

Dimethyldiphenylsiloxane copolymers synthesis by ion exchanger catalysis

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Dimethyldiphenylsiloxane copolymers were obtained by hydrolysis–copolymerization of diphenyldichlorosilane with octamethylcyclotetrasiloxane in the presence of water. A sulfonic cationite VIONIT CS-34C was used as catalyst. A macroporous, strongly basic anionite or a weakly basic gel were used to neutralize the HCl formed during the reaction. The formation of the copolymer was confirmed by ^{29}Si n.m.r. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Dimethylsiloxane elastomers have the highest thermo-stability among known elastomers but they do not possess any stability to ionizing radiation. In addition, because of their high crystallizing capacity, they cannot be used at temperatures below -55°C , while their glass temperature is -123°C ¹.

The crystallizing temperature, T_{cr} , of one polymer can be lowered by disrupting the ordered structure of the homopolymer. This can be done by introducing some bulky groups at the silicon atom. An interesting group for this purpose is phenyl because it is sufficiently bulky and has an intermolecular strength constant higher than methyl².

Lowering of the stiffening point can be obtained by introducing methylphenyl or diphenylsiloxane groups in the siloxane chain. However, Borisov *et al.*¹ found that for an elastomer with 8% diphenylsiloxane groups, a much higher radiation dose is necessary to crosslink it than for an elastomer with 18% methylphenylsiloxane groups. This might be a result of a better hindering of dimethyl groups by diphenylsiloxane groups than by methylphenylsiloxane groups. This 8% content of diphenylsiloxane groups is the optimum to assure cold resistance of the crosslinks.

The main method to synthesize dimethyldiphenylsiloxane copolymers is anionic copolymerization of octamethylcyclotetrasiloxane with octaphenylcyclotetrasiloxane, which was used in most papers^{3–7} because the Si–C₆H₅ bond is considered to be less stable towards acid reagents^{8,9}.

As is known¹⁰, cyclosiloxanes with phenyl groups polymerize with difficulty, and even more so in acid medium, because of the phenyl group effect. In octaphenylcyclotetrasiloxane, the Si–O bond cannot be cleaved with H₂SO₄ or acid activated clays¹¹. By using equilibrating catalysts it is possible to obtain siloxane polymers and copolymers in polycondensation–polymerization

processes using as monomers, simultaneously, silanes, siloxanediols and cyclosiloxanes^{11–14}. Such processes generally lead to statistical copolymers and also cyclics, except the case when the cyclization is thermodynamically unfavourable.

The purpose of this paper is to synthesize dimethyldiphenylsiloxane copolymers in a hydrolysis–copolymerization process using diphenyldichlorosilane with octamethylcyclotetrasiloxane in the presence of water, using an ion-exchanger for acid catalysis.

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane [(CH₃)₂SiO]₄, (D₄), supplied by Fluka AG, purum, >98%; mp 16–19°C; bp 175°C/760 mmHg; n_{D}^{20} 1.3960; d_4^{20} 0.955. Diphenyldichlorosilane (C₆H₅)₂Cl₂Si (DPDCS), supplied by Fluka AG, pract, >95%; bp 304°C/760 mmHg; n_{D}^{20} 1.582; d_4^{20} 1.22. Vionit CS-34 C: a macroporous, strongly acid cation exchanger with SO₃H groups, commercial product, having the following characteristics: granulation: 0.3–1.25 mm, porosity: 39–42%, specific surface: 39–42 m² g⁻¹, volumic weight: 900 g l⁻¹, exchange capacity: volumic, 1.8 meq ml⁻¹, gravimetric, 4.2 meq g⁻¹, granulation was chosen as 0.4–0.63 mm. Amberlite IRA-900, a strongly basic macroporous anion exchanger with benzyltrimethylammonium groups, supplied by Rohn & Haas and having the following characteristics: apparent density: 0.828 g ml⁻¹, strongly basic volumic exchange capacity (C_{VS}): 0.753 meq ml⁻¹, weakly basic volumic exchange capacity (C_{VW}): 0.062 meq ml⁻¹, total volumic exchange capacity (C_{VT}): 0.815 meq ml⁻¹, gravimetric exchange capacity (C_{G}): 3.044 meq ml⁻¹. XE-236, a gel, weakly basic anion exchanger with diethylenetriamine active groups, supplied by Rohn & Haas, having the following exchange capacities: C_{V} : 2.003 meq ml⁻¹, C_{G} : 4.879 meq ml⁻¹.

