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Notes

Equilibrium Cyclic Compositions in the Preparation of α,ω-Functionalized Poly(dimethylsiloxanes)

M. A. BUESE

General Electric Corporate Research and Development Center, Schenectady, New York 12301.

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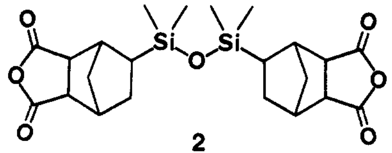
The preparation of block copolymers as materials with unique properties, due to phase separation of the various blocks, has generated increasing interest among polymer chemists.[1] The properties of these copolymers vary with the composition of the blocks. As the composition varies from rich in block A to rich in block B, the morphology of the copolymer changes. Therefore it is desirable to control the block size. Many of these block copolymers are produced by the reaction of an α,ω-functionalized polymer with another monomer or monomers or by the reaction between two or more different α,ω-functionalized polymers. The ability to prepare α,ω-functionalized polymers of predetermined length is very important.

If a soft block with relatively high temperature capabilities is desired, poly(dimethylsiloxane) is often used. Synthesis of α,ω-functionalized poly(dimethylsiloxanes) is often carried out by the equilibration of cyclic oligomers with an α,ω-functionalized dimer or oligomer. Since the reaction produces an equilibrium mixture of cyclic oligomers and linear polymer, the resulting linear polymer has an average molecular weight lower than that calculated from the total dimethylsiloxane repeat units (D units) divided by half of the end groups. Therefore, to determine the appropriate conditions to prepare a particular molecular weight polymer, one needs to know how the equilibrium conditions are defined by the starting conditions.

Although the equilibrium between cyclics and linears has been extensively studied, it has not been presented in a form that allows the synthetic chemist to readily determine the appropriate quantities of D units and end units to give the desired molecular weight of the α,ω-functionalized poly(dimethylsiloxane). This study was conducted to illustrate the dependence of the equilibrium composition on the concentration of D units and the proportion of D units to end groups. A simple expression relating these factors to the average degree of polymerization of the α,ω-functionalized poly(dimethylsiloxane is given. This expression is quite useful when polymers of less than 100 repeat units are desired. This range of molecular weights is used often in the preparation of block copolymers.

Experimental Section

Toluene solutions of octamethylcyclotetrasiloxane (D_4) and hexamethyldisiloxane (1) or 5,5′-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)bis[norborane-2,3-dicarboxylic anhydride] (2) were prepared in 10- or 25-mL volumetric flasks in a drybox and fitted with rubber septa. Trifluoromethanesulfonic acid was injected into the flasks through the septum, with 4 μL delivered into the 10-mL flasks and 10 μL into the 25-mL flasks. The reaction mixtures were kept at room temperature for 3 days[2] and then quenched by the addition of anhydrous MgO. The equilibrated solutions were filtered by using a clean, dry 5-mL syringe equipped with a 0.5-μm Millipore filter. In a 5-mL volumetric flask, 3 mL of the filtered equilibrated solution and a weighed portion of either hexamethylcyclotrisiloxane (D_3) or decamethyltetrasiloxane, depending on the end group, as internal standard were diluted to the mark with toluene. Analysis of the equilibrium cyclic composition was carried out on a Shimadzu GC-9A gas chromatograph with a 6-ft 10% OV101 column. The response of the thermal conductivity detector was observed to be proportional to weight for authentic samples of D_3, D_4, and D_5. This weight response was assumed to hold for all cyclic homologues. Molar concentrations of the cyclics through D_{11} were determined. The toluene was distilled from CaH_2 under a dry nitrogen atmosphere prior to use. Distillation from CaH_2 under nitrogen was used to purify D_4 and 1. The dianhydride 2 was recrystallized three times from toluene and dried for 48 h in a 120 °C vacuum oven.



