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## THE SYNTHESIS AND EXAMINATION OF ORGANOSILICON POLYCARBONATES\*

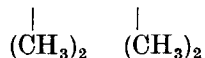
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The synthesis of polycarbonates containing silicon, from 1,1-di(4-hydroxyphenyl) cyclohexane, phosgene and organosilicon bis-chloroformates (BCF), has been studied and the optimal reaction conditions have been found. It was found that films cast from the copolymers so obtained are transparent, resistant to 40% NaOH solution and have good adhesion to glass. Copolymers from a mixture of the acid chlorides containing 30% of the BCF are best with respect to the above properties.

By synthesis of mixed polycarbonates containing organosilicon fragments of the type  $\text{—R—Si—O—Si—R—}$  (where R is a divalent organic radical) we



set ourselves the task of preparing from them modified polycarbonate materials with good adhesion to certain substrates such as silicate glasses [1].

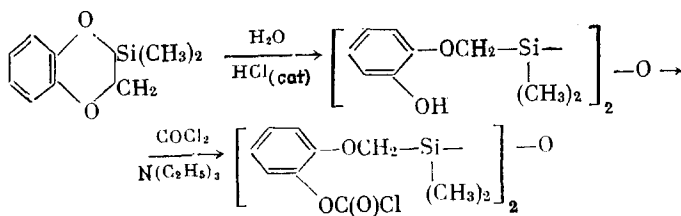
Polycarbonates prepared by partial replacement of phosgene by dimethyl-dichlorosilane or by organosiloxanes with terminal Cl atoms, which contain hydrolytically vulnerable Si—OC linkages in the main chain, are known [2, 6]. Information on silicon containing polycarbonates (PC) in which the silicon atoms are linked to the carbonate groupings by hydrocarbon bridges is more limited [7, 8].

### EXPERIMENTAL

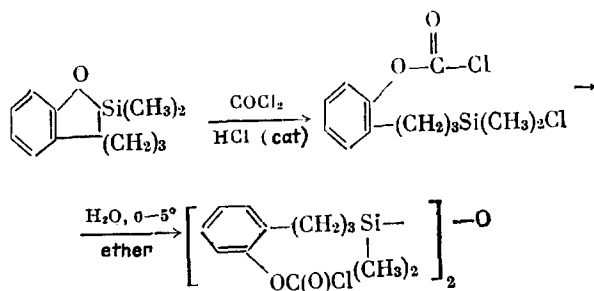
Modified PC's containing disiloxane units were prepared from 1,3-bis[*o*-(chloroformato)phenoxyethyl]-1,1,3,3-tetramethyldisiloxane (BCF-1) and 1,3-bis-[*γ*-(*o*-chloroformato-phenyl)propyl]-1,1,3,3-tetramethyldisiloxane (BCF-2). BCF-1 was synthesized from 1,1-

\* Vysokomol. soyed. **A16**: No. 9, 1940–1944, 1974.

dimethyl-1-sila-2,5-dioxa-3,4-benzocyclohexane by the following series of reactions:



BCF-2 was synthesized from 1,1-dimethyl-1-sila-2-oxa-3,4-benzocycloheptane



**Synthesis of BCF-1.** Forty five grammes (0.25 mole) of 1,1-dimethyl-1-sila-2,5-dioxa-3,4-benzocyclohexane, 500 ml of water and 10 ml of concentrated HCl were placed in a three necked flask provided with a stirrer, reflux condenser and dropping funnel. The mixture was refluxed for 10 min, then cooled and the organic layer was separated and the aqueous layer extracted with ether (3.25 ml). The combined organic layer and ethereal extract was distilled. This yielded 37.8 g (80% of theory) of 1,3-bis(*o*-hydroxyphenoxy-methyl)-1,1,3,3-tetramethyldisiloxane, with b.p. 175–177°/1.5 torr,  $d_4^{20}$  1.1160,  $n_D^{20}$  1.5282,  $MR_D$  104.48; calculated  $MR_D$  104.30 (according to the literature [9] b.p. 180°/4 torr).