Before use, the ion exchangers were washed with water, brought into active forms by repeated services and

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regenerations, washed again with water and dried using azeotrope distillation with toluene (for the cationite) and benzene (for the anionites). Finally, they were dried in vacuum at 110°C for cationite and 60°C for anionites.

Equilibration of D_4 with DPDCS in the presence of cationite

In a reaction vessel, equipped with stirring, reflux condenser, thermometer, nitrogen inlet and lateral tube for gas evacuation, mixtures of D_4 and DPDCS, in various molar ratios were introduced. The mixture was heated to the predicted temperature (70°C) and then the following introduced: water, in a small excess towards the stoichiometric amount calculated from the DPDCS hydrolysis reaction; the cationite, in a 2.5% ratio towards the weight of the monomers mixture.

The reaction was carried out at 70°C for 2 h and the stream of gases evacuated from the reaction vessel was solved in a determined volume of distilled water. This solution was titrated with NaOH aq. solution and a very small amount of HCl was taken over, the rest remaining in the reaction mixture. Finally, the cationite was separated from the reaction mixture by filtering and washing with toluene. The reaction mass was diluted with toluene and washed with distilled water to pH neutral.

During the reaction time, the higher the amount of DPDCS in the initial mixture, the more foamed the reaction mixture. The copolymers were separated from the mixture by repeated precipitating with methanol from the toluene solution and then they were dried in vacuum at 110°C to constant weight.

Equilibration of D_4 with DPDCS in the presence of cationite and anionite

We worked in the same way as above but an amount of anionite was also added to the reaction mixture. This amount was in excess (towards the necessary amount of anionite calculated according to its exchange capacity to adsorb the formed HCl). The system was closed, without nitrogen stream.

A macroporous, strongly basic anionite (IRA-900) or a weakly basic, gel (XE-236) were used. In this case, the reaction mixture did not foam anymore. The reaction mass washing water was collected in a marked bottle which was completed with distilled water and the HCl content was determined.

Measurements

^1H n.m.r. spectra were recorded on a JEOL C-60 HL spectrometer, at 50°C, using TMS as standard and CCl_4 as solvent. ^{29}Si and ^{13}C n.m.r. spectra were recorded on a AC-80-Bruker spectrometer using TMS as reference internal standard, $\text{Cr}(\text{AcAc})_3$ as relaxation agent and CCl_4 as solvent. I.r. spectra were recorded on a M-80 SPECTORD spectrophotometer using KBr tablets. The acidity (A) of the reaction mixture (in g HCl) was determined by titrating the washing water with 0.1 N NaOH solution. The molecular weights were determined by g.p.c. technique with a modular system Gilson HPLC, having a differential refractometer $R_{(132)}$ as detector.

RESULTS AND DISCUSSION

Equilibration of D_4 with DPDCS in the presence of cationite

The copolymers obtained at various composition of

the initial mixture were purified, dried and weighed in order to determine the conversion. They were analysed with ^1H n.m.r. and the composition of the copolymers were determined using the integral signals corresponding to the protons in methyl (near 0.0 ppm) and phenyl (7.0–8.0 ppm) group, respectively, according to the following relationship:

$$F = \frac{5h_1}{5h_1 + 3h_2} \quad (1)$$

where F is the molar fraction of the dimethylsiloxane units in copolymer; h_1 , h_2 are the heights of the integrals corresponding to the protons in the methyl and phenyl group, respectively. The results are presented in Table 1.

As can be seen (from the data presented in Table 1), the copolymers formed after 2 h have about the same content of diphenylsiloxane groups as the initial mixture and yields are sufficiently high (70%). For E_{16} copolymer, the molecular weights were determined by g.p.c.: $M_n = 14\,300$; $M_w = 29\,900$; $I = 2.03$.

The low values of the molecular weights can be explained by the presence of sufficient water in the reaction medium. The i.r. spectra of the copolymers formed show that the chlorine was not hydrolysed completely and it can be found at some chain ends ($\nu = 400\text{--}500\text{ cm}^{-1}$), the other ends being OH groups ($\nu = 3500\text{ cm}^{-1}$). This can be explained by the fact that the reactivity of chlorine decreases with the increase of the siloxane chain to which it is attached, as a result of consolidating the Si–Cl bond by the electron-withdrawing effect of the oxygen atoms on the chain.

