# CONCLUSIONS

(1) The reaction of hexamethylcyclotrisilazane and octamethylcyclotetrasilazane in the presence of alkali has been investigated and it has been shown that the reaction is accompanied by the evolution of methane and the formation of cyclolinear polymers.

(2) Polymers with chains of molecules with Si-N-Si bonds, with melting points up to 500° and with good solubility in benzene, have been synthesized.

Translated by B. J. HAZZARD

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# CARBOCHAIN POLYMERS AND COPOLYMERS-XL. POLYMERIZATION AND COPOLYMERIZATION OF METHACRYLIC AND ACRYLIC DERIVATIVES OF GERMANIUM\*

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WE SHOWED earlier [1, 2] that triethylgermanium methacrylate polymerizes by a radical mechanism and copolymerizes with styrene and methyl methacrylate. It was of interest to determine how the germanium atom influences the relative activity of the methacrylic group connected with it. With this object, we have carried out the copolymerization of triethylgermanium methacrylate with styrene at  $60^{\circ}$  to low degrees of conversion. The resulting copolymers were purified by reprecipitation from solutions in benzene with petroleum ether and dried in vacuum at  $60^{\circ}$  to constant weight, and their contents of carbon, hydrogen, and germanium were determined. The composition of the copolymers was calculated from the results of the analysis for the carbon content. To determine

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the relative activities, we used Mayo and Lewis's equation [3]. The results obtained are given in Table 1.

It can be seen from Table 1 that the relative activity of triethylgermanium methacrylate is somewhat lower than the relative activity of styrene. The product of the relative activities,  $r_1 \cdot r_2 \approx 1$ , which indicates a non-regular distribution of the residues of the two monomers in the chain of the copolymer. The ratio of  $r_1$  to  $r_2$  is 0.886 and is practically the same as the ratio of the relative activities of methyl methacrylate and styrene found at 60° [4], which is 0.885; from this, it may be concluded that the relative activity of the methacrylate group in copolymerization with styrene is not changed by the replacement of the CH<sub>3</sub> group by the Ge(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> group.

Amount used in the reaction (mmoles)		Yield of copolymer	Elementary com- position of the copolymer (%)		Did not react (mmole)		$r_1$	r <sub>2</sub>	
M <sub>1</sub> <sup>0</sup>	M <sub>2</sub>	(%)	C	н	Ge	M <sub>1</sub> <sup>1</sup>	M <sub>2</sub> <sup>1</sup>		
5	5	8.6	62.67 62.91	8·32 8·48	19·01 18·76	4.582	4.542		
10	20	4.2	74·11 73·95	8·31 8·34	7·35 7·51	9.672	18.94	0.93± 0.08	$1.05 \pm 0.02$
5	50	12.9	84·49 84·45	8·77 8·65	3.63 3.66	4.411	43.71		

TABLE 1. COPOLYMERIZATION OF TRIETHYLGERMANIUM METHACRYLATE ( $M_1$ ) with styrene ( $M_2$ )

In addition to triethylgermanium methacrylate, the synthesis and properties of which we have described earlier [1, 2], we synthesized other methacrylic and acrylic germanium derivatives; the properties of these compounds are given in Table 2. It was found that tributylgermanium methacrylate, tricyclohexylgermanium methacrylate, triethylgermanium acrylate, and tributylgermanium acrylate polymerize on heating in the presence of azoisobutyronitrile and copolymerize with styrene and with methyl methacrylate. The polymerization was carried out in an atmosphere of nitrogen in the presence of 0.6 mole-% of initiator. The initial temperature of polymerization was  $30^\circ$ ; after every 5 hours, the

