Size-Dependent Polycondensation of α,ω-Dihydroxyoligo(dimethylsiloxane)

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The ability to synthesize polymers with very narrow molecular weight distributions has had a significant impact on the study and understanding of macromolecular chemistry and physics. As part of an investigation of siloxane copolymers and networks, this laboratory has discovered a simple method to prepare α,ω-dihydroxypoly(dimethylsiloxane) of moderate molecular weight with a very narrow molecular weight distribution. The synthesis involves the size-dependent polycondensation of siloxanediols in the presence of a solid insoluble basic salt.

The pronounced use of relatively monodisperse mixtures began with the demonstration of living polymers by Szwarc and co-workers.[1] In principle, these systems produce a Poisson distribution of homologues.[2] The distribution becomes more narrow as the molecular weight increases by the relationship $\bar{X}_w/\bar{X}_n = 1 (\bar{X}_n - 1)/\bar{X}_n^2$. In practice the observed distribution is often broadened due to side reactions, slow initiation, termination by impurities, multiple active species, and the inherent difficulty of mixing monomer and initiator in a rapidly polymerizing system.[3] This synthetic method is used in the ring-opening polymerization of hexamethylcyclotrisiloxane.[4]

The task of preparing a monodisperse linear homopolymer by a polycondensation is formidable. It has been achieved for siloxane oligomers by laboriously adding one monomer at a time to a polymer.[5] The increase of molecular weight with conversion is that of a chain-growth polymerization where the composition of a reaction mixture is bimodal, containing only monomer and polymer.[6] Functional group reactivity is independent of molecular size in a typical homogeneous step-growth linear polycondensation reaction, and a normal molecular weight distribution is achieved.[7] The distribution becomes broader as the molecular weight increases to a limiting value of 2 as described by the equation $\bar{X}_w/\bar{X}_n = 2 - 1/\bar{X}_n$. For a homogeneous step-growth polymerization, the reactivity of homologues with complementary functionality must be inversely proportional to their degree of polymerization to observe a narrowing of the molecular weight distribution with conversion. Even in the case of copolymerization, or the polymerization of monomers with two or more functional groups with inherently different reactivities, the molecular weight distribution increases with conversion and is significantly narrower than a normal distribution only for very low degrees of polymerization.[8]

In a heterogeneous step-growth polymerization, it is possible to achieve a narrowing of the molecular weight distribution with conversion if the largest homologues are selectively removed from a reactive phase.[9] Conversely, if smaller homologues in the mixture are selectively partitioned into the reactive phase, narrowing of the distribution should occur. Examples where this may have occurred exist in the literature of phase-transfer-catalyzed polycondensation.[10]

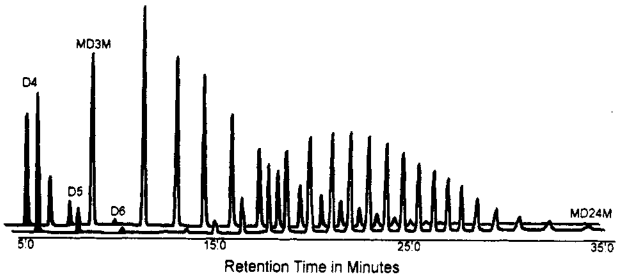


Figure 1. Composite gas chromatographic traces for the *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide-capped α,ω-dihydroxyoligo(dimethylsiloxane) after condensation over coarse CaH_2 at 105 °C for (back) 0 h (diol $\bar{X}_n - 4.4_9$) and (front) 10.5 h (diol $\bar{X}_n = 12.4_3$).