Equilibration of D_4 with DPDCS in the presence of anionite and cationite

In order to simplify the synthesis of these copolymers, a new procedure was tested. In this case an anionite in

Table 1 Results obtained for equilibration reaction of D_4 with DPDCS under various conditions (70°C, 2 h)

Sample code	f^a	Cationite (%)	Water (%)	F^a	Copolymer yield (%)
E_{22}	0.97	—	—		
E_{23}	0.97	—	1.2		Reaction did not take place
E_{24}	0.97	2.5	—		
E_{16}	0.97	2.5	1.25	0.97	71.5
E_2	0.94	2.5	2.5	0.98 ^b	66.1
					^b $E_{2/1} = 0.98$ ^b $E_{2/3} = 0.98$
E_{11}	0.94	2.5	2.5	0.96	67.2
E_7	0.90	2.5	3.8	0.95	61.4
E_1	0.88	2.5	4.1	0.89	58.4
E_9	0.80	2.5	6.4	0.75	60.5
E_{10}	0.73	2.5	8.1	0.62	53.6
E_{12}	0.63	2.5	9.5	0.39	54.5
E_{14}	0.50	2.5	11.0	—	50.4
E_{15}	0.31	2.5	12.5	0.25	44.3

$$^a f = \frac{[-(\text{CH}_3)_2\text{SiO}]_0}{[-(\text{CH}_3)_2\text{SiO}]_0 + [-(\text{C}_6\text{H}_5)_2\text{SiO}]_0}$$

$$F = \frac{[-(\text{CH}_3)_2\text{SiO}]}{[-(\text{CH}_3)_2\text{SiO}] + [-(\text{C}_6\text{H}_5)_2\text{SiO}]}$$

$[-(\text{CH}_3)_2\text{SiO}]_0$, $[-(\text{C}_6\text{H}_5)_2\text{SiO}]_0$: dimethyl and diphenylsiloxane unit concentrations respectively, in the initial mixture

$[-(\text{CH}_3)_2\text{SiO}]$, $[-(\text{C}_6\text{H}_5)_2\text{SiO}]$: dimethyl and diphenylsiloxane unit concentrations, respectively, in the obtained copolymers

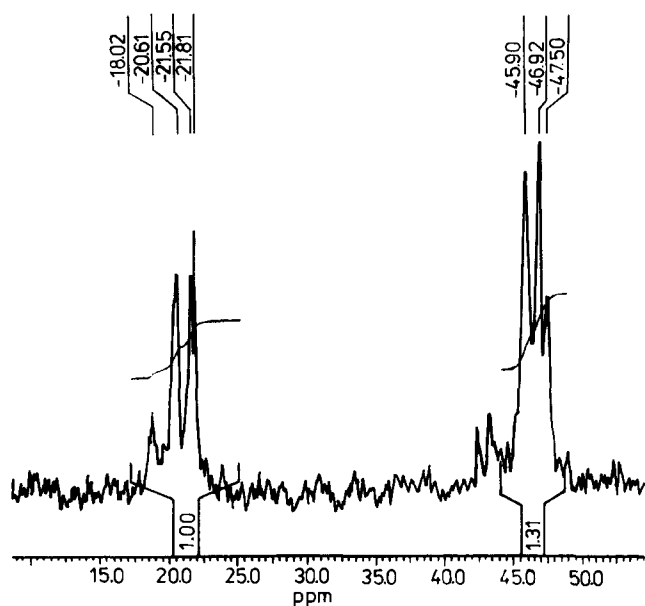
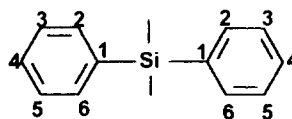
^b $E_{2/1}$, $E_{2/3}$: fractions 1 and 3, respectively of the copolymer E_2

Table 2 Results obtained for equilibration reaction of D₄ with DPDCS in the presence of cationite and anionite

Sample code	<i>f</i>	Cationite (%)	Anionite (%)	<i>F</i>	HCl am.exp. ^a × 10 ³ (g)	HCl am.th. × 10 ³ (g)
E ₁₈	0.97	2.5	—	0.94	152.25	312.21
E ₂₅	0.97	2.5	—	—	151.55	312.21
E ₁₇	0.97	2.5	12, XE-236	0.95	37.325	312.21
E ₁₉	0.97	2.5	24, XE-236	0.95	0.0	312.21
E ₂₁	0.97	2.5	24, XE-236	0.97	0.0	312.21
E ₂₀	0.97	2.5	20, IRA-900	0.97	0.0	312.21
E ₂₆	0.80	2.5	28, XE-236	—	34.37	2062.20
E ₂₇	0.80	2.5	—	—	807.6	2062.20

