

Polymer Communication

Preparation of poly(diethylsiloxane) with the NaOH/12-crown-4 catalyst

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Received 20 September 1999; received in revised form 17 December 1999; accepted 4 February 2000

Abstract

A new technique for the preparation of poly(diethylsiloxane) (PDES) is described. The monomer hexaethylcyclotrisiloxane is polymerized with NaOH as a catalyst in the presence of the promoter 12-crown-4 (1,4,7,10 tetraoxacyclododecane). The effects of NaOH concentration, 12-crown-4 concentration, and polymerization time on the molecular weight distribution are reported. A mechanism for the polymerization is proposed based on current knowledge of anionic ring-opening polymerization of cyclic siloxanes. The advantages and disadvantages of this synthesis relative to previously published PDES syntheses are discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(diethylsiloxane) synthesis; NaOH catalyst; Crown ether

1. Introduction

Poly(diethylsiloxane) (PDES) is a flexible-chain polymer which exhibits a complex phase behavior. PDES of relatively high molecular weight exhibits two or more crystalline phases at lower temperatures and a mesophase near room temperature [1–12]. Cross-linked films of PDES show complex phase behavior at low temperature and can also undergo an amorphous-to-mesophase transition under uniaxial tension [13–15].

In order to study the properties of the mesophase, it is necessary to have PDES macromolecules above a critical length. The mesophase can only be observed in melts with an average molecular weight of about 30,000 g/mol or higher [12]. The synthesis of PDES above this critical molecular weight is therefore necessary in order to study the properties of the mesophase.

There are already techniques available for producing PDES of high molecular weight, each with some limitations. The monomer hexaethylcyclotrisiloxane (hereafter abbreviated D_3Et_6) is the starting material for several techniques due to its high reactivity toward ionic catalysts.

D_3Et_6 monomer may undergo anionic polymerization in the presence of various alkylolithium initiators and the promoter cryptand [2.1.1] [12,15]. This technique can lead to PDES of high molecular weight and a narrow molecular weight distribution. However, this polymerization requires

conditions of stringent purity and high-vacuum break-seal equipment due to its extreme sensitivity toward water and other impurities. Also, the cryptand [2.1.1] ligand is expensive and difficult to purify.

Another technique for polymerization of D_3Et_6 is high temperature (approx. 150°C) bulk polymerization with KOH as a catalyst. This technique can lead to a strongly bimodal molecular mass distribution. There is also evidence (from an analogous poly(dimethylsiloxane) synthesis) that this type of polymerization leads to branched chains [16], especially at higher KOH concentrations. Whereas KOH-catalyzed polymerization is a very simple method of preparing PDES, it is not suitable for studies or applications where well-characterized, linear PDES is desired.

We have developed a new technique for preparing PDES of molecular weight up to 146,000 g/mol from the D_3Et_6 monomer. The monomer is polymerized with excess NaOH as a catalyst, and 12-crown-4 as a promoter. This technique does not require an elaborate apparatus, and the polymerization proceeds smoothly at room temperature. The molecular mass distribution obtained is reasonably narrow ($1.3 < M_w/M_n < 1.9$) and is unimodal. In this paper, we present the details of the synthesis and discuss the advantages and limitations of the technique.

2. Experimental

2.1. Materials

Hexaethylcyclotrisiloxane monomer was prepared as

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Table 1
Variation of NaOH concentration (polymerization time = 20.5 h; 0.411 g 12-crown-4/3 g monomer)

Batch	NaOH Conc. g NaOH/3 g mon.	M_w	M_w/M_n	Yield (%)
PDES-A	0.1	58,000	1.91	37
PDES-B	0.5	73,000	1.73	44
PDES-C	1.0	70,000	1.73	40

previously described [17], and was distilled over freshly ground calcium hydride powder shortly before the polymerization. The monomer was found to be of near 100% purity by gas chromatography.

Sodium hydroxide (electronics grade, 99.9%+) and 12-crown-4 (98%) were purchased from Aldrich. Toluene and methanol (HPLC grade) were obtained from Mallinckrodt. These materials were used as received.

