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REVIEW PAPER

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PREPARATION OF FUNCTIONALLY AND ORGANOFUNCTIONALLY TERMINATED OLIGO– AND POLYORGANOSILOXANES BY CATION EXCHANGE RESIN–CATALYZED EQUILIBRATION POLYMERIZATIONS

The intention of this review is to present and to give guide–lines for the preparation of linear siloxane compounds which bear different terminal groups. To achieve this purpose, the well–known siloxane equilibration reaction was applied. The specific items were the selection of the equilibration catalyst and the determination of all relevant reaction parameters. After the optimal conditions had been established, a number of differently terminated siloxane polymers was synthesized and it was also pointed out that their molecular weights could be predicted.

The equilibration reaction is one of the most familiar and, at the same time, one of the most important reactions in siloxane chemistry [1]. The basic process involves the continuous breaking and reforming of the siloxane, Si–O, bonds in the presence of ionic, both acidic and basic, catalysts. By sufficiently long reaction times, this redistribution ends with the formation of an equilibrium mixture which contains both cyclic and linear (poly)siloxanes. It is often used for the preparation of functionally (where functional groups are directly bonded to the terminal silicon atoms, Si–X) and organofunctionally (which means with organofunctional termination, Si–R–X, where R is a short chain hydrocarbon unit) terminated oligo– and polyorganosiloxanes, mostly dimethyl substituted [2]. In such a case, besides disiloxanex bearing the desired functional groups and serving also as molecular weight regulators, the other reaction participant is normally one of the so–called cyclic siloxane monomers, for example, octamethylcyclotetrasiloxane, D_4.

The catalysts used in the equilibrations involve a great number of ionic, either acidic or basic, substances. A detailed list of both types of catalysts can be found in the literature [3]. Among the great variety of acidic catalysts, some strong acid cation exchange resins appeared to be of special interest [4–6]. The main advantages of this catalyst type are: easy–to–handle form, easy separation from the reaction products after completion of the reaction, multiple usage without regeneration and so on.

The purpose of this article is to present in a summarized form the results obtained in this laboratory in the course of investigations dealing with siloxane equilibration reactions aimed at preparing differently terminated oligo– and polyorganosiloxanes using a specific cation exchange resin equilibration catalyst.

EXPERIMENTAL

Materials

Cyclic siloxanes and disiloxanes, octamethylcyclotetrasiloxane, D_4, pentamethylcyclopenta- siloxane, D_5^H, hexamethyldisiloxane, HMDS, divinyl– tetramethyldisiloxane, DVTMDS, tetramethyldisiloxane, TMDS, and dicarboxypropyltetramethyldisiloxane, DCPTMDS (ABCR GmbH and Co. KG, Germany), as well as a commercial grade dimethyldichlorosilane hydrolysate, DDSH (Dow Corning Fluid 2.0176, USA), were used as received. The composition of DDSH regarding the (cyclics)/(linear polymer) weight ratio was 46.4/53.6 [7]. A commercial grade macroporous strong acid cation exchange resin, MCER, Duolite C 26 (Diamond Shamrock Co. USA), having a total exchange capacity of 1.85 eq/L, was used after an overnight thermal treatment at 50°C.

Equilibration procedure

The equilibration reactions were typically performed in a 0.25 L, three–necked, round–bottomed flask which was equipped with a mechanical or a magnetic stirrer, reflux condenser and a thermometer. The reactor was placed in a constant temperature oil heating bath. A mixture of desired composition was prepared in a separate container and then charge into the reactor in which the weighed amount of MCER catalyst had already been placed. The amount of MCER catalyst used was 22 meq of active substance (H^+) per each 100 g of the reaction mixture in all cases [7]. Stirring was started and the mixture was allowed to heat to the desired reaction temperature. When the reaction was completed, the resulting mixture (equilibrate) was separated from the catalyst by decantation. The low temperature volatile components (cyclics) were separated from the polymer product by vacuum

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distillation up to 200°C at approximately 7 mm Hg. The polymer product which remained was characterized for its structure and molecular weight.

Viscosity measurements

Steady–state shear viscosities were determined using a Ferranti–Shirley cone–and–plate rotational viscosimeter. Its plate diameter was 3.5 cm and the cone angle was 0.0057 rad. Shear rates in the range of 0.46 to 0.00184 were applied at 25°C. Zero shear viscosities were determined by a standard extrapolation procedure.

Identification methods

IR analyses were carried out on a Perkin–Elmer model 1725X spectrophotometer and samples were films on KBr pallets. The identifying bands were: for Si–CH_3 at 1262 cm^{-1}, for Si–H at 2100–2200 cm^{-1} and for CO at 1720 cm^{-1}.

^1H NMR spectra were obtained on a Varian model FT–80A instrument of 80 MHz. The samples were solutions in $CDCl_3$ and the characteristic chemical shifts were: for Si–CH_3 at 0.04 and 0.07 ppm and for Si–H at 4.71–4.74 ppm.