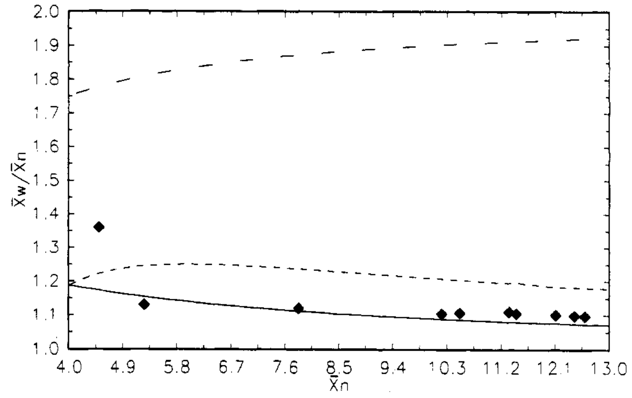
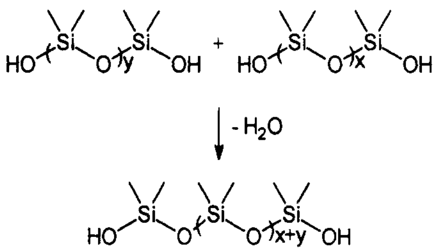
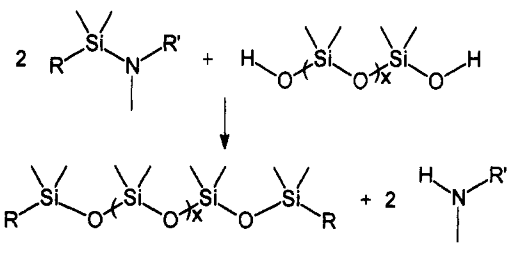


Figure 2. Plot of the dispersity index verses the average degree of polymerization for a size-dependent polycondensation (observed for conditions of Figure 1) (◆), a Poisson distribution for the hypothetical polymerization of silicone (—), an ideal living polymerization of hexamethylcyclotetrasiloxane (- - -), and a normal distribution (– · · · · –).

Scheme I



Scheme II



R = CH₃, R' = C(O)CF₃ R = H, R' = CH₃

The system presently under investigation in our laboratory involved the self-condensation of an α,ω-dihydroxyoligo(dimethylsiloxane) fluid in the presence of a solid base as shown in Scheme I. A polydisperse silanol fluid (Hüls PS340) was used in this study. The fluid was characterized by gas–liquid chromatography immediately after exhaustively end-capping the fluid by the addition of *N*-(trimethylsilyl)-*N*-methyltrifluoroacetamide or (dimethylsilyl)dimethylamine (Scheme II).[11] The average degree of polymerization was determined to be 4.49, and the dispersity was found to be 1.36. Dehydration began upon mixing the fluid with CaH_2 (Fisher) as indicated by the vigorous evolution of gas. Aliquots were removed with time and immediately end-capped and analyzed by gas–

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liquid chromatography (Figure 1).[12] A significant narrowing of molecular weight distribution accompanied the increase of molecular weight (Figure 2). The breadth of the molecular weight distribution was smaller than that of a normal distribution throughout the reaction. The dispersity index, $\bar{X}_w/\bar{X}_n$, quickly became similar to that of the Poisson distribution for the hypothetical living polymerization of silicone, $(CH_3)_2SiO$, and significantly narrower than that for an ideal polymerization of hexamethylcyclotrisiloxane.[13] The reaction was followed until an average degree of polymerization of 13 was achieved.[14]

The narrowing of the distribution with conversion occurred in the presence of CaH_2 or other solid bases.[15] Condensation of the silanols stopped upon removal from the base. The rate at which the condensation occurred depended on the quantity and mesh of the CaH_2 used.[16] Stirring increased the rate of condensation. Heating increased the rate of the condensation yet gave nearly identical molecular weight distributions for equivalent degrees of polymerization.

Another interesting feature of this process is that almost no cyclization occurred.[17] The lack of cyclization contrasts to that of the hydrolytic bulk polycondensation of difunctional dimethylsilanes, in which a significant portion of the resulting mixture consists of cyclocondensation products.[18] Under conditions where redistribution occurs, cyclosiloxanes are formed by backbiting and are a significant portion of the resulting mixture.[19] As in the acid-catalyzed polymerization of hexamethylcyclotrisiloxane, an end-to-end condensation can enhance the proportion of cyclics in the mixture.[20]

End-capping can be carried out with a variety of functionalized silanes in a manner similar to the capping used for the analysis of the fluids. This permits the preparation of a host of telechelic poly(dimethylsiloxanes) with narrow molecular weight distribution.

