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Functionalized oligopolysiloxanes by heterogeneously catalyzed equilibration polymerization reactions

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Summary

A new general procedure for preparation of functionalized oligopolysiloxanes of predetermined molecular weight is described. It utilizes heterogeneously catalyzed siloxane equilibration polymerization reactions which do not require troublesome and sometimes difficult post-preparative work-up procedures usually encountered with the well known homogeneously catalyzed corresponding reactions. The method is described using as example the preparation of α,ω-telechelic vinyldimethylsiloxy-oligopolydimethylsiloxanes from octamethylcyclotetrasiloxane and 1,3-divinyltetramethyldisiloxane, but reference to the preparations of trimethylsiloxy-, dimethylsiloxy- and carboxypropyldimethylsiloxyoligopolydimethylsiloxanes, oligopolymethylhydridosiloxanes or their copolymers is also made.

Introduction

It has been well documented in the literature that linear oligopolysiloxanes with potentially reactive functional groups at their chain ends, known as α,ω-telechelic oligopolysiloxanes, can be prepared by the so-called equilibration polymerization reactions of cyclic siloxanes and functional disiloxanes in the presence of appropriate reaction catalysts (1). These catalysts can be different compounds, but, without any exception, until present, they were all soluble in the siloxane reaction mixtures, and their action, that is the reaction catalysis, was always homogeneous.

On the other hand, it has long been known that siloxane equilibration polymerization reactions can also be catalyzed by the catalysts which are insoluble in the respective reaction mixtures and that the resulting heterogeneous catalysis exhibits many practical advantages over the homogeneous one (2). Thus, the heterogeneously catalyzed equilibration polymerization reactions generally do not require time consuming and sometimes very tedious post-polymerization work-up procedures, including catalyst deactivation, neutralization and isolation, and they utilize cheaper, easy to handle and commercially available catalysts. Generally,

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these catalysts can also be recuperated, permitting their multiple usage after simple separation, washing and drying.

Among many different types of insoluble catalysts examined, including carbon treated with acids, silicates treated with acids, acidified diathomeus earths or clays, etc., particular attention has been devoted to various crosslinked polymers, of which the well-known cation exchange resins, CER, based on the sulfonated crosslinked polystyrenes have successfully reached even into industrial practice (3).

However, despite these clear advantages, heterogeneous catalysis of the siloxane equilibration polymerization reactions is still generally limited to the preparation of nonfunctional polysiloxanes, that is to the synthesis of polymers with unreactive trimethylsiloxy end groups, the well-known "silicon oils", and no successful attempts have been reported on its use for preparation of functionalized oligopolysiloxanes. Therefore, we recently attempted to combine these two approaches, that is to examine if heterogeneously catalyzed siloxane equilibration polymerization reactions could be developed for preparation of functionalized oligopolysiloxanes, and in this report we wish to describe some preliminary results obtained from this investigation.

Experimental

Materials: Octamethylcyclotetrasiloxane, D_4, pentamethylcyclopentasiloxane, D^H_5, hexamethyldisiloxane, HMDS, 1,3-divinyltetramethyldisiloxane, DVTMDS, 1,3-tetramethyldisiloxane, TMDS, and 1,3-*bis*(3-carboxypropyl)tetramethyldisiloxane, DCTMDS, were purchased from ABCR GmbH and Co. KG, Germany, and used in the equilibration polymerizations as received. "Duolite C26" cation exchange resin from "Diamond Shamrock", USA, having total ion exchange capacity of 1.85 eq/L, was used as the reaction catalyst after preliminary drying by vacuum filtration and an overnight warming at 50°C.

Equilibration polymerization reactions: A typical equilibration polymerization reaction was performed as follows. A 100 mL, four-necked, round-bottomed flask, was equipped with a mechanical stirrer, reflux condenser and a termometer and placed in a constant temperature silicon oil bath. A mixture of desired composition of D_4 and selected disiloxane was prepared in the flask and, with constant stirring, warmed up to the reaction temperature, which in this work was 95°C, except for the case of preparation of the dimethylsiloxy- terminated oligopolysiloxane, when this temperature was 50°C because of high volatility of TMDS, b.p.=70°C. After this was completed, the weighted amount of CER, necessary to achieve concentration of 16.3 meq of $-SO_3H$ active catalytic cites, per each mol of Si-O units, was charged into the reactor to start the reaction.