2.2. Polymerization procedure

The polymerizations described here were conducted at 23°C. 3.0 g of D_3Et_6 monomer was placed in a 25 ml round-bottom flask equipped with a magnetic spin bar. The promoter 12-crown-4 was added in the desired quantity, and the mixture was homogenized by stirring for 5 min. Sodium hydroxide was quickly ground into a fine powder using a mortar and pestle. It was not necessary to grind the hygroscopic NaOH under a dry atmosphere as long as the grinding was done quickly. The polymerization can tolerate trace amounts of water without adverse effects. An appropriate amount of the NaOH powder (see quantities in Tables) was added to the polymerization flask and quickly stirred into the monomer. Much of the NaOH was dissolved into the monomer/crown mixture, with excess NaOH sinking to the bottom in some cases. The flask was sealed with a rubber septum. In some of the trials, the stirring ceased when the viscosity became too high for the spin bar to turn. A polymerization time between 6 min and seven days was examined to study its effect on the molecular weight obtained.

2.3. Termination and washing

The polymerization mixture was dissolved in 10–15 ml toluene to reduce the viscosity. The solution was decanted from the excess NaOH into a separatory funnel containing about 20 ml deionized water. The two-phase mixture was

Table 2
Variation of 12-crown-4 concentration (polymerization time = 20.5 h; 1.0 g NaOH/3 g monomer)

Batch	Crown conc. g crown/3 g monomer	M_w	M_w/M_n	Yield (%)
PDES-D	0.290	14,000	1.53	42
PDES-C	0.411	70,000	1.73	40
PDES-E	0.822	61,000	1.80	28

shaken vigorously for a few minutes to neutralize the chain ends and remove the NaOH/crown complex. The wastewater was discarded, and the water washing was repeated for three more times. This procedure is expected to yield chains that are primarily Si–OH endcapped.

The organic (top) layer was retained, and the polymer was precipitated from its toluene solution by adding about 15 ml methanol. The top layer was discarded, and the polymer layer was washed three more times with 15 ml methanol to remove most of the toluene. The toluene/methanol precipitation procedure also removed most of the oligomeric byproducts. The polymer was then dried for 24 h at 60°C in a vacuum oven. The yield of PDES based on monomer weight is about 40–45% under optimum conditions.

2.4. Molecular weight determination

Polymer fractions were analyzed by gel permeation chromatography (GPC) in order to determine the polystyrene-equivalent number average and weight average molecular weights. The GPC consisted of a Waters Model 6000A solvent delivery system, two Waters Ultra-Styrigel columns (10^4 and 10^5 Å pore sizes), and a Waters model R401 refractive index detector. Calibration was conducted with polystyrene standards from Scientific Polymer Products, Inc. Polystyrene-equivalent molecular weights are reported throughout this study. The PDES chains were assumed to be linear.

3. Results and discussion

The effects of reaction conditions on polymer yield and molecular weights were investigated. The variables studied were NaOH concentration, 12-crown-4 concentration, and polymerization time. The temperature was kept constant at 23°C to avoid the side reactions that can occur in high-temperature siloxane polymerizations. For example, chain branching has been documented in high-temperature PDMS polymerizations, especially when the concentration of the metal counter-ion (K^+) was high [16].

3.1. NaOH concentration

The effects of bulk NaOH concentration can be seen from the data in Table 1. At high NaOH loadings, the molecular weight distribution is independent of the amount of NaOH added. Increasing the NaOH concentration from 0.5 g NaOH/3 g monomer (PDES-B) to 1.0 g NaOH/3 g monomer (PDES-C) resulted in no significant change in the molecular weight distribution or yield. There is likely a limiting solubility of the Na^+ ion in the polymerization mixture that has been reached in both of these experiments. As the concentration of NaOH is lowered (PDES-A), the molecular weight obtained at 20.5 h. decreases. At NaOH concentrations much lower than that reported for PDES-A, no polymer was formed on the time scale of these experiments. In

Table 3
Effects of polymerization time

Batch	Polymerization time	M_w	M_w/M_n	Yield (%)
PDES-F	6 min.	6000	1.27	41
PDES-G	3 h	15,500	1.46	43
PDES-C	20.5 h	70,000	1.73	40
PDES-H	168 h	146,000	1.57	36

contrast to many anionic polymerizations, decreasing the initiator concentration does not lead to longer chains in this system.

3.2. 12-crown-4 concentration

Several experiments were conducted with different concentrations of the promoter, 12-crown-4 (Table 2). The NaOH concentration (1.0 g NaOH/3 g monomer) and polymerization time (20.5 h) were fixed for this set of experiments. Low concentrations of the crown ether (0.290 g crown/3 g monomer) produce PDES of relatively low molecular weight (PDES-D). A 12-crown-4 concentration of 0.411 g crown/3 g monomer (PDES-C) produced PDES of higher molecular weight under these conditions. However, raising the concentration to 0.822 g crown/3 g monomer (PDES-E) resulted in a substantial decrease in yield and a slight reduction of molecular weight under these reaction conditions.