20.1 g (0.2 mole) of  $\text{COCl}_2$  was condensed into a four-necked flask provided with stirrer, thermometer, dropping funnel, gas inlet tube and reflux condenser cooled in a mixture of  $\text{CO}_2$  and acetone. A solution of 37.8 g (0.1 mole) of diphenol obtained above, in 200 ml of dry ether was first added, then at 0–5° 20.2 g (0.2 mole) of triethylamine was added dropwise. After the reaction mixture had been held under reflux for 1 hr it was filtered, the filtrate was evaporated and the residue redistilled. This yielded 42.2 g (83.8% of theory) of BCF-1, with b.p. 210–212°/torr,  $d_4^{20}$  1.2130,  $n_D^{20}$  1.5130,  $MR_D$  123.72.

Found, %: C 47.52, H 4.74, Si 10.67, Cl 14.33.  $\text{Si}_2\text{C}_{20}\text{H}_{24}\text{O}_7\text{Cl}_2$ .  
 Calculated, %: C 47.70, H 4.70, Si 11.15, Cl 14.08,  $MR_D$  124.20.

**Preparation of BCF-2.** 1,1-Dimethyl-1-sila-2-oxa-3,4-benzocycloheptane (38.4 g, 0.2mole) was placed in a three necked flask provided with a gas bubbler, a reflux condenser and a thermometer, a weak current of dry HCl was first passed in (3 min) followed by  $\text{COCl}_2$ , until absorption ceased. The temperature of the reaction mixture was held at 130–195°. The cessation of absorption of  $\text{COCl}_2$  was taken as an indication of the end of the reaction. The mixture was cooled to 0°, 100 ml of ether and 150 ml of water containing finely crushed ice was added and it was then stirred for 1 hr. The organic layer was separated, dried over

$\text{Na}_2\text{SO}_4$  and distilled, yielding 44.9 g (85.2 % of theory) of BCF-2, with b.p. 227–230°/1.5 torr,  $d_4^{20}$  1.1349,  $n_D^{20}$  1.5160,  $MR_D$  140.20.

Found, %: C 56.22, H 5.79, Si 10.10, Cl 13.47,  $\text{Si}_2\text{C}_{22}\text{H}_{32}\text{O}_5\text{Cl}_2$ .  
 Calculated, %: C 56.30, H 6.11, Si 10.64, Cl 13.43,  $MR_D$  139.06.

The silicon-containing PC's were prepared by interfacial polycondensation in a large test tube fitted with a stirrer. Methylene chloride was added to a previously prepared solution of 1,1-di-(4-hydroxyphenyl)cyclohexane (DHPC) in alkali and after the mixture had been stirred for 5 min 1% of triethylamine calculated on the DHPC and the calculated quantity of the BCF in methylene chloride was added. After 10 min a solution of phosgene

#### PROPERTIES OF POLYCARBONATES

BCF used	Quantity of BCF in the PC, mole %	$\eta_{\text{red}}$ , dl/g	Yield, %	M.p., °C	Si, %			Elongation at break,	$\sigma_{\text{br}}$ , kg/cm <sup>2</sup>
					calculated	found			
						A	B		
BCF-1	15	0.49	82	230–235	2.38	2.59	2.48	17.5	345
BCF-2	10	0.50	85	232–237	1.67	1.35	1.51	16.0	300

A—from PMR spectra; B—by elementary analysis.

in methylene chloride was added to the mixture, then stirring was continued for 45–60 min. At the end of the reaction the mixture separated into two layers. The upper, aqueous alkaline layer was decanted off and 10% HCl was added to the organic layer, which contained the polymer, until a weakly acid reaction was obtained. The acidified layer was stirred for 10–20 min then washed with distilled water until the wash water gave a neutral reaction. The polymer obtained after evaporation of the solvent was freed from unreacted monomer and fractions of low molecular weight by reprecipitation by hexane from solution in chloroform. Depending on the preparative conditions, the silicon-containing PC was obtained in the form of a light yellow, viscous mass or a white powder with m.p. from 70° to 230°. The properties of the copolymers obtained are presented in the Table.