The course of the reaction was monitored by withdrawing small amounts of the reaction mixtures after selected time intervals for analysis of their contents and for molecular weight determination. This was performed by using a narrow glass tube with a stainless steel net sealed to its bottom end to filter the catalyst and stop the reaction in withdrawn reaction mixture samples. All reactions examined, were carried out until no further changes in the followed properties could be observed.

At the reaction end point, the stirring was stopped, the reaction mixture was filtered through a stainless steel net filter to remove the catalyst, and the filtrate was fractionated by distillation under reduced pressure. This distillation was carried out by heating the liquid filtrate up to 200°C at 5-10 mm Hg until complete removal of the volatiles, which in the case of dimethylsiloxanes usually amounted to about 8-10$\%_{mas.}$ of the starting filtrate, while in the cases of methylhydridosiloxanes this amount was usually reduced to only 1-3$\%_{mas.}$. The composition of the volatile fractions was analyzed by capillary gas chromatography, CGC, while molecular weights of the remaining polymer products were determined by melt rheometry.

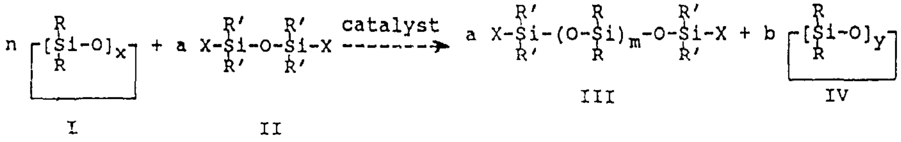
Monitoring methods; Rheometry: Rheological flow curves, viscosity vs. shear rate, of the reaction mixtures and of the resulting functionalized oligopolysiloxanes were determined by using a Feranty-Shirley cone-and-plate rotational viscometer at 25°C. The plate diameter was 8.3 cm, the cone diameter was 3.5 cm and the cone angle was 0.0057 rad. The shear rate interval from 18.4 to 1.84 10^3 s^{-1} was scanned and the zero shear viscosities, η_o, were determined by standard extrapolation procedure of the linear, low shear rate parts of the η vs. $\dot{\gamma}$ double logarithmic plots to zero shear rate.

High performance liquid chromatography: A Varian liquid chromatograph model 1250 with Supelco Pl-Gel columns and refractive index detector was used at 25°C. Three columns with crosslinked polystyrene stationary phase having pore sizes of 10^5, 10^4 and 10^3 A, respectively, were connected in line and chloroform was used as the mobile phase. This system was calibrated with polydimethylsiloxane constant viscosity standards: B1 (98.84 cP; $\bar{M}_w$ = 7250), B2 (466.56 cP; $\bar{M}_w$ = 19 950) and B4 (4724 cP; $\bar{M}_w$ = 49500) purchased from "Brookfield Laboratories", USA and molecular weight standards: PSAW 101 ($\bar{M}_{GPC}$ = 67500), PSAW 104 ($\bar{M}_{GPC}$ = 166000) and PSAW 106 ($\bar{M}_{GPC}$= = 357000) purchased from "Petrarch Silanes and Silicones", USA. 10 μL of 10$\%_{mas.}$ sample in chloroform solutions were injected in all cases.

Capillary gas chromatography: A Varian 3400 gas chromatograph with a 4m long DB-wax column and a flame ionization detector was used. Injector temperature was 250°C, the column temperature program was: 3 min at 50°C followed by heating at 15°C/min to 270°C, and detector temperature was 300°C.

