SHORT COMMUNICATION

Activity of some disiloxanes toward the cation exchange resin-catalyst in the siloxane equilibration reaction

M. N. GOVEDARICA[*]

ICTM, Centre of Chemistry, Department of Polymeric Materials, Njegoševa 12, YU-11000 Belgrade, Yugoslavia

The relative activities of four disiloxanes toward the cation exchange resin, which was used as an equilibration catalyst, were determined in such a way that the equilibrium initially present in an arbitrary chosen equilibrate was disturbed by adding the respective disiloxanes to it, and then by recording the viscosity of the equilibrating mixtures as a function of reaction time. As a result, a set of different viscosity-reaction time relationships was obtained, which implies different activities of disiloxanes toward the catalyst. In this way the following decreasing order of acitivites was established: 1,3-tetramethyldisiloxane > 1,3-divinyltetramethyldisiloxane > hexamethyldisiloxane > 1,3-bis(3-carboxypropyl)tetramethyldisiloxane.

Keywords: cation exchange resin, catalyzed siloxane equilibration, activities of disiloxanes, acidic equilibration catalyst.

INTRODUCTION

In the presence of ionic substances, either basic or acidic, the siloxane, Si–O, bonds undergo the process of continuous breaking and reforming. If the reaction time is sufficiently long, these redistribution reactions end with the formation of an equilibrium mixture consisting of both linear and cyclic siloxanes. In such a case, this process is called the equilibration reaction.[1] It is often used for the preparation of different polysiloxane compounds, for example of α, ω-difunctionally terminated oligo- and polysiloxanes, which implies the use of a variety of difunctional disiloxanes.[2] For this reason, it would be advantageous to know how these disiloxanes behave under equilibration conditions.

Another important feature of an equilibration process is the choice of an appropriate catalyst. A detailed list of catalysts used for equilibrations can be found elsewhere.[3]

It should be also mentioned that the literature data on the activities of disiloxanes toward catalysts are rather scarce. Almost forty years ago, the following

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* Serbian Chemical Society active member.

decreasing order of activities toward sulfuric acid-catalyst was established[4]: MM > MM' > M'M' > M"M" (where: M: $(CH_3)_3SiO_{1/2}$; M': $BrCH_2(CH_2)_2SiO_{1/2}$ and M": $ClCH_2(CH_3)_2SiO_{1/2}$).

In this investigation, an acidic catalyst, a macroporous cation exchange resin, MCER, was used, because of its easy-to-handle form[5] and particularly because of its importance in commercial processes.[6] The activities of four disiloxanes toward the selected MCER-catalyst were determined. They are, hexametyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$, (HMDS), 1,3-tetramethyldisiloxane, $H(CH_3)_2SiOSi(CH_3)_2H$, (TMDS), 1,3-divinyltetramethyldisiloxane, $CH_2=CH(CH_3)_2SiOSi(CH_3)_2CH=CH_2$, (DVTMDS) , and 1,3-bis(3-carboxypropyl)tetramethyldisiloxane, $HOOC(CH_2)_3(CH_3)_2SiOSi(CH_3)_2(CH_2)_3COOH$, (DCPTMDS).

EXPERIMENTAL

Materials

Octamethylcyclotetrasiloxane, D_4, as well as all disiloxanes: HMDS, TMDS, DVTMDS and DCPTMDS, were obtained from ABCR GmbH & Co KG, Germany, and used as received. A commercial grade macroporous cation exchange resin, MCER, Duolite C 26, from Diamond Shamrock, USA, having a total exchange capacity of 1.85 eq/L, was used as the acidic equilibration catalyst after preliminary drying by vacuum filtration and an overnight warming at 50 ºC.