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Results and Discussion

The treatment of the problem of the distribution of cyclopoly(dimethylsiloxanes) at equilibrium predates the Jacobson–Stockmayer theory[3] with the study by Scott.[4] Applying Flory's statistical mechanical treatment of heterogeneous polymer solutions,[5] Scott derived an expression for the number-average degree of polymerization for an equilibrium mixture of cyclics and linears resulting from the reaction of hexamethyldisiloxane with D_4 in the presence of an acid catalyst. In his treatment he used the following equations to describe the concentration of linear and cyclic species, respectively, where A and p were described as constants for a given equilibrium mixture.

$$[c_y] = Ap^y \tag{1}$$

$$[r_x] = K_x p^x \tag{2}$$

This constant p was used in all subsequent treatments of cyclic equilibria where it was identified as the extent of reaction,[3] the fraction of reacted end groups,[6] the fraction of unreacted end groups,[7] or the extent of reaction of functional groups for the acyclic constituents.[8,9] Thus, the value of p relates directly to the number-average degree of polymerization of the acyclic portion of the mixture.

$$\bar{X}_n = 1/(1 - p) \tag{3}$$

Scott related the cyclic equilibrium constant to the ring size by the expression

$$K_x = ab^x \tag{4}$$

where a and b are constants determined experimentally. This is in contrast to the Jacobson–Stockmayer relationship

$$K_x = a'x^{b'} \tag{5}$$

where a' and b' were derived considering the entropy change for the reaction $c_{x+y} \rightarrow c_y + r_x$, yielding $b' = -^5/_2$.[3] Equation 5 has been supported by the good fit of experimentally determined values of the equilibrium constants for $x > 16$.[9,10] The fit does not extend to the smaller cyclics, which dominate the mixture. The experimentally determined values of K_4 to K_{10} can be fitted equally well to eq 4 and 5. Since the mathematical treatment is simpler, eq 4 shall be used and only the conditions where small errors

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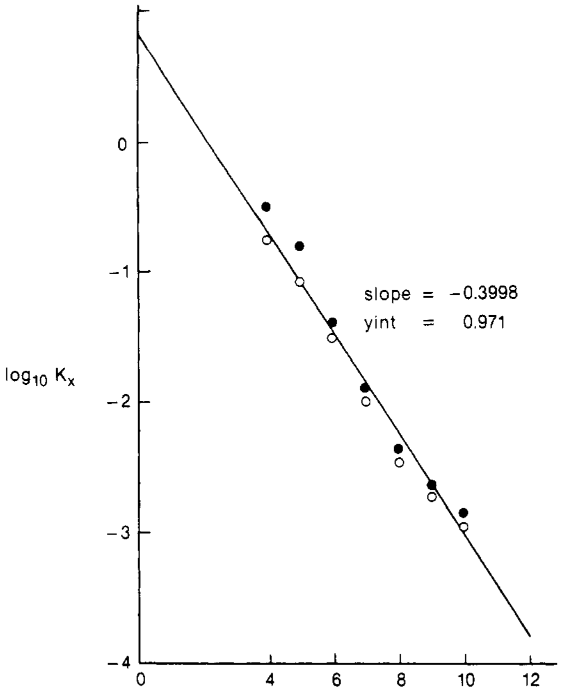

Figure 1. log K_x vs. ring size x: (●) K_x determined in solution;[10] (○) K_x determined in bulk.[9]

are introduced by this relationship will be considered. A plot of log K_x vs. x (Figure 1) yields a = 9.355 and b = 0.398.