Results and discussion

Equilibration polymerization reactions of cyclosiloxanes in the presence of disiloxane end-capping agent, or chain end terminator, can be represented by the following generalized equation:



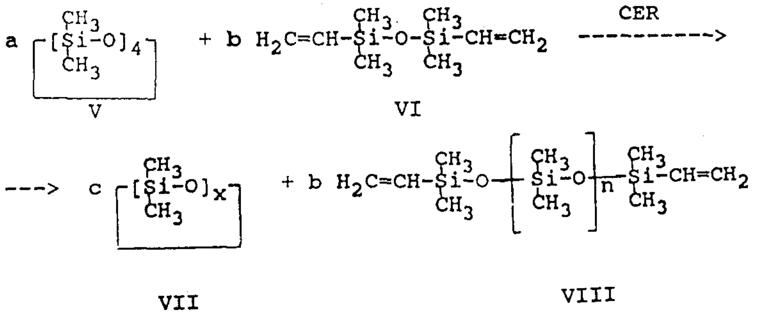
$$n \left[\underset{R}{\overset{R}{Si}}-O\right]_x + a\; X-\underset{R'}{\overset{R'}{Si}}-O-\underset{R'}{\overset{R'}{Si}}-X \xrightarrow{\text{catalyst}} a\; X-\underset{R'}{\overset{R'}{Si}}-(O-\underset{R}{\overset{R}{Si}})_m-O-\underset{R'}{\overset{R'}{Si}}-X + b \left[\underset{R}{\overset{R}{Si}}-O\right]_y \quad (1)$$

I II III IV

The basic reaction in these processes is, of course, the siloxane redistribution reaction, which represents a series of consecutive breaking and reforming of the siloxane bonds induced by the attack of ionic species supplied by the reaction catalyst (3). If such processes are carried out until the equilibrium of the reactants and the reaction products is reached, they can be referred to as the equilibration polymerizations (4).

Sulfonated crosslinked polystyrene cation exchange resin, CER, used in this work, may be considered as a reservoir of H^+ ions which can act as catalytically active species for the equilibration polymerization. The degree of polymerization of the linear polymer product and the chemical structure of its end groups may be regulated by selecting the type and the concentration of the reacting disiloxane end-capping agent (5). All reactions performed were monitored by following the course of their occurrence by several monitoring methods, including viscometry, high performance liquid chromatography and capillary gas chromatography.

Heterogeneously catalyzed equilibration polymerization reaction of octamethylcyclotetrasiloxane, D_4, V, and 1,3-divinyltetramethyldisiloxane, DVTMDS, VI, to obtain an α,ω-telechelic vinyldimethylsiloxy terminated oligopolydimethylsiloxane, VIII (further referred to as VDM-OPDMS), can be represented by the following equation:



$$a \left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_4 + b\; H_2C=CH-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH=CH_2 \xrightarrow{\text{CER}}$$

V VI

$$\longrightarrow c \left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_x + b\; H_2C=CH-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-\underset{CH_3}{\overset{CH_3}{Si}}-CH=CH_2 \quad (2)$$

VII VIII

The results obtained by monitoring the course of this reaction are shown in Figures 1 and 2.

It can be seen from Figure 1 that the reaction mixture viscosities increased with time, until plateaus were reached after which the viscosities ceased to increase further. This indicated that the reactions were completed and that the states of equilibrium were reached in the resulting reaction mixtures (6). The corresponding HPLC results are shown in Figure 2. These results clearly showed that the observed

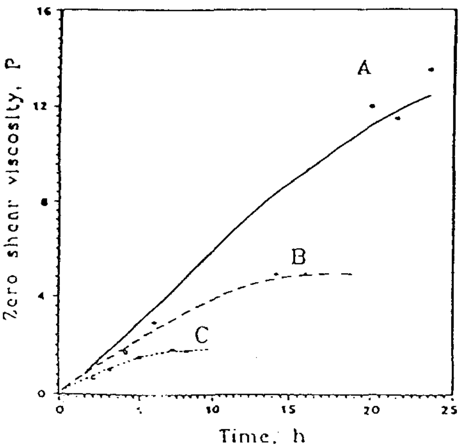


Figure 1: Monitoring of the CER catalyzed equilibration polymerization reactions of D_4 and DVTMDS by rheometry. Initial siloxane reaction mixture compositions in mol % D_4/mol % DVTMDS: A=99.2/0.8; B=98.4/1.6 and C=96.85/3.15.