Determination procedure

The determination was performed by registrating the viscosity as a function of reaction time for reaction mixtures consisting of exactly weighed and constant amounts of an equilibrate, here called "the basic equilibrate",[*] and respective disiloxanes the amounts of which were also exactly weighed and equimolar. The procedure was as follows: at first, both the basic equilibrate and the respective disiloxane were charged into a reactor flask and the viscosity (as inherent viscosity), η_{inh} (initial), was determined. Then, the MCER-catalyst was added and, at various arbitrarily selected time intervals, samples were withdrawn, and the viscosities of these samples, η_{inh} (actual), were determined. After a sufficiently long time, long enough for equilibrium to be attained (cca. 50 hours), the viscosity was again determined, η_{inh} (final).

Equilibrations

All equilibrations were carried out in a three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser and a thermometer. The flask was placed into a constant temperature oil bath. The amount of MCER-catalyst was in all cases 2.2 meq/10 g of reaction mixture. In equilibrations aimed at the determination of relative activities, the reaction temperature was held at 50 ºC, while the basic equilibrate was prepared by equilibrating the mixture at 95 ºC for 24 hours. A more detailed description of the equilibration procedure can be found elsewhere.[5,7]

Viscosities

Inherent viscosities, $\eta_{inh} = \ln(\eta_s/\eta_0)/c \cong \ln(\tau_s/\tau_0)/c$ (where: η_{inh}: inherent viscosity, cm^3/g; η_s, τ_s: solution viscosity and solution flow time, respectively; η_0, τ_0: pure solvent viscosity and pure solvent flow time, respectively, and c: solution concentration, g/cm^3), were determined using an Ubbelohde-type viscosimeter at 30 ºC. Toluene was used as a solvent and the concentrations of the solutions were approximately 0.15 g/mL.

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* An equilibrate obtained by equilibrating a mixture of 99 wt% of D_4 and 1 wt% of HMDS, which was an arbitrary choice, as many other compositions could also have been used as long as they represent a real equilibrate.

RESULTS

Table I gives the compositions of the starting equilibration mixtures and the results obtained by measuring the inherent viscosities at arbitrarily selected reaction time intervals, including both the initial and final viscosity values.

TABLE I. Starting equilibration compositions[*] and inherent viscosities at different reaction time intervals

Disiloxan	g	Inherent viscosities[**] cm^3/g after reaction time of							Total viscosity change cm^3/g
		0	20	40	75	150	300	3000	
					minutes				
HMDS	0.1528	11.32	11.07	10.49	10.32	10.06	9.77	8.16	3.16
TMDS	0.1264	11.34	10.67	10.47	10.18	9.94	9.69	9.18	2.16
DVTMDS	0.1754	12.12	11.56	11.38	11.02	10.67	10.37	9.06	3.05
DCPTMDS	0.2884	11.39	11.35	11.09	10.95	10.82	10.49	8.83	2.57

[*]In all experiments the amounts of basic equilibrate and MCER were constant and totaled 20 g and 0.9 g, respectively. [**]These values are averages obtained from 6 or 7 individual runs. Each individual run did not differ by more than ± 5 % from the average value.

Viscosity, although it represents only one of the mechanistic features of the process and hence does not permit interpretation at the molecular level of what occurs in the reaction, is at least a qualitative measure of the average molecular weight; its total change, $\Delta\eta_{inh}$ (total) = η_{inh} (initial) − η_{inh} (final), reflects the change in molecular weights between the initial reaction mixture and the final equilibrium state.