^a Determined from the washing waters**Table 3** ¹³C n.m.r. chemical shifts in copolymer E₁₄

Group	>Si(CH ₃) ₂	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
δ, ppm	0	134.00	134.00	127.22	129.47	127.22	134.00

**Figure 1** ²⁹Si n.m.r. spectrum of E₁₄ (*f*₁ = 0.50) copolymer

excess towards the stoichiometric amount was calculated according to its exchange capacity. This amount must be enough to neutralize the HCl formed during the reaction.

The yields and the compositions of the formed copolymers as well as the acidities of the reaction mass are presented in Table 2. The acidity of the reaction mixture, calculated from equation (2) was actually absent and the band in the i.r. spectrum, corresponding to the Si—Cl bond decreased, while the band corresponding to the Si—OH bond increased.

$$A = \frac{36.5mcV}{40n} \quad (2)$$

where *m* is the NaOH solution volume for titration (ml); *c* is the concentration of the NaOH solution (g ml⁻¹); *V* is

the total volume of washing waters (ml); *n* is the volume of washing waters used for titration (ml).

In order not to charge the reaction mass too much with solid phase, we tried to use a weakly basic, gel anionite, XE-236, with a higher exchange capacity (4.879 meq g⁻¹). Such anionites are very appropriate¹⁵ to retain mineral acids from solutions. Also in this case, the reaction mixture was finally neutral (Table 2, E₁₉, E₂₁, E₂₆).

To prove that copolymer was obtained and not a homopolymers mixture, we used the fraction technique¹⁸. From ¹H n.m.r. spectral data it was shown that all the separated fractions have the same composition (Table 1, E_{2/1}, E_{2/3}).

For the copolymers obtained using both procedures, the ¹³C n.m.r. spectra were recorded (Table 3). The ²⁹Si n.m.r. spectra were also recorded. In the ²⁹Si n.m.r. spectrum of the purified E₁₄ copolymer (Figure 1) we can see that between -45.6 and -47.5 ppm some specific signals appeared for the silicon in the diphenylsiloxane units which are part of a polymeric chain, while the silicon in dimethylsiloxane units appears between -20.6 and -21.6 ppm, the appearance of several signals for the silicon in dimethyl- and diphenylsiloxane units is due to the different neighbourhoods at the triad level. The ²⁹Si n.m.r. spectra of the copolymers show two sets of multiplets, one between -20.61 and -21.81 ppm for Me₂SiO groups, and one between -45.90 and -47.50 ppm for Ph₂SiO groups. For the dimethyl- and diphenylsiloxane sequences, respectively, the structures shown in Table 4 can appear at the triad level.

Using integral areas of the indicated Me₂SiO— and Ph₂SiO— centred triads the integral ratio factors, *f*_{Me} and *f*_{Ph} were calculated by different combinations of the triad signal intensities, *F*₀, *F*₁ and *F*₂, respectively²⁰.

The experimental run number, *R*_{exp} (average number of comonomer sequences in 100 repeat units) was calculated²¹.

$$R_{\text{exp}} = f_{\text{Me}} \cdot \% \text{Me}_2\text{SiO} = f_{\text{Ph}} \cdot \% \text{Ph}_2\text{SiO} \quad (3)$$

Table 4 ²⁹Si n.m.r. chemical shifts for comonomer sequences at triad level in the copolymer chains

Sequence	Triad	δ , ppm	Rel. intensities (F_0, F_1, F_2)
Me₂SiO-centred triads			
–Me ₂ SiO– Me ₂ SiO–Me ₂ SiO–	[0]	–21.81	0.45
–Me ₂ SiO– Me ₂ SiO–Ph ₂ SiO–	[1]	–20.61	0.35
–Ph ₂ SiO– Me ₂ SiO–Ph ₂ SiO–	[2]	–18.02	0.20
Ph₂SiO-centred triads			
–Ph ₂ SiO– Ph ₂ SiO–Ph ₂ SiO–	[0]	–45.90	0.64
–Me ₂ SiO– Ph ₂ SiO–Ph ₂ SiO–	[1]	–46.92	0.41
–Me ₂ SiO– Ph ₂ SiO–Me ₂ SiO–	[2]	–47.50	0.26

