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Silyl sulfonate approach to the synthesis of a block copolydimethylsiloxane-polydioxepane

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ABSTRACT

Block copolydioxepane-polydimethylsiloxane has been synthesized by the "silyl sulfonate approach." The nucleophilic macromer, lithium polydimethylsiloxane, was reacted with chlorodimethylsilane or allylchlorodimethylsilane to produce the corresponding macromers with a labile substituent, namely an allyl or a hydride, on silicon. These macromers were then converted to the electrophilic polydimethylsiloxane arylsulfonates, which initiated the cationic polymerization of 1,3-dioxepane to yield block polydimethylsiloxane-polydioxepane in the presence of 2,6-di-t-butylpyridine.

INTRODUCTION

We have been interested in the study of a new type of electrophilic initiator, i.e. trialkylsilyl esters, to polymerize electron-rich monomers such as 1,3-dioxepane. In an exploratory survey, we showed that trimethylsilyl triflate readily polymerized oxacyclic monomers.[1,2] However, the silyl triflate was too reactive and molecular weight control was not achieved. Subsequently, we found that the less reactive trialkylsilyl methanesulfonate is able to initiate dioxepane polymerization in the presence of hindered base.[3]

The aim of this study was to use a silyl ester macromer to synthesize a block copolymer of polydioxepane (polyDOX) and poly-dimethylsiloxane (poly DMS). The main problem in the synthesis of a block copoly-DMS/poly-DOX is that the best controlled polymerizations of cyclosiloxanes proceed anionically, while 1,3-dioxepane can only be polymerized with cationic initiators. Therefore, we had to design a system to convert the anionic end of living polysiloxane into an electrophilic center, namely a silyl methanesulfonate end group.

RESULTS

Model Study

We attempted to convert a nucleophilic SiO^- end group to the electrophilic $SiOSO_2R$ end group directly by reaction with sulfonic anhydrides or sulfonyl chlorides, but were unsuccessful. The formed silylsulfonate reacted too rapidly with remaining silanolate ends. Therefore, two alternative synthesis routes were explored: via hydrosiloxane or via allylsiloxane.

Via Silicon Hydride Ends

Lithium trimethylsilanolate, a model for the living polysiloxane macromonomer with SiO^- end group, was prepared by reaction of excess hexamethyldisiloxane with n-butyllithium, according to the method of Seyferth and Alleston.[4] Excess Me_2SiHCl was added to this solution at -70°C, which yielded the desired hydrosiloxane, $Me_3SiOSiMe_2H$, in 86% yield.

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$$Me_3SiOLi + Me_2SiHCl \xrightarrow[-LiCl]{} Me_3SiOSiMe_2H$$

$$Me_3SiOSiMe_2H + MeSO_3H \xrightarrow[-H_2]{\text{toluene, } 0^\circ} Me_3SiOSiMe_2OSO_2Me$$

If the reaction of Me_3SiOLi with Me_2SiHCl was run at relative high temperature, some hydride displacement occurred, even though chloride is a better leaving group than hydride, and octamethyltrisiloxane was formed in two consecutive reactions.

$$Me_3SiOSiMe_2Cl + Me_3SiOLi \xrightarrow[-LiCl]{} Me_3SiOSiMe_2OSiMe_3$$

To avoid the formation of this byproduct, slowly adding Me_3SiOLi into Me_2SiHCl at low temperature, vigorous stirring and a nonpolar solvent were necessary.

The labile hydride of $Me_3SiOSiMe_2H$ was next replaced by a sulfonate function by CH_3SO_3H. Hydrogen evolution was quite slow. When 2% of Pd-C was added to the solution, the reaction was rapid, and 86% yield was achieved. However, $Me_3SiOSiMe_2H$ and $MeSO_3H$ were not miscible in high concentration. Therefore, benzene-, p-toluene- and t-butylbenzenesulfonic acids were studied. The t-butylphenylsulfonic acid gave the highest yield, probably because of improved miscibility.

Via Allylsilane Ends

Allyldimethylchlorosilane was prepared from the reaction of dichlorodimethylsilane with one equivalent of allyl magnesium bisinide an was then added to a solution of Me_3SiOLi, leading to $Me_3SiOSiMe_2CH_2CH{=}CH_2$ (88% yield). The allyl substituent was then replaced by sulfonate group[5] by reaction with CH_3SO_3H. The allyl cleavage reaction was slow at 0°C, but could be accelerated with the addition of small amounts of CF_3SO_3H (96% yield after six hours).

$$CH_2{=}CHCH_2MgBr + Me_2SiCl_2 \xrightarrow[-MgBrCl]{THF} Me_2ClSiCH_2CH{=}CH_2$$

$$Me_3SiOLi + Me_2SiClCH_2CH{=}CH_2 \xrightarrow[-LiCl]{} Me_3SiOSiMe_2CH_2CH{=}CH_2$$

$$Me_3SiOSiMe_2CH_2CH{=}CH_2 + CH_3SO_3H \xrightarrow[-C_3H_6]{} Me_3SiOSiMe_2OSO_2CH_3$$

Synthesis of Oligomeric Functionalized Polysiloxane

On the basis of these model reactions, we could now turn to the synthesis of oligomeric siloxane initiators.

