THE EFFECTS OF SUBSTITUENTS ON THE REACTIVITY OF ORGANOCYCLOSILOXANES IN ANIONIC POLYMERIZATION*

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POLYMERIZATION of inorganic heterocyclic compounds is used extensively for synthesis of polymers with inorganic chain molecules. Much attention is given in the literature to study of the polymerization of organocyclosiloxanes. Qualitative studies of the polymerization of organocyclosiloxanes with different organic substituents attached to the silocon atom have shown that the reactivity of the ring is dependent to a considerable extent on the organic groups surrounding the inorganic ring.

The present communication describes an attempt to determine the effect of the polarity of the substituent in a series of organocyclosiloxanes on their polymerizability, making use of the Hammett–Taft equation for this purpose. In a study of anionic polymerization of a number of these compounds octamethylcyclotetrasiloxane was chosen as a reference compound in which the polarity of the substituent was assumed to be zero. The other members of the series were otbained by replacing a methyl group in the octamethyl derivative by vinyl, ethyl, phenyl and chlorophenyl groups. All these organocyclosiloxanes were obtained by simultaneous hydrolysis with water under acid conditions, according to the reaction:

$$nR_2SiCl_2+mR'RSiCl_2 \xrightarrow{(n+m)H_2O} (R_2SiO)_n\,(RR'SiO)_m+(n+m)HCl$$

$$R=CH_3,\ R'=CH_3,\ C_2H_5,\ CH=CH_2,\ C_6H_5,\ C_6H_4Cl$$

The main characteristics of the products are given in Table 1.

The cyclosiloxanes were polymerized at 120° in an atmosphere of argon, in the presence of 0·1% of KOH. It was found that the rate of polymerization of the organocyclosiloxanes is directly proportional to the monomer concentration and satisfies the equation of a first-order reaction. This relationship holds up to a degree of conversion of 40%. From the experimental results data were obtained on the dependence of the yield of polymer on polymerization time (Figs. 1 and 2).

It is seen from Fig. 2 that at low degrees of conversion the relationship between log c and polymerization time is linear. The values of the rate constants

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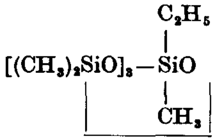
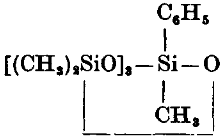
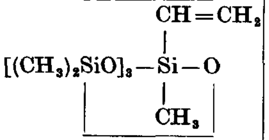
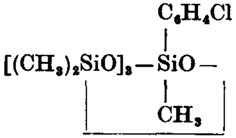
TABLE 1. ORGANOCYCLOSILOXANES

Monomer	B.p., °C/mm	d_4^{20}	n_D^{20}	MR_D		C, %		H, %		Si, %	
				found	calculated	found	calculated	found	calculated	found	calulated
$[(CH_3)_2SiO]_4$	175	0·9558	1·3975	74·67	74·78	32·90	32·45	8·12	8·10	37·41	37·90
 $[(CH_3)_2SiO]_3{-}\overset{C_2H_5}{\underset{CH_3}{SiO}}$	60–65/10	0·9584	1·4021	78·83	78·43	34·85	34·55	8·42	8·38	36·24	36·20
 $[(CH_3)_2SiO]_3{-}\overset{C_6H_5}{\underset{CH_3}{Si}}{-}O$	105–107/3	1·0166	1·4488	94·66	94·52	43·41	43·60	7·45	7·25	31·71	31·30
 $[(CH_3)_2SiO]_3{-}\overset{CH=CH_2}{\underset{CH_3}{Si}}{-}O$	61–61·5/1·5	0·9706	1·4095	78·90	78·92	35·83	35·10	7·75	7·89	38·82	39·01
 $[(CH_3)_2SiO]_3{-}\overset{C_6H_4Cl}{\underset{CH_3}{SiO}}{-}$	115–120/2	1·0613	1·4560	98·09	98·81	39·95	39·75	6·54	6·37	29·89	28·55*

* Found 8·75% Cl, calculated 9·40% Cl.

(k_1) of polymerization of the substituted organocyclosiloxanes and the ratio of these to the rate constant of polymerization of octamethylcyclotetrasiloxane are shown in Table 2.