Raising the crown ether concentration past a certain level is detrimental to the formation of linear chains. If there are already enough crown molecules present to promote polymerization effectively, then raising the crown ether concentration only serves to dilute the concentrations of total siloxanes. In siloxane polymerizations where a typical ring-chain equilibrium may be present, the usual effect of dilution is to lower the yield of polymer and favor cyclic byproducts [18,19].

3.3. Polymerization time

The polymerization time was found to be the most convenient means of controlling the molecular weight distribution. The molecular weights of some samples are listed in Table 3 as a function of polymerization time.

Stopping the reaction after 6 min results in a reasonable yield (41%) of short chains with a narrow molecular mass distribution ($M_w/M_n = 1.27$). As polymerization time proceeds, the molecular weight gradually increases, and the distribution of chain sizes broadens. The largest molecular weight we have obtained is $M_w = 146,000$ g/mol after a polymerization time of about one-week. Fig. 1 shows the molecular weight distribution obtained from GPC traces of the samples in Table 3.

3.4. Comments on the polymerization mechanism

In this section, we analyze some features of this polymerization in the context of the current understanding of siloxane polymerizations. We propose a mechanism based on a general model of anionic ring-opening polymerization in siloxanes [18].

3.4.1. Initiation

Initiation takes place by reaction of NaOH with the monomer. The crown ether may increase the solubility of the NaOH in the siloxane monomer.

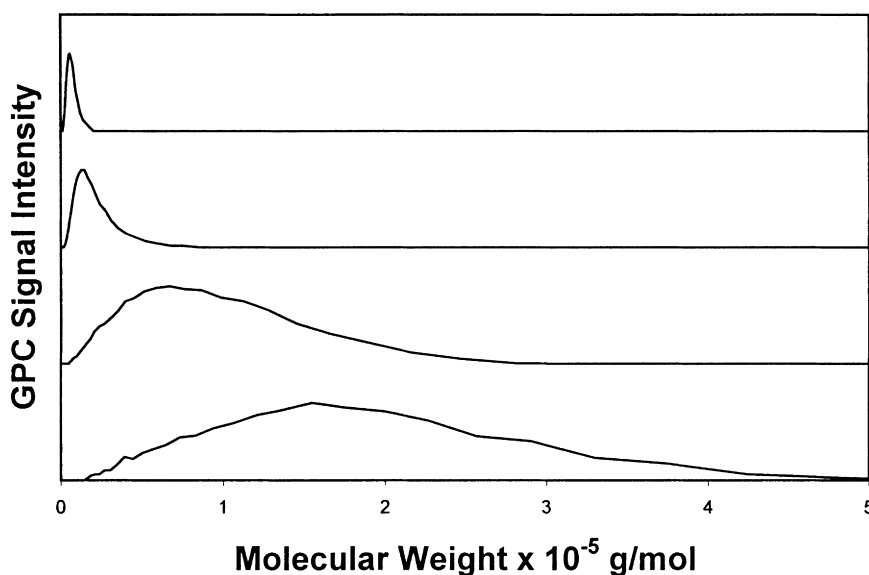
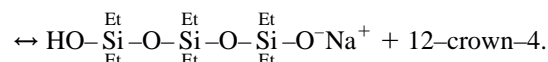
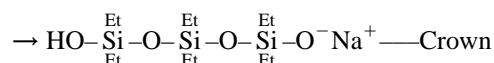
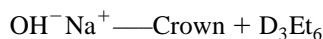


Fig. 1. Molecular weight distributions as a function of polymerization time from GPC traces of the samples listed in Table 3.

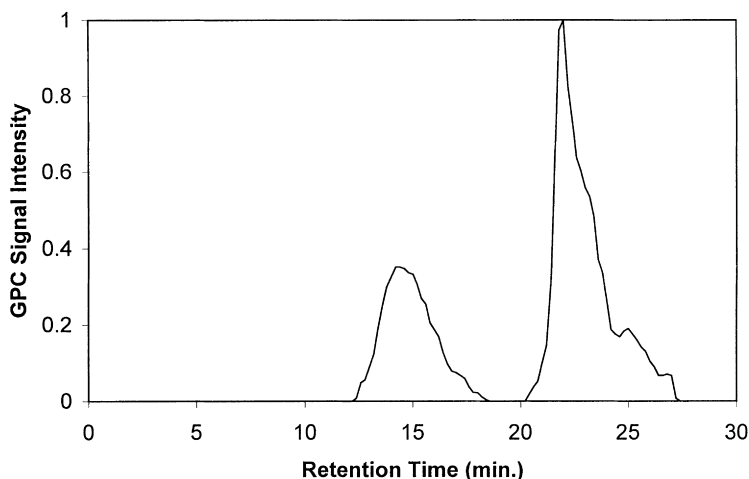


Fig. 2. Gel permeation chromatograph showing low-molecular-weight byproducts.