The vinyl gropus were determined by the mercury acetate titration method [8].

The well–known acid number determination procedure (for COOH determination) was performed by titrating sample solutions in a 1:1 toluene–acetone mixture with a methanolic KOH solution.

RESULTS AND DISCUSSION

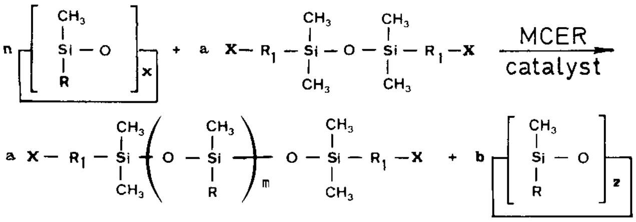
The first step in this investigation was to select the cation exchange resin catalyst. Several types and forms of strongly acidic cation exchange resins were tested for their efficiency and applicability as equilibration catalysts: two gel–type resins, Duolite C 20, a standard gel–type resin of Diamond Chamrock Co. and a gel–type resin prepared at a proper time in this laboratory [9], then the same resins, but in powdered form, and finally two macroporous resins, a commercial grade Duolite C 26 and again one of macroporous resins prepared in this laboratory [10]. The examination was carried out by equilibrating a number of arbitrary chosen reaction mixtures consisting of different portions of DDSH and HMDS at 120° C. The results showed that the gel–type resin catalyzed equilibrations progressed too slowly to permit any reasonable use in practice. On the other hand, both gel–type resins when used in powdered form, demonstrated an extremely high catalytic effect. It was, however, very strenuous work to separate them from the reaction products after the reaction was completed, which eliminated them as possible candidates. Anyway, both macroporous resins seemed to be an optimal choice, because of their sufficiently high catalytic activity and of their good separability from the equilibration products. For the sake of standardization, a commercial grade Duolite C 26 resin was finally selected as the equilibration catalyst.

After the catalyst had been selected, the relationship reaction temperature–reaction time was examined. This was done in a series of equilibrations performed on DDSH/HMDS mixtures of constant composition, which contained 2.5 wt% of HMDS. The data of Table 1 show that the increase of the reaction temperature shortened the reaction time needed to attain the equilibrium [7].

Table 1. Effect of the reaction temperature on the reaction times needed for equilibrium to be attained

Reaction temperature °C	Reaction time, hours	Polymer viscosity at equilibrium mPa · s
20	47	230
35	6	202
50	5.5	207
75	5	–
95	4.5	200
120	4	230

It should be emphasized that all of these preliminary investigations were carried out using DDSH, the linear part of which was OH–terminated. This means that the obtained siloxane polymers could have two different kinds of terminal groups, not only the desired ones (from disiloxanes intentionally added to the reaction mixture), but possibly also OH–groups originating from DDSH. This subject will be separately discussed elsewhere [11]. Hence, in order to avoid such an eventuality, all equilibrations which were performed afterwards, were caried out solely with cyclic monomers. In this case, the following generalized equation represents the equilibration reaction:



$$n\left[\mathrm{Si(CH_3)(R)}-\mathrm{O}\right]_x + a\ \mathrm{X}-\mathrm{R_1}-\mathrm{Si(CH_3)_2}-\mathrm{O}-\mathrm{Si(CH_3)_2}-\mathrm{R_1}-\mathrm{X} \xrightarrow[\text{catalyst}]{\text{MCER}} a\ \mathrm{X}-\mathrm{R_1}-\mathrm{Si(CH_3)_2}\left(\mathrm{O}-\mathrm{Si(CH_3)(R)}\right)_m\mathrm{O}-\mathrm{Si(CH_3)_2}-\mathrm{R_1}-\mathrm{X} + b\left[\mathrm{Si(CH_3)(R)}-\mathrm{O}\right]_z$$

where: x = 4 or 5, z = 4 and higher, R = CH_3 or H, R_1 = an organic radical and X = a functional group.

Another important reaction parameter was the reaction temperature, which was held constant at 95°C, except for the case of preparing dimethylsiloxy terminated polymers, when this temperature was 50°C because of the high volatility of TMDS, b.p. = 70°C. Each polymer type was synthesized with three different molal fractions of the respective disiloxane in the starting reaction mixture, and they amounted to 0.8%, 1.6% and 3.15%.

It was shown [12] that the molecular weights (in terms of viscosities) of the obtained polymers corresponded well, at least qualitatively, to the values expected from the reaction mixture compositions, Figure 1. Table 2 gives the general overview of the synthesized polymer classes and indicates the applied structure identification methods [12].