As indicated by Scott, the molar concentration of end groups [E] and dimethylsiloxy repeat units [D] may be expressed as a summation of the linear and cyclic species in the equilibrium mixture, with $RSi(CH_3)_2OSi(CH_3)_2R = c_1$.

$$[E] = \sum_{y=1}^{\infty} 2Ap^y = 2Ap/(1-p) \tag{6}$$

$$[D] = \sum_{y=1}^{\infty} (y-1)Ap^x + \sum_{x=4}^{\infty} xab^x p^x = Ap^2/(1-p)^2 + (4ab^4p^4 - 3ab^5p^5)/(1-bp)^2 \tag{7}$$

These equations may be combined to yield the polynomial

$$0 = 6ab^5p^6 - (6ab^5 + 8ab^4)p^5 + 8ab^4p^4 + (Eb^2 + 2Db^2)p^3 - (2Eb + 4Db + 2Db^2)p^2 + (E + 2D + 4Db)p - 2D \tag{8}$$

Since the determination of cyclic siloxanes by gas chromatography is rapid and reasonably accurate (Figure 2), their composition was determined rather than a determination of the molecular weight of the linears. Thus eq 8 was solved for p with a given concentration of [D] and [E]. The resulting value of p was then used to determine the mole fraction of the charged D units which reside in cyclics at equilibrium by the expression

$$\text{mole fraction of D in cyclics} = (4ab^4p^4 - 3ab^5p^5)/(1-bp)^2[D] \tag{9}$$

As seen in Figure 3 the fraction of D units in cyclics determined by GC analysis agrees well with those predicted by eq 9, independently of the end group.[11]

The use of eq 4 to define the cyclic equilibrium constants leads to only small errors in the mole fraction of D units in cyclics for the range of [D]/[E] plotted for Figure 3. As X_n increases, the error introduced by the use of this relationship increases. At X_n = 100, the fraction of D units in D_{12} through D_{200} of all D units in cyclics is 0.144 using the equilibrium constants determined by Brown.[10] Thus the error introduced by the use of eq 4 is less than 14% at X_n = 100. Only at the extreme lower right portion of Figure 3 are the molecular weights of the resulting polymers near this size. For example, with [D] = 12 M and in [D]/[E] = 4.1, the use of Brown's experimental constants through K_{200} would predict that 0.12 of the D units would reside in cyclics rather than the value of 0.11 from Figure 3.

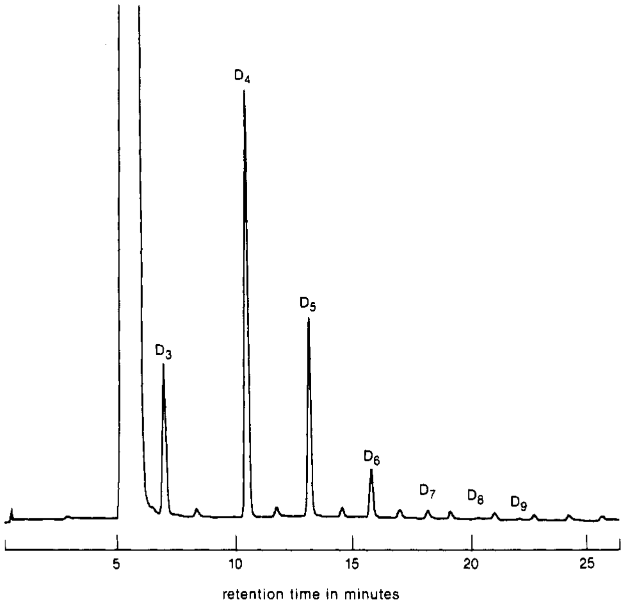

Figure 2. GC trace of the low molecular weight portion of the equilibrium composition resulting from 0.3 M 1 and 0.30 M D_4 with D_3 added as an internal standard.