Formula	B. p., °C (mm)	$d_{_{20}}^{_{20}}$	$n_{\mathbf{D}}(t)$
$CH_2 = C(CH_3)COOGe(C_4H_9)_3$	130-132 (4)	1.0166	1.4602 (20)
$CH_2 = C(CH_3)COOGe(C_6H_5)_3$	M. p. 180°	_	—
$CH_2 = C(CH_3)COOGe(C_6H_{11})_3$	M. p. 82–84°		-
$CH_2 = CHCOOGe(C_2H_5)_3$	88-90 (12)	1.1530	1.4582 (20)
$CH_2 = CHCOOGe(C_4H_9)_3$	131 (4)	1.0131	1.4609 (22)
$CH_2 = CHCOOGe(C_6H_5)_3$	M. p. 178–178,5°	-	· · ·

TABLE 2. METHACRYLIC AND ACRYLIC GERMANIUM DERIVATIVES

temperature was raised by  $10^{\circ}$ . Tricyclohexylgermanium methacrylate was an exception, the polymerization of this substance being carried out at  $100^{\circ}$  for 5 hours and then at  $120^{\circ}$  for 40 hours. Polymerization was continued until a non-fluid mass was formed. The polymers and copolymers were isolated by precipitation with petroleum ether from their solutions in dichloroethane, amyl acetate, or dimethylformamide.

In the copolymerizations with styrene and with methyl methacrylate, the content of germanium-containing monomer in the mixture of monomers was 20 moles-% in each case. Azoisobutyronitrile, taken in an amount of 0.5 mole-% of the sum of the monomers, was used as the initiator. The temperature conditions for copolymerization were the same as in polymerization. The results obtained are given in Tables 3 and 4.

Monomer	Polymeri- zation time (hr)	Yield of polymer (%)	[ŋ] (solvent)
$CH_2 = C(CH_3)COOGe(C_4H_9)_3$	75	60	0.57 (pyridine)
Ditto	60*	50	0.68 (pyridine)
$CH_2 = C(CH)_3 COOGe(C_6H_{11})_3$	45	40	0.10 (dichloroethane)
$CH_2 = CHCOOGe(C_2H_5)_3$	10	30	1.20 (dimethylformamide)
$CH_2 = CHCOOGe(C_4H_9)_3$	27	40	0.30 (dimethylformamide)

TABLE 3. POLYMERIZATION OF ACRYLIC AND METHACRYLIC GERMANIUM DERIVATIVES

\* Initiator: benzoyl peroxide (0.5 mole-%).

TABLE 4. COPOLYMERIZATION OF ACRYLIC AND METHACRYLIC GERMANIUM DERIVATIVES WITH STYRENE AND WITH METHYL METHACRYLATE

Germanium-containing monomer	Comonomer	Reac- tion time (hr)	[ŋ] dimethyl- formamide	Content of germanium in the co- polymer (mean) (%)	Yield of polymer (%)
Tributylgermanium	Styrene		1		
methacrylate	-	80	1.10	0.93	58.5
Ditto	Methyl meth-				
	acrylate	75	1.03	0.35	60
Triethylgermanium	Styrene				
acrylate		56	0.35	Traces	60 ·
Ditto	Methyl meth-				
	acrylate	10	0.90	7.43*	50 .
Tributylgermanium	Styrene				
acrylate		60	0.26	0.20	53
Ditto	Methyl meth-				
	acrylate	10	1.45	7.58†	52

\* Germanium content in the initial mixture of monomers 10.50%.

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† Germanium content in the initial mixture of monomers 10.15%.

It can be seen from Tables 3 and 4 that the polymers and copolymers of the methacrylic and acrylic germanium derivatives possess fairly high molecular weights. It is interesting to note that the germanium-containing monomers given in Table 4, in contrast to triethylgermanium methacrylate, polymerize poorly with styrene, as is shown by the low germanium content in the copolymers. In copolymerization with methyl methacrylate, the activity of the acrylic germanium derivatives is quite high, and the germanium content in the copolymers is lower than in the initial mixtures of monomers by a factor of only  $\sim 1.5$ .

It was also found that tributylgermanium methacrylate and the triethylgermanium methacrylate which we described earlier undergo emulsion polymerization in the presence of potassium persulphate. Triethylgermanium methacrylate rapidly polymerizes on irradiation with UV light and after 40 minutes' irradiation the yield of polymer with  $[\eta]$  0.75 (pyridine) was 45%.