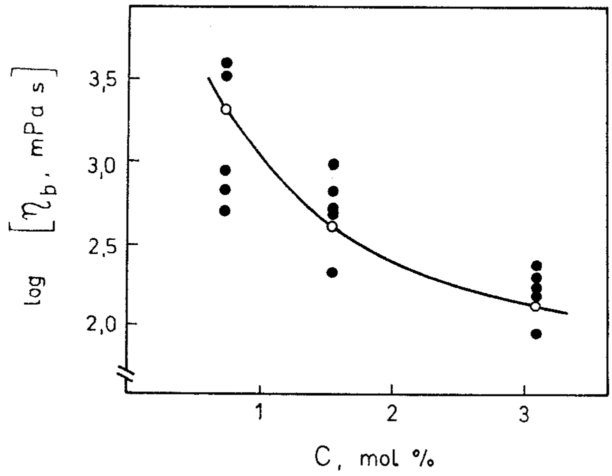


Figure 1. Effect of the disiloxane concentration "c" in the starting reaction mixtures on the polymer bulk viscosity "η_b". Open circles correspond to the values calculated from the starting mixture compositions

Table 2. The structure of the synthesized polymers and the applied structure identification methods

Structure units of eq. (1)			Structure identification methods*
R	R_1	X	
CH_3	–	CH_3	^{1}H NMR, FTIR
CH_3	–	$CH = CH_2$	HgAc titration
CH_3	–	H	FT IR
CH_3	$(CH_2)_3$	COOH	FTIR, acid number determination
H	–	CH_3	^{1}H NMR, FTIR
H	–	$CH = CH_2$	^{1}H NMR, FTIR, HgAc titration
CH_3-co-H	–	CH_3	^{1}H NMR, FTIR

*Identifying characteristic signals are given in the experimental part

Finally, the question yet to be answered, was: was it possible to predict the product molecular weight for a given starting reaction mixture composition, i.e. was it possible to predetermine the polymer molecular weight by proper choice of the reaction mixture composition? This problem was investigated and solved in a separate experimental series carried out very carefully on D_4/DCPTMDS equilibration systems. A detailed treatment of this problem, concerning both the experimental determination, as well as the elements of the theory-based molecular weight predestination procedure, can be found in a recently published article [13]. Here, only the final results, i.e. the experimentally determined molecular weight values (from the compositions of equilibrium mixtures) and values calculated on the basis of the theoretical considerations, are presented. Table 3 gives this comparison, which, as can be seen, shows extraordinary agreement.

Table 3. Compositions and polymer molecular weights for D_4/DCPTMDS equilibration systems

Initial mixtures		Equilibrium mixtures weight fractions of		Polymer molecular weights	
D_4, g	DCPTMDS, g	Polymer	Cyclics	exp.	calc.
20.0	1.66	0.88	0.12	3520	3520
20.5	2.83	0.89	0.11	2250	2240
20.3	5.14	0.90	0.10	1370	1370
20.1	8.83	0.92	0.08	920	920
5.0	5.17	0.95	0.05	570	580

The application of the described synthetic route and practical use of the siloxane oligo– and polymers so obtained, has been presented in a number of publications [14–17].

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IZVOD

DOBIJANJE OLIGO– I POLIORGANOSILOKSANA SA ZAVRŠNIM FUNKCIONALNIM I ORGANOFUNKCIONALNIM GRUPAMA METODOM EKVILIBRACIONE POLIMERIZACIJE SA KATJONSKOM JONOIZMENJIVAČKOM SMOLOM KAO KATALIZATOROM

(Pregledni rad)

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Polisiloksani sa završnim funkcionalnim i organofunkcionalnim grupama čine važnu skupinu siloksanskih intermedijera. U radu je opisan jedan od mogućih postupaka za dobijanje ovih jedinjenja, i to primenom poznate reakcije tzv. siloksanske ekvilibracije, odnosno ekvilibracione polimerizacije. Pošto je ovo katalizovana reakcija, najpre je izvršen odabir katalizatora. Izabrana je jedna makroporozna katjonska jonoizmenjivačka smola tipa jake kiseline, Duolite C 26. Po određivanju svih parametara značajnih za odvijanje reakcije, pristupljeno je izvođenju sinteze. Početnu reakcionu smešu činili su uvek neki ciklik, obično D_4 i odgovarajući disiloksan. Struktura dobijenih polimera proverena je instrumentalnim metodama (IR, ^{1}H NMR) i metodama hemijske analize završnih grupa. Pokazano je takođe, a na osnovu rezultata nekih teorijskih razmatranja, da je moguće sintetizovati polimere sa željenom, unapred zadatom srednjom molskom masom; drugim rečima, polazeći od zadate molske mase polimera, moguće je računskim putem odrediti potreban sastav početne reakcione smeše.

Ključne reči: Polisiloksani • Polimerizacija • Katjonske izmenjivačke smole • Molske mase • Procena •
Key words: Functionally terminated polysiloxanes • Equilibration polymerization • Cation–exchange resin • Predetermination of molecular weight •