Comparison of the values of k_1 for the substituted dimethylcyclotetrasiloxanes with k_{CH_3} for octamethylcyclotetrasiloxane shows that the introduction of electron-donating substituents causes reduction in the reactivity of organocyclosiloxanes in polymerization, but introduction of electron-accepting substituents causes an increase in polymerizability.

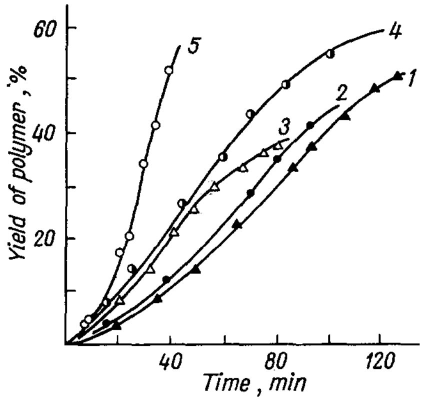


FIG. 1

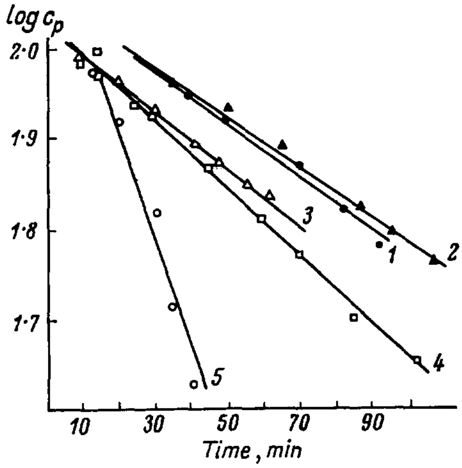
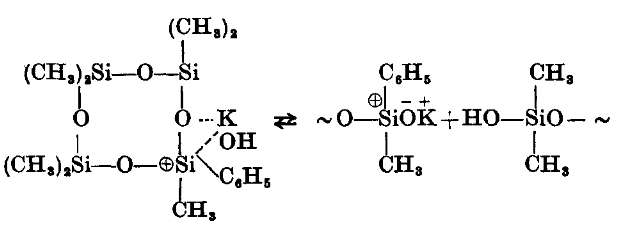


FIG. 2

FIG. 1. Dependence of polymer yield on polymerization time.

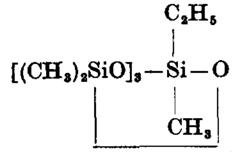
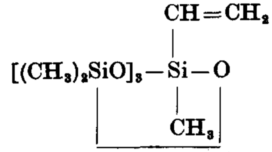
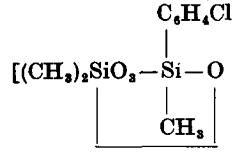
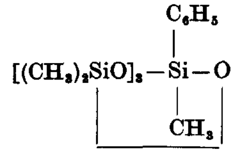
FIG. 2. Dependence of the logarithm of polymer concentration on polymerization time.

This confirms that the initial step in the reaction is attack of the nucleophilic OH group mainly at the most electropositive silicon atom as follows:



The reactivity of the organocyclosiloxanes of this series in anionic polymerization increases as the electron-accepting properties of the substituent increases and is directly proportional to Taft's induction constant σ^*, and there is a linear relationship between σ^* and log k_1/k_{CH_3} in the Hammett–Taft equation log $k_1/k_{CH_3} = \sigma^*\rho^*$, for the substituents, CH_3, $CH{=}CH_2$, C_2H_5, C_6H_5 and C_6H_4Cl. This relationship is shown in Fig. 3.

TABLE 2. DEPENDENCE OF THE POLYMERIZABILITY OF ORGANOCYCLOSILOXANES ON THE POLARITY OF THE SUBSTITUENT ON THE SILICON ATOM

Monomer	$k \times 10^3$ min^{-1}	$\frac{k_1}{k_{CH_3}}$	$\log \frac{k_1}{k_{CH_3}}$	σ^*	E, kcal/mole
$[(CH_3)_2SiO]_4$	4·58	1	0	0	19·6
 $[(CH_3)_2SiO]_3-\overset{C_2H_5}{\underset{CH_3}{Si}}-O$	4·09	0·893	0·0492	0·1	–
 $[(CH_3)_2SiO]_3-\overset{CH=CH_2}{\underset{CH_3}{Si}}-O$	5·73	1·252	0·097	0·4	–
 $[(CH_3)_2SiO_3-\overset{C_6H_4Cl}{\underset{CH_3}{Si}}-O$	6·97	1·521	0·1838	0·8	18·91
 $[(CH_3)_2SiO]_3-\overset{C_6H_5}{\underset{CH_3}{Si}}-O$	7·79	1·700	0·2305	0·6	17·85