It can be seen that the viscosities in Table I decreased as a function of reaction time. This result is an expected one, because disiloxanes act as chain transfer agents and are therefore used to control molecular weights.
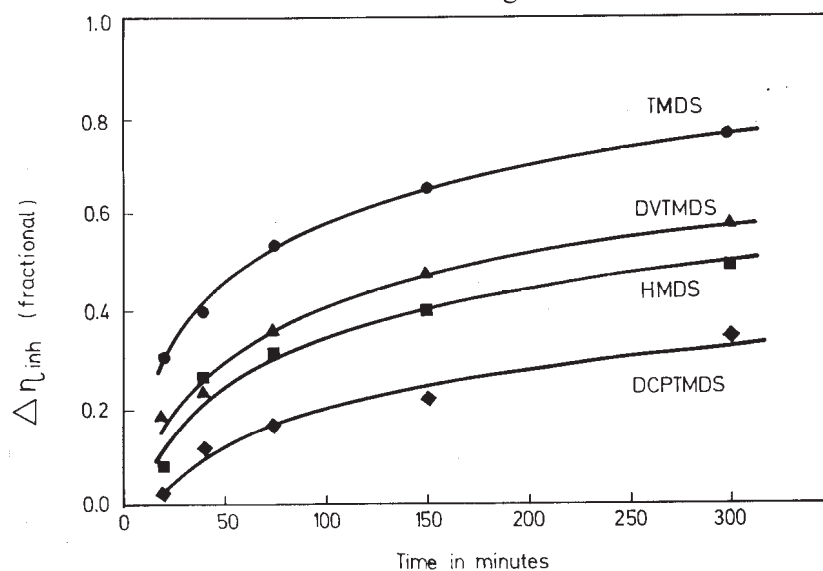

Fig. 1. η_{inh} (fractional) as a function of reaction time.

It is also clear that various disiloxanes could possess different activities toward the equilibration catalyst. Thus, in order to determine their activities, the viscosities, *i.e.*, the viscosity changes of a reaction mixture, can be used, as it was done here. For this purpose, the actual viscosity change, expressed as a fraction of the total change, η_{inh} (fractional) = [η_{inh} (initial) − η_{inh} (actual)]/Δ η_{inh} (total), was calculated and the results are presented as a function of reaction time in Fig. 1.

According to the figure, the following decreasing order of activities toward MCER-catalyst was obtained:

$$TMDS > DVTMDS > HMDS > DCPTMDS$$

CONCLUSION

A simple, precise and, at least in principle, generally applicable method for the determination of the relative activities of siloxane compounds toward the equilibration catalyst is presented. It is based on the assumption that the viscosity change of an equilibrating reaction mixture, consisting of the siloxane compound the activity of which is to be determined, and of an arbitrary chosen equilibrate (the basic equilibrate), could be used as a measure of the activity of the respective siloxane compound. The reason for this assumption is simple: as the basic equilibrate alone can not change its composition, it follows that the added siloxane compound is the only ingredient of the equilibrating mixture that can cause such a change. Taking the measured viscosity changes as fractions of its total change for the duration of the equilibration reaction, enables the direct determination of the activity of the respective siloxane compound. The application of the method was demonstrated using a number of disiloxanes as examples.

И З В О Д

АКТИВНОСТ ДИСИЛОКСАНА ПРЕМА КАТЈОНСКОЈ ЈОНОИЗМЕЊИВАЧКОЈ СМОЛИ - КАТАЛИЗАТОРУ РЕАКЦИЈЕ СИЛОКСАНСКЕ ЕКВИЛИБРАЦИЈЕ

М. Н. ГОВЕДАРИЦА

ИХТМ, Центар за хемију, Одељење за полимерне материјале, Његошева 12, 11000 Београд

Одређене су релативне активности четири дисилоксана према катјонској јоноизмењивачкој смоли, катализатору реакције еквилибрације, и то тако што је додатком дисилоксана поремећена првобитно присутна равнотежа у произвољно одабраном еквилибрату, а затим је праћен вискозитет у зависности од времена трајања реакције еквилибрације. Као резултат, добијене су различите зависности вискозитет-време трајања реакције, што указује на различиту активност дисилоксана према катализатору. На овај начин установљен је следећи опадајући редослед активности: 1,3,-тетраметилдисилоксан > 1,3-дивинилтетраметилдисилоксан > хексаметилдисилоксан > 1,3-бис(3-карбоксипропил)тетраметилдисилоксан.

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