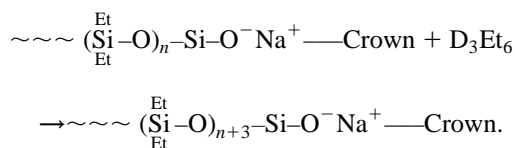
3.4.2. Propagation

In many anionic siloxane polymerizations, the ion pairs at the chain ends are able to aggregate into clusters or complexes [20–22]. The chain ends may exist either as: (a) single ion pairs complexed with one or more promoter molecules, or (b) aggregates of ion pairs. Polymerization takes place only at the single ion pairs. This problem can often be overcome by addition of a “promoter” molecule that disrupts formation of ion clusters. Previous researchers have used tetrahydrofuran [22–28], dimethylsulfoxide [29–32], diglyme [33], and other solvents [18] as promoters for producing various polysiloxanes. The promoter molecule is usually able to associate with the metal counter-ion, which increases the amount of single ion pairs present.

We believe that the presence of the crown ether promotes the formation of single ion pairs in this polymerization. This idea is based on the observation that no polymerization will take place (at this temperature) in the absence of the crown ether.

Propagation takes place by addition of a monomer unit to a free ion pair (growing chain end) in the presence of one or more crown ether molecules.

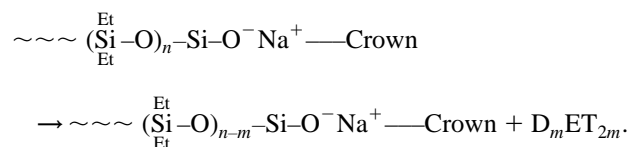
Propagation at a free (non-aggregated) chain end:



3.4.3. Depolymerization and chain scrambling

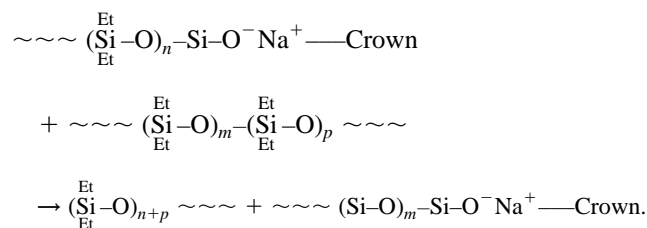
We also expect that this system is able to generate cyclic byproducts by depolymerization, as is often the case with siloxane polymerizations [18]. These cyclic molecules have the structure D_4Et_8 , D_5Et_{10} , D_6Et_{12} , etc. In the depolymerization process, the growing end of a chain-reacts with the

backbone of the same chain, producing a cyclic molecule:



The presence of cyclic byproducts would explain why the polymer yield is typically below 50%. Fig. 2 shows a gel permeation chromatograph of a PDES sample showing the byproducts after 47 h of polymerization. (This sample was washed with water to remove most of the 12-crown-4 and NaOH, but was not precipitated from toluene with methanol.) The peak at higher retention time represents some low molecular weight material. This peak has a retention time approximately the same as the D_3Et_6 monomer, but is much broader, indicating that it may be a group of several different compounds. We did not confirm the identity of the byproducts by other methods, since we were only interested in the polymeric products. However, since ring–chain equilibria are present in many siloxane polymerizations, it is probably a good assumption that these byproducts are indeed cyclics.

Other side reactions that may be present are the so-called “chain scrambling” processes. In these reactions, a growing chain end reacts with the Si–O backbone of another chain, transferring the ion pair to the other chain:



The polymerization/depolymerization and chain scrambling processes may explain the mechanism for formation of long PDES chains. Looking at the data in Table 3, one can see that much of the monomer has already been converted to

very short chains after 6 min of polymerization. Therefore, monomer addition alone cannot be responsible for the formation of long PDES chains. The combination of chains by chain scrambling and the depolymerization/polymerization processes must favor an equilibrium state where long linear species form a significant fraction of the material. In this case, one would expect that the value of M_w/M_n would approach 2.0 at long times [23]. In our long-time polymerizations reported here, M_w/M_n was usually slightly less than 2.0. We expect that this slight narrowing of the molecular weight distribution is actually due to the washing procedure used. The toluene/methanol precipitations are basically crude fractionations that remove some of the short polymer chains along with the byproducts.