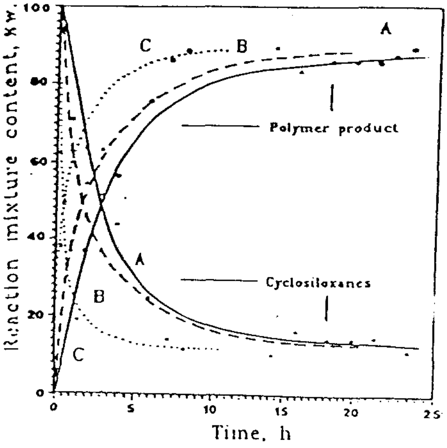


Figure 2: Monitoring of the course of the CER catalyzed equilibration polymerization reactions of Figure 1 by HPLC. Component contents were calculated from the areas of the corresponding peaks by using a chromatogram weighting method. Lettering system is the same as in Figure 1.

viscosity changes were caused by disappearance of the cyclic siloxane monomer, D_4, V in Equation 2, and by simultaneous formation of the linear VDM-OPDMS product, VIII. The final yield of the latter was about 90% in all cases, which was in good agreement with the expected content of the dimethylsiloxane equilibrates calculated from the Jacobson-Stockmayer theory (7).

The polymers thus obtained were isolated from the respective reaction mixtures by simple filtration, to separate the catalyst, and distillation of the cyclic siloxanes, by heating up to 200°C under reduced pressure of about 5-10 mm Hg.

The products were clear, viscous liquides, which had molecular weights, $\overline{M}_w$, calculated from zero shear viscosity using $\log \eta_0(\mathrm{cs}) = 1.00 + 0.0123\ \overline{M}_w^{1/2}$ (8), as listed in Table 1. Table 1 also lists other α,ω-telechelic oligopolysiloxanes and their respective $\overline{M}_w$ values obtained in the same manner, which generally agreed well with the expected target values calculated from the initial reaction mixture compositions given in Figure 1. These target molecular weights, assuming perfect equilibration of the two reactants, i.e. without formation of cyclic siloxanes, VII in eq. 2, and neglecting the end groups, were approximately 9100, 18200 and 36800; taking the formation of cyclic siloxanes - in amount of 10% - into account, the target $\overline{M}_w$'s were 8200, 16400 and 33100, respectively. It can be seen from these data that, with only few exceptions, obtained mo-

Table 1: Structures and Some Properties of the Functionalized α,ω-Telechelic Oligopolysiloxanes, OPS, III, Prepared

OPS samples	R	R′	X	Structure identification methods	OPS $\bar{M}_w$
	from eq. (1)				
1	CH_3	CH_3	CH_3	^1H NMR, FTIR	11 000 19 000 22 500
2	CH_3	CH_3	$CH=CH_2$	HgAc titration	13 000 26 000 43 000
3	CH_3	CH_3	H	FTIR	10 400 - -
4	CH_3	CH_3	$(CH_2)_3COOH$	FTIR	32 000[a] - 85 800[a]
5	$(CH_3)(H)$	CH_3	CH_3	^1H NMR, FTIR	12 000 19 000 20 000
6	$(CH_3)(H)$	CH_3	$CH=CH_2$	^1H NMR, FTIR HgAc titration	6 200 12 000 26 000
7	$(CH_3)_2$-co-$(CH_3)(H)$	CH_3	CH_3	^1H NMR, FTIR	10 000 22 000 46 000

[a] These values probably indicate COOH associations in the polymer melts.

lecular weights agreed rather well with the targeted values and were very sensitive to changes in the ratios of the reactant concentrations, confirming the expected chemistry of this polymerization reaction.