Table 5 Microstructure parameters for E₁₄ copolymer

Parameter	Value
% –Me ₂ SiO–	43.3
% –Ph ₂ SiO–	56.7
\bar{R}_{exp}	51.56
R_{th}	49.10
% Linkages	
% –Me ₂ SiO–Ph ₂ SiO– = % –Ph ₂ SiO–%–Me ₂ SiO–	25.78
% –Me ₂ SiO–Me ₂ SiO–	17.52
% –Ph ₂ SiO–Ph ₂ SiO–	30.92
Average sequence lengths (\bar{l})	
\bar{l} (–Me ₂ SiO–)	1.68
\bar{l} (–Ph ₂ SiO–)	2.20
Probabilities of diads (P)	
P(–Me ₂ SiO–Me ₂ SiO–)	0.40
P(–Me ₂ SiO–Ph ₂ SiO–)	0.60
P(–Ph ₂ SiO–Ph ₂ SiO–)	0.55
P(–Ph ₂ SiO–Me ₂ SiO–)	0.45
Product of reactivity ratios	
$r_{Me} \cdot r_{Ph} = [\bar{l}(-Me_2SiO-) - 1] \cdot [\bar{l}(-Ph_2SiO-) - 1]$	0.82

and was compared with theoretic run number R_{th} , calculated from

$$R_{th} = \frac{\% Me_2SiO \cdot \% Ph_2SiO}{50} \quad (4)$$

Using the value of run number, \bar{R}_{exp} , the other quantitative parameters describing the microstructure of the copolymer chain were calculated (Table 5) using Harwood–Ritchey relationships²².

Because $\bar{R}_{exp} > R_{th}$ and $r_{Me} \cdot r_{Ph} < 1$, it can be concluded that the distribution of the comonomer units in the chain is a statistic with a high tendency to alternate.

It can be seen that, both when we used only the cationite and a cationite–anionite mixture, almost the same values for yields and copolymer compositions were obtained. We presume that the anionite does not participate in the reaction itself. On the other hand, from Table 1 (E₂₂, E₂₃, E₂₈) we can see that the reaction can occur in the presence of cationite and water only.

Regarding the reactions between halogenosilanes and cyclosiloxanes, according to Andrianov and Severni^{18,19} more than one Si–O–Si bond can be cleaved, both in cycles and linear polymers. Thus, oligomers with a number of siloxane units not necessarily a multiple of 3 or 4 are obtained. Taking into account the cationite activity, this can catalyse the D₄ polymerization, the DPDCS hydrolysis and also the cyclization of the formed (C₆H₅)₂Si(OH)₂. The condensation of diols

with chlorosiloxanes or chlorosilanes, the redistributions of siloxane chains and cyclization may also occur.

From the ²⁹Si n.m.r. spectrum of the unpurified copolymers it is shown that cyclic compounds are present in the sample. Some specific signals for the diphenylsiloxane units contained in the cyclic compounds appear between –34 and –39 ppm. Therefore, the signals at $\delta = 34.00$ ppm corresponds to the tricyclic compounds and $\delta = 37.49$ ppm to the tetracyclic compounds containing diphenylsiloxane units. The width of the signals can be explained by the co-existence of different conformers in dynamical equilibrium²³. Therefore, it is presumed that the process is very complex and difficult to represent.

CONCLUSIONS

Dimethyldiphenylsiloxane copolymers in good yields can be obtained by equilibration of D₄ with DPDCS in the presence of VIONIT CS-34 C and a determined amount of water. Water plays the role of co-catalyst and hydrolysing agent. Thus, the diphenylsiloxane cycles stage is eliminated.

Using simultaneously cationite and anionite as adsorbent for HCl, the same results are obtained and, in addition, the reaction mass is practically free of HCl. Thus, the supplementary operations of neutralizing the reaction mass are eliminated and possible secondary reactions are prevented. Both the macroporous, strongly basic anionite and the weakly basic gel are equally efficient.

The dimethyldiphenylsiloxane copolymer formation was proved by the identity of compositions for various fractions of the copolymer and also by ²⁹Si n.m.r. spectra which show specific signals for diphenyl and dimethylsiloxane units, respectively, in the copolymer.

The obtained copolymer has a predominant statistical distribution of the co-monomer units.

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