The deviation of the points from the straight line indicates that the values of σ^* are only approximately universal, especially for compounds containing silicon, because no account is taken of $p_\pi - d_\pi$ conjugation effects, which are possible in organocyclopolysiloxanes. However, the correlation coefficient $r=0{\cdot}93$ indicates a completely satisfactory correlation between the polymerization rates and Taft's induction constants. In this series of organocyclopolysiloxanes steric effects do not arise.

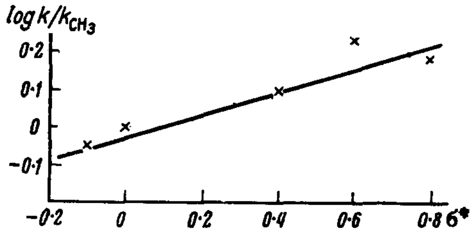
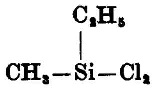
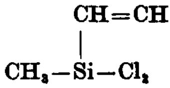
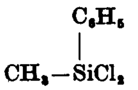
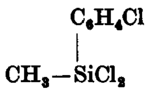


FIG. 3. Dependence of the ratio of the rate constants on the induction effect of the substituent on anionic polymerization of organocyclosiloxanes: $r=0{\cdot}93$, $\rho=0{\cdot}41$.

It is seen from Fig. 3 that σ^* changes sign on passing from electron-donating

TABLE 3. ALKYL(ARYL)DICHLOROSILANES

Alkyl(aryl)dichlorosilane	B.p., °C/mm	Cl, %	
		calculated	found
$(CH_3)_2SiCl_2$	70	55·00	55·08
 $CH_3-Si(C_2H_5)-Cl_2$	100/747	49·70	49·70
 $CH_3-Si(CH{=}CH_2)-Cl_2$	91–93	50·45	50·35
 $CH_3-Si(C_6H_5)Cl_2$	207–205	37·18	37·10
 $CH_3-Si(C_6H_4Cl)Cl_2$	161–164/100	31·15	31·48

to electron-accepting substituents. The value of ρ^* obtained is +0·41. This indicates that the groups surrounding the silicon atom affect the polymerization reaction, but their effect is relatively small. The reduced sensitivity of this reaction to the effect of substituents is probably explained by the fact that the organocyclosiloxanes contain other silicon atoms capable of undergoing nucleophilic attack in addition to the silicon attached to the substituent. Consequently the total inductive effect of the substituent is lower than if the reacting molecule had only one active centre.

The calculated values of the energy of activation (Table 2) for polymerization of phenylheptamethylcyclotetrasiloxane and chlorophenylheptamethylcyclotetrasiloxane are similar and close to the corresponding value for octamethylcyclotetrasiloxane.

The variation in the rate of polymerization with temperature was measured for phenylheptamethylcyclotetrasiloxane and chlorophenylheptamethylcyclotetrasiloxane. The results are presented in Fig. 4.

EXPERIMENTAL

The dimethyldichlorosilane and the aryl(alkyl)dichlorosilanes used for hydrolysis had the characteristics shown in Table 3. The alkyl(aryl)cyclotetrasiloxanes were prepared by simultaneous hydrolysis of dimethyldichlorosilane and the aryl(alkyl)dichlorosilanes by the method of references [1] and [2]. Their physicochemical constants are given in Table 1.