Structure of polymer samples listed in Table 1, were verified by ^1H NMR and/or FTIR. For IR analyses a Perkin-Elmer model 1725X spectrofotometar was used and samples were films on KBr pallets; for ^1H NMR a Varian model FT-80A instrument of 80 MHz was used and samples were OPS solutions in $CDCl_3$; all ^1H NMR chemical shifts are relative to tetramethylsilane. Identifying characteristic signals were: for sample 1: standard polydimethylsiloxane spectra; for sample 3: Si-H at 2128 cm^{-1}; for sample 4: C=O at 1720 cm^{-1}; for sample 5 and 6: Si-H at 2168 cm^{-1} and at 4.71-4.74 ppm (singlet); for sample 7: Si-H at 2157-2168 cm^{-1} and at 4.71-4-74 ppm (singlet), Si-CH_3 at 0.04 and at 0.07 ppm (two singlets). The identification of vinyl groups was not possible by either of the two spectrometers used, probably because molecular weights of the polymers prepared were to high for useful signal to noise ratio. Nevertheless, the vinyl groups were easily determined by the mercury acetate titration method (9), which in all cases gave an average of 1.9 vinyl groups per polymer molecule, in excellent agreement with the expected value of 2.

Conclusions

It was shown in this work that equilibration polymerization of cyclic siloxanes and various functional linear disiloxane end-capping agents can be successfully catalyzed heterogeneously by sulfonated crosslinked polystyrene cation exchange resin, CER, to yield α,ω-telechelic functional oligopolysiloxanes of predetermined molecular weights as the reaction products. This represents a novel and extremely practical route to preparation of these reactive polymers, because of very high purity of the products and simplicity of preparation which retains all practical advantages characteristic for this mode of catalysis. Therefore, this approach clearly offers very promising possibilities for easy and routine preparation of a wide variety of functionalized oligopolysiloxanes, which are highly desirable as reactive precursors for numerous synthetic applications. Detailed investigations of these and other related reaction systems are in progress in our laboratories and the results obtained will be described in our forthcoming publications.

References

1. (a) Summers JD, Elsbernd CS, Sormani PM, Brandt PJA, Arnold CA, Yilgor I, Riffle JS, Kilic S, Mc Grath JE (1988) Recent advances in organosiloxane copolymers. In: Zeldin M, Wynne KJ, Alcock HR (eds) Inorganic and organometalic polymers. ACS Symp Series, 360, p. 180 (b) Elsbernd Cs, Spinu M, Krukonis VJ, Gallagher PM, Mohanty DK, Mc Grath JE (1990) Synthesis and fractination studies of functionalized organosiloxanes. In: Ziegler JM, Gordon Fearon FW (eds) Silicon based polymer science: a comprehensive resource. Adv Chem Ser, Am Chem Soc, 224, p. 145
2. (a) Hyde JF (1975) US Pat 2 779 776 (b) Evans (1978) US Pat 4 122 247 (c) Finke U, Moretto HH (1982) US Pat 4 310 679
3. Noll W (1968) Chemie und Technologie der Silicone Verlag Chemie, Weinheim/Bergstr, p. 188
4. Dvornic PR, Lenz RW (1990) High temperature siloxane elastomers. Huthig a. Wepf, Heidelberg New York, p. 30
5. Govedarica MN, Dvornic PR (1991) J Serb Chem Soc 56, 7
6. Kantor SW, Grubb WT, Osthoff RC (1954) J Am Chem Soc 76, 5190
7. (a) Jacobson H, Stockmayer WH (1950) J Chem Phys 18, 1600 (b) Flory PJ, Semlyen JA (1966) J Am Chem Soc 88, 3209 (c) Flory PJ (1953) Principles of polymer chemistry. Cornell, Ithaca New York
8. (a) Barry AJ (1946) J Appl Phys 17, 1020 (b) Charlesby A (1955) Proc R Soc (London) A 320, 120 (c) Dvornic PR, Jovanovic JD, Govedarica MN (1993) J Appl Polym Sci 49, 1497
9. Angellotti NC (1991) in Smith AL (ed) The analytical chemistry of silicones. Wiley New York p. 203