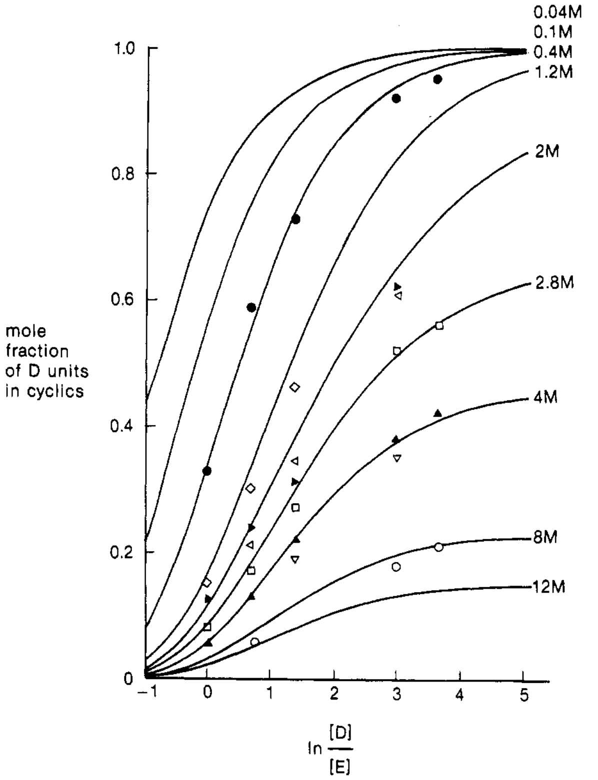

Figure 3. Mole fraction of D units in cyclics for various compositions of D and E. Curves calculated by eq 9. Experimental points are as follows: (●) 0.4 M in D, end group 1; (◇) 1.2 M, 1; (▶) 2.0 M, 1; (◁) 2.0 M, 2; (□) 2.8 M, 1; (▽) 4 M, 1; (▲) 4 M, 2; (○) 8 M, 1.

As seen in Figure 3, the slopes at the inflection point of the curves increase rapidly with decreasing concentration of D, up to [D] = 1 M. Below this concentration, the slopes at the inflection point remain reasonably constant and the curves are displaced to the left. This behavior illustrates the limitations one encounters in preparing an α,ω-functionalized poly(dimethylsiloxane). If the miscibility of the α,ω-functionalized dimer or oligomer in a dimethylsiloxane medium is low, the introduction of a solvent may enhance the incorporation of D units. However, the introduction of solvent will also limit the amount which may be incorporated. Often in these cases the miscibility of the linear species will increase as its molecular weight builds. Therefore removal of the solvent as the reaction progresses will increase the conversion of cyclics to linears. Conversely, if one removes solvent during the polymerization, or before introduction of the catalyst to dry the system, careful control of the final volume must be made if a specific molecular weight is desired. As the size of the end group increases there is a natural dilution for a given [D]/[E] ratio. Particularly, when one tries to incorporate cyclic siloxane into a preformed copolymer, dilution by the end group must be considered.

In conclusion, the relationship between the concentration of end groups and repeat units charged in an equilibration mixture and the resulting composition at equilibrium has been illustrated for the range of $[D]/[E] < 50$. By use of eq 8, a close approximation of the initial conditions necessary to produce a desired equilibrium molecular weight of the linear polymer may be made for $X_n = 100$ or less.

References and Notes

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(10) Brown, J. F., Jr.; Slusarczuk, G. M. J. *J. Am. Chem. Soc.* **1965**, *87*, 931.

(11) Changes in volume due to polymerization were very small. The experimental points were determined for initial concentrations, and calculated lines correspond to the final conditions. The good agreement is expected as the density of low molecular weight silicone fluids does not differ greatly from that of D_4.

Poly(phenylsiloxanes) Electronic Spectra

C. SALOM,[†] A. HORTA,[‡] I. HERNÁNDEZ-FUENTES,[†] and I. F. PIÉROLA*[†]

Departamento de Química-Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 28040, Spain, and Departamento de Química General y Macromoléculas, Facultad de Ciencias, UNED, Madrid 28040, Spain.