In conclusion, a size-dependent polycondensation of α,ω-dihydroxyoligo(dimethylsiloxane) has been demonstrated. It suggests that the selectivity for condensation results from the higher affinity of the smallest oligomer for the catalyst surface. This simple process permits the preparation of α,ω-disubstituted poly(dimethylsiloxanes) which exhibit narrower molecular weight distribution than is possible via the living polymerization of hexamethylcyclotrisiloxane for low degrees of polymerization.[21]

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(11) A 0.2-mL aliquot was removed at various times and 0.2 mL (approximately a 2- or 4-fold excess relative to the starting diol using *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide or dimethylsilyldimethylamine, respectively) of the end capping agent, as received from Hüls, was then added via a syringe. The end-capping reaction occurred exothermically, and within 5 min crystals of *N*-methyltrifluoroacetamide formed if the agent was *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide The odor of dimethylamine was obvious immediately upon addition of (dimethylsilyl)dimethylamine. The mixture was immediately analyzed by gas chromatography. Slow redistribution was observed after the addition of *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide.

(12) The relative response factors for pure octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, and octamethyltrisiloxane were determined relative to dodecane and hexamethylcyclotrisiloxane, which was added as an internal standard in some cases to verify that the anticipated mass of siloxanes was observed in a gas chromatographic trace. In these cases, more than 97% of the mass of siloxane fluid could be accounted for by the homologues observed. The relative response factors for the MD_nM homologues were assigned as the following function: response factor $MD_nM = 2.17 + n$. The relative amounts of homologues determined using these factors for low molecular weight poly(dimethylsiloxanes) (degree of polymerization < 3) prepared by the redistribution of octamethylcyclotetrasiloxane with hexamethyldisiloxane agreed well with the normal distributions and the molar ratio of adjacent homologues known to form under these conditions. The molecular weight of dimethylsilane end-capped fluids as determined by gas chromatrography agreed well with the relative areas of the Si–H and $Si-CH_3$ proton signals of 300-MHz ^1H NMR spectra when corrected for the cyclics observed in the gas chromatographic trace.

(13) The distribution of a living polymer is dependent upon the kinetic chain length which is one-third of the number-average degree of polymerization for a hexamethylcyclotrisiloxane polymerization. Reported molecular weight distributions for polymers prepared via the living polymerization of hexamethylcyclotrisiloxane are narrow but generally not as narrow as the theoretical limit for the Poisson distribution. Though the dispersity index is similar to the one expected for a living polymerization, the relative amount of homologues is different. The calculated Poisson distribution for a hexamethylcyclotrisiloxane polymerization of DP 12 contains both lower and higher molecular weight homologues than that observed for the size-dependent polycondensation. However, the weight fraction of the homologue that is nearest the average molecular weight in a Poisson distribution should be greater than that observed for the homologue nearest the average molecular weight homologue in the size-dependent polycondensation.

(14) Homologues through the 26-mer were observable under the conditions of the experiment. At degrees of polymerization of 13 some 25-mer was observed. Distribution for higher degrees of polymerization could exhibit errors because of unobserved higher members of the series.

(15) It is presently not clear that CaH_2 is a catalytic species, as its replacement with $Ca(OH)_2$ gave similar results. Other alkali-earth hydroxides gave similar results. Sodium hydroxide initially narrowed the distribution but quickly caused redistribution and rapid molecular weight build. The use of lithium

hydroxide resulted in a product which suggested no redistribution, but the molecular weight distribution broadened with conversion which began immediately upon mixing. A small amount of cyclics through the nonamer was formed, as would be anticipated if a significant portion of the condensation occurred in a homogeneous phase. After a few minutes in the presence of LiOH the distribution was too broad to analyze all of the homologues by gas chromatography.

(16) That the base truly catalyzed the condensation rather than acting only as a water scavenger was indicated by the lack of any molecular weight build or redistribution when dehydration was promoted by the distillation of water from the system as a toluene azeotrope.

(17) Some cyclic tetramer, pentamer, and hexamer were in the original fluid. Their proportion increased only slightly during the course of the reaction. No larger cyclic oligomers formed.

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(21) It is not clear that this method will give polymers which are more narrow in distribution for high molecular weight polymer. The difference in the relative affinity of the siloxanediols for the surface should decrease as the molecular weight builds. If at some point the surface is efficiently nonselective, a broadening of the molecular weight could commence.