Thermomechanical properties: a-copolymers with styrene; 1-triethylgermanium acrylate; 2-tributylgermanium acrylate; 3-tributylgermanium methacrylate. b-polymer of triethylgermanium acrylate (3) and copolymers of methyl methacrylate with triethylgermanium acrylate (1) and tributylgermanium acrylate (2).

The thermomechanical properties of some of the polymers and copolymers obtained are given in Figures a and b.

#### EXPERIMENTAL

Tetrabutylgermanium was obtained by the reaction of *n*-butylmagnesium bromide with germanium tetrabromide in absolute ether [5-7]. 110 g of *n*-butyl bromide, 19.3 g of magnesium, and 62.8 g of germanium tetrabromide in 560 ml of ether yielded 28 g of tetrabutylgermanium with b.p. 153-155/°18 mm,  $n_D^{20}$  1.4575; yield 58.5% of theoretical.

Tributylgermanium bromide. A solution of 15.8 g of bromine in 140 ml of dibromoethane was added to 28.7 g of tetrabutylgermanium. The reaction mixture was heated to a gentle boil for 4 hours with a reflux condenser. The unchanged bromine and the dibromoethane was distilled off and the residue was distilled in vacuum. This gave 27 g of a substance in the form of a mobile colourless liquid with a sharp smell, b.p.  $176^{\circ}/7$  mm,  $n_D^{22.5}$  1.4702; yield 87.8% of theoretical.

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Found, %: Ge 22.03, 21.86. C<sub>12</sub>H<sub>27</sub>GeBr. Calculated, %: Ge 22.41.

Tributylgermanium methacrylate. 5 g of anhydrous potassium methacrylate, 50 ml of absolute methanol, and a small amount of cuprous chloride were placed in a 3-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel. 13 g of tributylgermanium bromide was run in slowly, and the mixture was boiled for 1 hour and left overnight. The potassium bromide which had separated was filtered off, the filtrate was evaporated in vacuum (15–20 mm) at a bath temperature not higher than 50°, and the residue was distilled in vacuum. This yielded 7 g of a substance in the form of a mobile colourless liquid with a sharp odour, b.p.  $130-132^{\circ}/4$  mm,  $n_D^{20}$  1.4602,  $d_{20}^{20}$  1.0166; yield 54% of theoretical.

Found, %: C 58:35, 58:11; H 9:21, 9:77; Ge 21:58, 21:62. C<sub>15</sub>H<sub>32</sub>O<sub>2</sub>Ge. Calculated, %: C 58:38; H 9:81; Ge 22:07.

Tetraphenylgermanium. 24.3 g of magnesium and 400 ml of absolute ether were placed in a four-necked flask fitted with a reflux condenser, a stirrer, a dropping funnel, and a tube for the introduction of nitrogen. 157 g of bromobenzene was added and the contents of the flask were boiled for 1 hour. Then the ether was distilled off, 400 ml of absolute toluene was poured on to the residue, and a solution of 39.2 g of germanium tetrabromide in 39 ml of absolute toluene was added to the hot mixture at such a rate that it boiled gently, after which it was boiled for a further two hours. It was then cooled to room temperature and decomposed with dilute hydrochloric acid (1:1). It was transferred to a separating funnel, 250 ml of hot toluene was added, the toluene layer was separated, and the toluene was distilled off in vacuum until the volume of the solution had been reduced to 100–150 ml. The solution was cooled and the crystals which deposited were separated and washed with cold toluene and alcohol. The tetraphenylgermanium was purified by recrystallization from benzene; m.p. 225–226°. Yield 30.9 g or 81.6% of theoretical.

Triphenylgermanium bromide. 80 ml of dibromoethane and 5 ml of bromine were added to 28 g of tetraphenylgermanium, the mixture was heated to a gentle boil for 20-30 min, and the dibromoethane and unchanged bromine were distilled off. The residue was recrystallized from absolute *n*-heptane. The yield of substance with m.p. 136-137° was 15 g or 53% of theoretical.