#### RESULTS AND DISCUSSION

The effect of various factors on the preparation of polycarbonates from DHPC has been studied previously [10]. The optimal conditions for carrying out this preparation were used for preparation of similar containing PC's, but the need to investigate the effect of the most important factors affecting copolycondensation in the preparation of silicon modified PC's remained. Polycondensation of the silicon-containing bis-chloroformates for the purpose of investigating the dependence of the yield and molecular weight of the polymer on the composition of the phosgene : BCF mixture was carried out on a total quantity of acid chlorides of 125% of theory and the proportion of the BCF in this mixture was varied between 0 and 100%. In all experiments the reduced viscosity

was determined with a 0.5% solution of the polymer in methylene chloride at 20°.

An acid chloride mixture containing 15% of BCF-1 or 10% of BCF-2 gave copolymers with the highest  $\eta_{\text{red}}$  in highest yield (Fig. 1). Films from these copolymers possess the best mechanical characteristics, whereas further increase in the silicon content of the polymer lowers its mechanical properties.

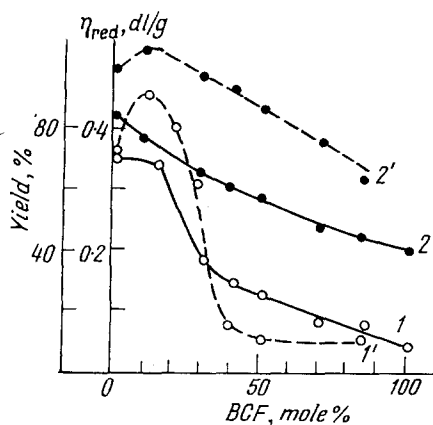


FIG. 1

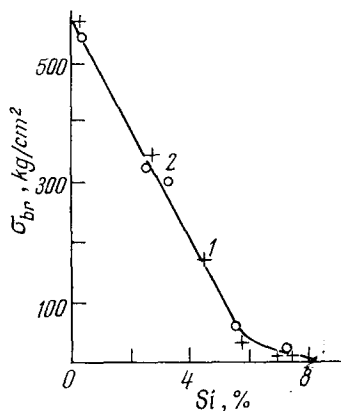


FIG. 2

FIG. 1. The dependence of  $\eta_{\text{red}}$  (1, 1') and the yield (2, 2') of the copolymers on the proportion of BCF in the acid chloride mixture: 1, 2—polymer based on BCF-1; 1', 2'—BCF-2.

FIG. 2. Dependence of the breaking strength ( $\sigma_{\text{br}}$ ) of films of silicon-modified PC's based on BCF-1 (1) and BCF-2 (2) on their silicon content.

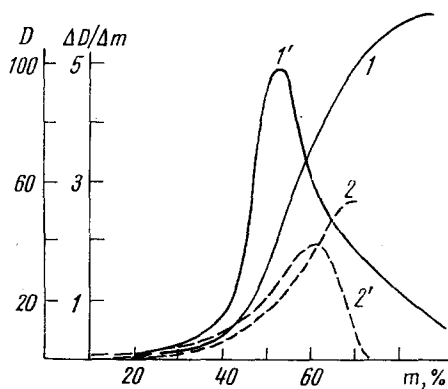


FIG. 3. Integral (1, 2) and differential (1', 2') MWD curves of silicon-modified copolymers, from turbidimetric titration measurements: 1, 1'—PC based on BCF-1; 2, 2'—BCF-2.

Judging by the change in the silicon content of the copolymers as the BCF content of the original acid chloride mixture was varied, the two BCF's react at approximately the same rate. It is seen from Fig. 2 that the dependence of the breaking strength ( $\sigma_{br}$ ) of the films on the silicon content of the copolymer is of the same nature for BCF-1 and BCF-2.