Polymerization. The required quantity of alcoholic KOH was placed in a round-bottomed flask provided with a sealed stirrer and reflux condenser. The alcohol was removed *in vacuo* in a current of dry argon, at a temperature not exceeding 60°. The monomer, previously evacuated to 10^{-3} mm in another vessel and treated with dry argon, was transferred to the flask containing the catalyst in a current of argon. The flask was then placed in a thermostatically controlled oil bath previously heated to 120°. Test samples were removed by means of a pipette during the polymerization period, transferred to beakers, weighed on an analytical balance, and neutralized with CH_3COOH. Weighed samples were placed in a water-heated vacuum pistol and monomer was removed *in vacuo* (1–2 mm). The yield of polymer was found from the weight of the solid residue. The Taft σ^* constants were taken from published Tables [3, 4]. The value of σ^* for the *p*-chlorophenyl group in a ring was calculated from the corresponding values of the σ^0_x constants by means of the fromula

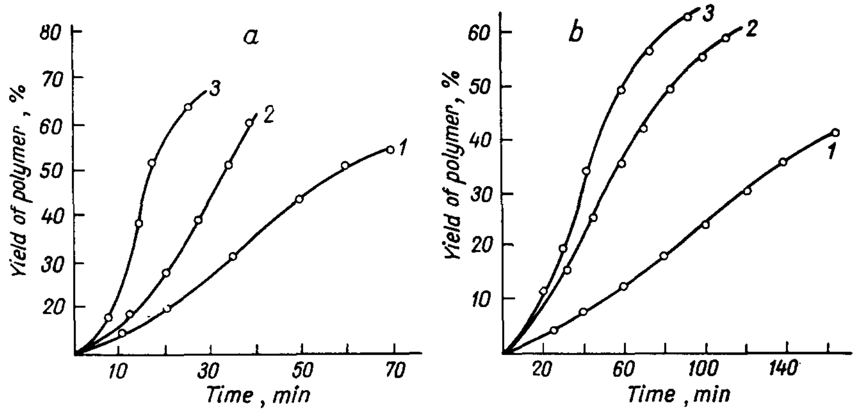


FIG. 4. Dependence of the yield of polyphenylmethylsiloxane (*a*) and polychlorophenylmethylsiloxane (*b*) on polymerization time at: *1*—110°; *2*—120°; *3*—130°.

$$\sigma^*_x C_6H_4 = \sigma^0_x + 0{\cdot}600; \quad \sigma^0_x = 0{\cdot}20 \ [5].$$

The value of ρ^* was calculated by the method of least squares from empirical data. The correlation coefficient for the five points, $r = 0{\cdot}93$, is good and is significant at the 2% significance level [6].

CONCLUSIONS

(1) The anionic polymerization of octamethylcyclotetrasiloxane, ethylheptamethylcyclotetrasiloxane, phenylheptamethylcyclotetrasiloxane, chlorophenylheptamethylcyclotetrasiloxane and vinylheptamethylcyclotetrasiloxane has been studied. A possible correlation between polymerization rate and Taft's induction constants (σ^*) is shown.

(2) The numerical value of ρ^*, of $+0{\cdot}41$, found for this reaction indicates that the substituents studied have only a small effect on the rate of anionic polymerization of organocyclosiloxanes.

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ELECTRONIC SPECTRA OF POLYMERS WITH CONJUGATED BONDS*

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IN THE synthesis of conjugated polymers the probability that when a new monomer unit is added conjugation already does not extend along the entire polymer chain is always greater than zero. This can happen as a result of bending of the polymer chain, caused by steric effects that deflect the chain from coplanarity or as a result of the specific conditions of synthesis. It was therefore of interest to study the relationship between the molecular weight of a conjugated polymer and the length of the conjugation sequence.

Let the probability of propagation with maintenance of conjugation be α, and with disruption of conjugation β, and the probability of chain termination γ; $\alpha+\beta+\gamma=1$. Then the average number of conjugated segments can be found as

$$\bar{n}_c=\sum_{n=1}^{\infty} n\alpha^n(\beta+\gamma)=(\beta+\gamma)\alpha\frac{d}{d\alpha}\sum_{n=0}^{\infty}\alpha^n=\frac{\alpha}{1-\alpha},$$

and the average number of monomer units in the polymer [1]

$$\bar{n}_p=\sum_{n=1}^{\infty} n(\alpha+\beta)\gamma=\frac{\alpha+\beta}{1-(\alpha+\beta)}.$$

If $\alpha\ll\beta$ then $\bar{n}_p=\beta/(1-\beta)$ and $\bar{n}_p>\bar{n}_c$. If such a polymer is fractionated the average length of the conjugation sequences in the fractions should not be dependent on molecular weight if the number of units in the fraction is greater than $\bar{n}_c$, and the electronic absorption spectrum should not vary from fraction to

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