4. Conclusions

The NaOH/12-crown-4 catalyst provides a relatively straightforward method for the synthesis of PDES. Although it cannot produce PDES with polydispersities as low as those obtained with the Li + /cryptand [2.1.1] synthesis [12,15], this method offers simplicity and lower cost due to its less stringent requirements of purity. The method described here is probably a better choice than the KOH catalyst if a unimodal molecular mass distribution is desirable. The most obvious disadvantage of this technique is that the polymer yield is only about 40–45% under optimum conditions.

Acknowledgements

This work was supported by NSF Polymers Program, grant DMR-9706066.

References

- [1] Lee CL, Johansson OK, Flanigan OL, Hahn P. ACS Polym Prepr 1969;10(2):1319–26.
- [2] Beatty CL, Pochan JM, Froix MF, Hinman DD. Macromolecules 1975;8(4):547–51.
- [3] Froix MF, Beatty CL, Pochan JM, Hinman DD. J Polym Sci: Polym Phys 1975;13:1269–74.
- [4] Beatty CL, Karasz FE. J Polym Sci: Polym Phys 1975;13:971–5.
- [5] Pochan JM, Beatty CL, Hinman DD. J Polym Sci: Polym Phys 1975;13:977–83.
- [6] Papkov VS, Godovsky YK, Svistunov VS, Litinov VM, Zhdanov A. J Polym Sci: Polym Phys 1984;22:3617–32.
- [7] Tsvankin DY, Papkov VS, Zhukov VP, Godovsky YK, Svistunov VS, Zhdanov AA. J Polym Sci: Polym Phys 1985;23:1043–56.
- [8] Godovsky YK, Papkov VS. Macromol Chem: Macromol Symp 1986;4:71–87.
- [9] Pochan JM, Hinman DD, Froix MF. Macromolecules 1976;9(4):611–6.
- [10] Wiedemann HG, Wunderlich B, Wesson JP. Mol Cryst Liq Cryst 1988;155:469–75.
- [11] Kögler G, Loufakis K, Möller M. Polymer 1990;31:1538–45.
- [12] Molenberg A, Möller M. Macromolecules 1997;30:8332–7.
- [13] Zhdanov AA. Polym Sci USSR 1989;31(8):1729–37.
- [14] Godovsky YK. Angew Makromol Chem 1992;202/203:187–212.
- [15] Out G, Turetskii A, Snijder M, Möller M, Papkov VS. Polymer 1995;36(16):3213–21.
- [16] Kucera M. J Polym Sci 1962;58:1263–81.
- [17] Out G, Klok H, Möller M, Oelfin D. Macromol Chem:Phys 1995;196:195–210.
- [18] Chojnowski J. In: Clarson SJ, Semlyen JA, editors. Siloxane polymers, Chichester, New York: Ellis Horwood–PTR Prentice Hall, 1993 (chap. 1).
- [19] Semlyen JA. Cyclic polymers. Amsterdam: Elsevier, 1986 (p. 1).
- [20] Chojnowski J, Mazurek M. Makromol Chem 1975;176:2999–3023.
- [21] Gladkova NK, Durgaryan SG, Nametin NS. Dokl Akad Nauk SSSR 1979;244:86–88.
- [22] Wilczek L, Kennedy JP. Polym J 1987;19:531–8.
- [23] Bajaj P, Varshney SK, Misra A. J Polym Sci: Polym Chem 1980;18:295–309.
- [24] Kawakami Y, Miki Y, Tsuda T, Murthy RAN, Yamashita Y. Polym J 1982;14:913–7.
- [25] Zilliox JG, Roovers JEL, Bywater S. Macromolecules 1975;8:573–8.
- [26] Bostick E. ACS Polym Prepr 1969;10:877–84.
- [27] Gnanou Y, Rempp P. Makromol Chem 1988;189:1997–2005.
- [28] Kawakami Y, Murthy RAN, Yamashita Y. Makromol Chem 1984;185:9–18.
- [29] Veith CA, Cohen RE. J Polym Sci: Polym Chem 1989;27:1241–58.
- [30] Lee CL, Frye CL, Johansson OK. ACS Polym Prepr 1969;10(2):1361–7.
- [31] Lee CL, Johansson OK. J Polym Sci: Polym Chem 1976;14:729–42.
- [32] Suzuki T. Polymer 1989;30:333–7.
- [33] Clarson SJ, Semlyen JA. Polymer 1986;27:1633–6.