The amount of alkali in excess and the initial reactant concentration affect the molecular weight of the copolymers to a great extent. At a reactant concentration of 0.2 mole/l. the highest yields and reduced viscosities were obtained with an excess amount of alkali of 175% for a copolymer with a 15% content of BCF-1 and 150% for a copolymer with 10% of BCF-2. The maxima in the reduced viscosity and yield as the reactant concentration is varied between 0.1 and 0.5 mole/l. occur at 0.3 mole/l.

The above optimal conditions were used for further preparation of copolymers containing silicon. Some characteristics of the copolymers are given in the Table.

Molecular weight distribution curves obtained by turbidimetric titration (Fig. 3) show that both polycondensation products are copolymers and not mixtures of two homopolymers. The infrared spectra of the copolymers confirm the functional group composition. They contain bands corresponding to the organosilicon ( $\text{Si}-\text{CH}_3$  at 750, 812, 850 and  $1265\text{ cm}^{-1}$ ;  $\text{Si}-\text{O}-\text{Si} \sim 1070\text{ cm}^{-1}$ ) and organic ( $\text{C}-\text{O}$  at  $1015\text{ cm}^{-1}$ ;  $\text{C}=\text{C}$   $1500\text{ cm}^{-1}$  and  $1265\text{ cm}^{-1}$ ;  $\text{C}=\text{O}$   $1770\text{ cm}^{-1}$ ;  $\text{C}-\text{H}_{\text{arom}}$   $3050$  and  $3075\text{ cm}^{-1}$ ) parts of the molecule.

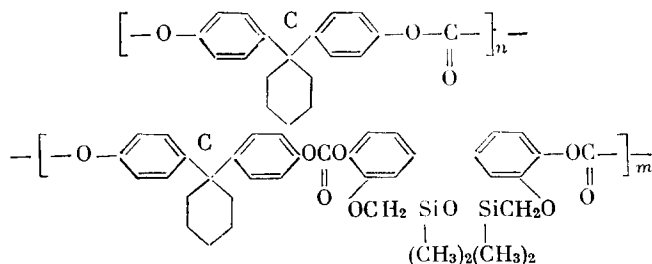
The PMR spectrum of the polymer from BCF-1 contains signals of the  $\text{Si}-\text{CH}_3$  (0.05 ppm),  $-\text{CH}_2-\text{CH}_2-$  (1.50 p.p.m.),  $-\text{C}-$  (2.22 p.p.m.) and  $\text{OCH}_2$

$\begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 \end{array}$ 
 $\begin{array}{c} \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ | \qquad | \end{array}$

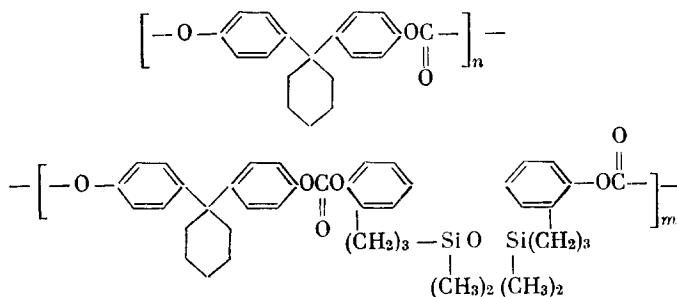
(3.58 p.p.m.) groups of protons. The chemical shifts of the signals corresponding to Si—CH<sub>3</sub> and the two types of methylene protons in the PC based on BCF-2 are 0.05, 1.57 and 2.32 p.p.m. respectively.

According to calculation from the integral spectral curve of the deviation of the actual ratio of the intensities of the signals of the  $\text{>Si-CH}_3$  and  $-\text{CH}_2-\text{CH}_2-$  groups of protons from the theoretical (2 : 1 as in homopolycar-

bonates), it was found that the main units in the polymer containing BCF-1



are present in the ratio  $n : m = 6 : 1$ , and in the polymer based on BCF-2



in the ratio  $n : m = 13 : 1$ .