Triphenylgermanium methacrylate was obtained in a similar manner to tributylgermanium methacrylate (see above). The yield of material with m.p.  $180^{\circ}$  (from benzene) was 48% of theoretical.

Found, %: C 68·20; H 5·40. C<sub>22</sub>H<sub>20</sub>O<sub>2</sub>Ge. Calculated, %: C 67·92; H 5·18.

Triethylgermanium acrylate. 6 g of anhydrous potassium acrylate, 60 ml of absolute methanol, and a small amount of cuprous chloride were placed in a three-necked flask fitted with a reflux condenser, a stirrer, and a dropping funnel. 13 g of triethylgermanium bromide was added slowly and the mixture was boiled for 1 hour and left overnight. The potassium bromide which had separated was filtered off, the filtrate was evaporated in the vacuum of a water-jet pump (~20 mm) at a temperature not exceeding 50°, and the residue was distilled in vacuum. This gave 6 g of a substance with b.p. 88–90°/12 mm,  $n_D^{20}$  1.4582; yield 50% of theoretical.

Found, %: C 46.27, 46.38; H 7.98, 8.02; Ge 33.02, 32.79. C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>Ge. Calculated, %: C 46.83;, H 7.80; Ge 31.48.

Tributylgermanium acrylate was obtained in a similar manner to triethylgermanium acrylate. The yield of material with b.p.  $131^{\circ}/4$  mm,  $n_{D}^{22}$  1.4609, was 45% of theoretical.

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Found, %: Ge 22.82; 22.72.

C<sub>15</sub>H<sub>30</sub>O<sub>2</sub>Ge. Calculated, %: Ge 23.05.

Triphenylgermanium acrylate was obtained in a similar manner to triethylgermanium acrylate. The yield of material with m.p.  $178-178\cdot5^{\circ}$  (from benzene) was 40% of theoretical.

Found, %: Ge 19.25. C<sub>21</sub>H<sub>18</sub>O<sub>2</sub>Ge. Calculated, %: Ge 19.36.

Tricyclohexylgermanol. 163 g of cyclohexyl bromide 300 ml of absolute ether, and 24.5 g of magnesium turnings were placed in a three-necked flask fitted with a reflux condenser a stirrer, and a dropping funnel. When the reaction was complete, a solution of 21.4 g of germanium tetrachloride in 200 ml of absolute benzene was added. The mixture was boiled for 2 hours and then distilled with steam. The solid residue was filtered off, well pressed out, and dissolved in alcohol, and the tricyclohexylgermanol was precipitated by pouring the aqueous solution into water. Recrystallization from petroleum ether gave 10 g of white crystals m.p.  $171-173^{\circ}$ ; yield 29.6% of theoretical, calculated on the germanium tetrachloride. According to data in the literature [8], tricyclohexylgermanol melts at  $175-176^{\circ}$ .

Tricyclohexylgermanium methacrylate. 4.5 g of tricyclohexylgermanol 1.2 g of freshlydistilled methacrylic acid, and 40 ml of dry acetone were placed in a flask fitted with a stirrer and reflux condenser. The mixture was boiled with stirring for 2 hours and left overnight. The acetone was distilled off, the residue was dissolved in dichloroethane, the solution was filtered, and the dichloroethane was distilled off until the volume was decreased to 1/3of the original volume; it was then cooled and the crystals which separated were filtered off. The yield of substance with m.p.  $82-84^{\circ}$  was 0.6 g or 11% of theoretical.

> Found, %: C 64.57; H 9.55; Ge 17.28, 17.88. C<sub>22</sub>H<sub>35</sub>O<sub>2</sub>Ge. Calculated, %: C 64.57; H 10.00; Ge 17.72.

## CONCLUSIONS

(1) The relative activities of triethylgermanium methacrylate and styrene when they are copolymerized have been determined.

(2) Six new acrylic and methacrylic germanium derivatives have been synthesized, and germanium-containing polymers and copolymers with styrene and methyl methacrylate have been obtained.

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