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The photophysics of siloxane polymers containing phenyl groups as substituents has not yet been studied, as opposed to the situation with polysilanes and short-chain silanes containing aryl groups whose fluorescence and phosphorescence have been extensively studied.[1-4] The objective of this work is to examine the electronic spectra of methylphenylsiloxane polymers, namely, the homopolymer poly(methylphenylsiloxane) (PMPS) and copolymers of methylphenylsiloxane with dimethylsiloxane (MPS-DMS). The spectroscopic behavior of these polymers is compared with that of polystyrene (PS) because this is a purely organic polymer whose structure is very closely related to that of PMPS and whose photophysics is quite well-known.[5-7]

Experimental Section

The homopolymer sample PMPS was kindly provided by Dow Corning Co. It was fractionated by precipitation at 25 °C in toluene-methanol as solvent-precipitant system. One of the fractions with $M_w/M_n = 1.71$ (as determined by GPC) was selected for the present work. Its M_w measured by light scattering in cyclohexane (Ch) is 1.15×10^5 and its tacticity, determined by ^{1}H NMR, is, in diads, 51% meso and 49% racemic.[8] A description of the PMPS network is in ref 8.

We also examined a monodisperse PS sample from Pressure Chemical Co. with $M_n = 1.11 \times 10^5$ and $M_w/M_n = 1.05$ and an isotactic PS sample with $M_v = 3 \times 10^5$. They were previously purified by precipitation to eliminate monomer impurities.

Three copolymers of MPS and DMS have been employed in this work. The samples called copolymer 8240 (molar fraction of methylphenylsiloxane $x_{MP} = 0.095$) and copolymer 8241 ($x_{MP} = 0.543$) were provided by Polysciences Ltd, and sample copolymer 710 ($x_{MP} = 0.663$) was provided by Siliconas Hispania S.A. The three samples are fluid, and their molecular weights are M_n = 6400, 4200, and 2500, respectively.

Solvents used, cyclohexane (Ch) and dioxane, were from Carlo Erba and of RS quality, special for fluorescence.

Emission spectra were recorded on a Perkin-Elmer LS-3 spectrofluorometer. Front-face excitation was employed for solid samples and transmission spectra for dilute solutions. Absorption spectra were measured on a Perkin-Elmer 560 UV-vis spectrometer.

Results and Discussion

Absorption spectra of PMPS and copolymers in dilute Ch solutions resemble those of PS ($\lambda_{max} \simeq 260$ nm) and have practically the same extinction coefficient ($\epsilon_{PMPS} = 247$ L mol^{-1} cm^{-1} vs. $\epsilon_{PS} = 193$ L mol^{-1} cm^{-1}). A hyperchromic effect and red shift have been observed for polysilanes containing phenyl[2] and naphthyl[1] groups. They have been explained by an increased conjugative interaction between the $2p\pi$ orbital of the aromatic ring and the $3d\pi$ orbital of the silicon backbone. None of these effects are observed in our samples, which have a different electronic and geometric structure in their molecular skeleton.

Figure 1 shows the emission spectra of PMPS and copolymers in a very dilute Ch solution (chromophore concentration 5.0×10^{-3} M in all cases). It can be observed that the spectra show two bands with monomer emission centered around 285 nm and excimer emission around 325 nm. The excimer-to-monomer intensity ratio increases with the methyl phenyl content in the polymer chain as expected for intramolecular excimers. The fluorescence spectra of naphthyl polysilanes have also been shown to consist of monomer and excimer bands.[1] Emissions from a dimer state[1] stabilized at low temperatures and from a charge-transfer complex with a planar aryl-Si-Si configuration[3] have also been considered for polysilanes, but they have not been clearly established.

PMPS has a larger efficiency of excimer formation than PS: e.g., in dioxane solutions 5×10^{-3} M after N_2 bubbling, the ratio I_E/I_M is 2.3 for PS and 3.8 for PMPS. A similar result was found for poly(α-methylstyrene) (PαMS) with respect to PS.[9,10] PαMS exhibits a larger distance between

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[†] Departamento de Química-Física, Universidad Complutense.

[‡] Departamento de Química General y Macromoléculas, UNED.