It is seen from Fig. 4 that when BCF-1 or BCF-2 is introduced into the polymer chain of a polycarbonate the loss in weight when it is heated in air is reduced.

Some properties of films cast from 15–20% solutions of the copolymers in chloroform were investigated. These films proved to be very resistant to water, their absorption of water in 10 days being practically nil. Experiments on the resistance of films to 40% NaOH solution at 20° showed that the loss in weight of the copolymers with 15% of BCF-1 and 10% of BCF-2 is 45% in 9 days, whereas when Diflon is immersed in 40% NaOH solution at 20° it loses 64% of its

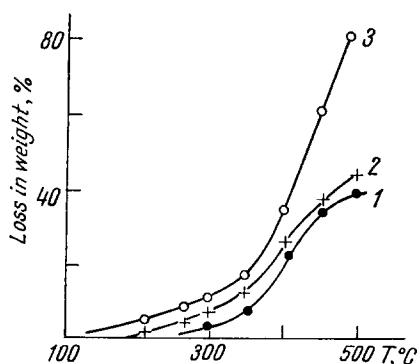


FIG. 4

FIG. 4. Thermogravimetric analysis curves of polymers based on BCF-1 (1) and BCF-2 (2), and a homopolycarbonate (3).

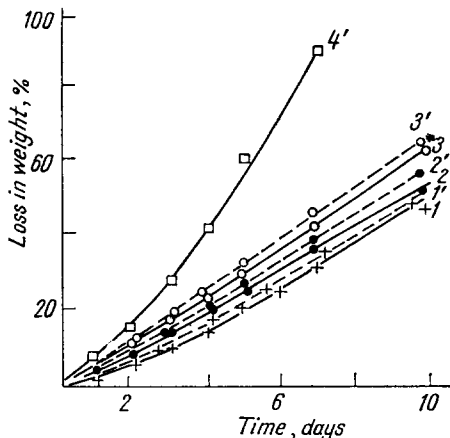


FIG. 5

FIG. 5. Resistance to 40% aqueous NaOH solution of films of PC's based on BCF-1 (1–3) and BCF-2 (1'–4'), with quantities of BCF in the copolymer of 30 (1, 1'); 15 (2); 40 (2', 3); 10 (3') and 70 mole % (4').

weight in 3 days and after 12 days it is completely hydrolysed. The introduction of siloxane linkages into the polycarbonate chain improves the resistance of the copolymers to hydrolysis. It was interesting to compare the effect of alkali on

copolymers with different amounts of the BCF in the mixture of acid chlorides. It is seen from Fig. 5 that copolymers from reactant mixtures containing 30% of a BCF are the most resistant to alkali. The above results can be explained by the considerably reduced molecular weight of copolycarbonates containing siloxane units, the reduction being greater the higher the proportion of silicon in the copolymer.

The most important property of these silicon containing polycarbonates is their good adhesion to glass. A relative assessment of the adhesion of copolymers containing different amounts of the BCF's was given by the cross hatch method according to the specification GOST-15140-60, in which adhesion is rated according to a four point scale. The results of the tests are given below.

Quantity of BCF in reactant mixture, mole %	15	30	50	70	85
Adhesion rating (the numerator is for the PC from BCF-1 and the denominator from BCF-2)	3/4	2/3	3/2	3/3	3/4

It was found that the copolymers with the best adhesion contain 30% of BCF.

*Translated by E. O. PHILLIPS*

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## EMULSION POLYMERIZATION IN THE PRESENCE OF WEAK INHIBITORS\*

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A study has been made of the effect of the chemical activity of inhibitors and of some parameters of the emulsion process (solubility of the monomer and inhibitor in the aqueous phase and latex particles, the number of particles, the rate of generation of primary radicals) on the kinetics of emulsion polymerization of styrene and methyl methacrylate. It is shown that the rate and degree of polymerization of styrene in emulsion is inversely proportional to the quantity of m-dinitrobenzene present.

\* Vysokomol. soyed. A16: No. 9, 1945-1950, 1974.