For C<sub>6</sub>H<sub>7</sub>Cl<sub>3</sub>O<sub>2</sub> calculated: 33.13% C, 3.24% H, 48.91% Cl; found: 33.79% C, 3.36% H, 48.88% Cl. For C<sub>5</sub>H<sub>5</sub>Cl<sub>3</sub>L<sub>2</sub> (203.5) calculated: 29.51% C, 2.48% H, 52.28% Cl; found: 29.85% C, 2.53% H, 51.87% Cl.

*b*) A mixture of 44.8 g of 2,2,2-trichloroethanol, 60 ml of benzene, 2.9 aluminium foil and several grains of iodine and mercuric chloride was kept simmering until aluminium was dissolved. A solution of 31.5 methacryloyl chloride (27.5 g acryloyl chloride) and 0.1 g 1,4-benzoquinone in 50 ml of dry benzene was added dropwise while stirring for about 20 min to the above solution cooled in an icy bath. The reaction mixture was stirred for 15 min more; 80 g of crushed ice was added to it while still stirring. After an addition of 10 ml of concentrated hydrochloric acid the benzene solution was separated and dried with anhydrous sodium sulphate. Fractionation (*cf.* *a*) gave 35 g of *I* (33 g *II*) b.p. 31.3°C/0.4 Torr (29.8°C/0.3 Torr); the fractions were chromatographically pure. Lower yields of *I* were obtained by heating equimolar amounts of 2,2,2-trichloroethanol with methacryloyl chloride, similarly to the preparation of 2,2,2-trichloroethyl acetate<sup>12</sup>, and also by reaction of methacryloyl chloride with 2,2,2-trichloroethanol in a benzene solution while using an equimolar amount of pyridine or powdered potassium carbo-

nate. Attempts at the reesterification of methyl methacrylate with 2,2,2-trichloroethanol while using concentrated sulphuric acid, benzenesulphonic acid and aluminium 2,2,2-trichloroethyl-alkoxide as catalysts were unsuccessful.

### Polymerization

An ampoule containing 3 ml of freshly redistilled monomer and 0.0049 g of 2,2'-azobisisobutyronitrile was first cooled to  $-78^{\circ}\text{C}$ , then evacuated several times, filled with nitrogen and immersed into cool water when evacuated. On melting of the monomer, the ampoule was cooled again to  $-78^{\circ}\text{C}$ , evacuated and sealed *in vacuo*. After 24 h at  $60^{\circ}\text{C}$  the monomers polymerized to form hard colourless clear blocks. One part of the polymers was dissolved in benzene and precipitated from the solution with a sevenfold volume of hexane. After drying to constant weight, poly(2,2,2-trichloroethyl methacrylate) (*III*),  $d_4^{20}$  1.4611 and poly(2,2,2-trichloroethyl acrylate) (*IV*),  $d_4^{20}$  1.5632 were analyzed. For *III* ( $M_n = 1190000$ ) calculated: 33.13% C, 3.24% H, 48.91% Cl; found: 33.34% C, 3.30% H, 48.31% Cl. For *IV* ( $M_n = 672000$ ) calculated: 29.51% C, 2.48% H, 52.28% Cl; found: 29.86% C, 2.54% H, 51.22% Cl.

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