Anionic ring-opening polymerization of cyclotrisiloxane (D_3).

This polymerization was carried out according to the literature.[6,7] After quenching living oligomer 1 with Me_3SiCl, terminated polymer 2 was subjected to SEC analysis, to show that molecular weight control was obtained (Table 1).

$$nBuLi + m\ D_3 \longrightarrow Bu(SiMe_2O)_nSiMe_2O^-\ Li^+$$

(m=n+1) 1

$$Bu(SiMe_2O)_nSiMe_2O^-\ Li^+ + Me_3SiCl \xrightarrow[-LiCl]{} Bu(SiMe_2O)_{n+1}SiMe_3$$

1 2

Synthesis of polysiloxane sulfonate through hydride-terminated polysiloxane.

Adding living siloxane oligomer 1 into excess Me_2SiHCl yielded hydropolysiloxane 3, identified by NMR. Hydride-terminated polysiloxane 3 was then reacted with methanesulfonic acid in the presence of Pd-C, yielding polysiloxane methanesulfonate 4. Again, t-butylbenzenesulfonic acid gave better results than methanesulfonic acid because of greater miscibility with 3.

$$Bu(SiMe_2O)_nSiMe_2OLi + Me_2SiHCl \xrightarrow[-LiCl]{} Bu(SiMe_2O)_{n+1}SiMe_2H$$

1 3

$$Bu(SiMe_2O)_{n+1}\ SiMe_2H + CH_3SO_3H \xrightarrow[-H_2]{\text{Pd-C, toluene, } 0^\circ} Bu(SiMe_2O)_{n+2}\ SO_2CH_3$$

3 4

$$Bu(SiMe_2O)_{n+1}SiMe_2H + t\text{-}C_4H_9C_6H_4SO_3H \xrightarrow[-H_2]{\text{Pd-C, } 0^\circ} Bu(SiMe_2O)_{n+2}SO_2C_6H_4\text{-}t\text{-}Bu$$

3 5

To investigate if the polysiloxane backbone was left intact in the presence of t-butylbenzenesulfonic acid, polysiloxane sulfonate 5 was quenched with an equivalent amount of nBuLi and subjected to SEC analysis.

$$nBu(SiMe_2O)_{n+2}SO_2\ C_6H_4\text{-}t\text{-}Bu + BuLi \xrightarrow[-tBuC_6H_4SO_3Li]{} Bu(SiMe_2O)_{n+1}SiMe_2Bu$$

5 6

The molecular weight distribution of oligomer 6 is somewhat broader than of 2 (Table 1).

Synthesis of polysiloxane sulfonate through allyl-terminated polysiloxane

Adding siloxane oligomer 1 with a lithium silanolate end group into excess allyldimethylchlorosilane led to polysiloxane 7 with an allyl substituent on the terminal Si. Oligomer 7 was identified by ^1H NMR spectra and the yield, calculated from NMR, was 92%. Allyl-terminated polysiloxane 7

was then reacted with t-butylbenzenesulfonic acid at room temperature for two days, yielding polysiloxane t-butylbenzenesulfonate 5 in 90% yield. To see if there was any influence of acid on the polysiloxane's backbone, polysiloxane sulfonate 5 was also quenched by the addition of BuLi.

$$\underset{1}{Bu(SiMe_2O)_nSiMe_2O^-\ Li^+} + Me_2SiClCH_2CH{=}CH_2 \xrightarrow[-LiCl]{\text{excess}} \underset{7}{Bu(SiMe_2O)_{n+1}SiMe_2CH_2CH{=}CH_2}$$

$$\underset{7}{Bu(SiMe_2O)_{n+1}SiMe_2CH_2CH{=}CH_2} + t\text{-}BuC_6H_4SO_3H \xrightarrow[-C_3H_6]{} \underset{5}{Bu(SiMe_2O)_{n+2}SO_2C_6H_4\text{-}tBu}$$

$$\underset{5}{Bu(SiMe_2O)_{n+2}SO_2C_6H_4t\text{-}Bu} + BuLi \xrightarrow[-tBuC_6H_4SO_3Li]{} \underset{8}{Bu(SiMe_2O)_{n+1}SiMe_2Bu}$$

Oligomer 8 was then subjected to SEC analysis. The molecular weight distribution of oligomer 8 is broader than that of oligomer 2 (Table 1).

The Preparation of Block Copolydimethylsiloxane-Polydioxepane

The electrophilic polysiloxane arylsulfonate 5 (Mn = 1349) was treated with a hindered pyridine (2,6-di-t-butylpyridine) to remove unreacted t-butylbenzenesulfonic acid. 1,3-Dioxepane was then added to the dichloroethane solution. Because polysiloxane arylsulfonate 5 is not miscible with 1,3-dioxepane in high concentration, the reaction was done in quite low concentration in 1,2-dichloroethane: [polysiloxane arylsulfonate]=0.05M, [1,3-dioxepane]=0.1M. The solution was kept at 0°C and stirred occasionally for four days.

$$\underset{5}{Bu(SiMe_2O)_{n+2}SO_2C_6H_4t\text{-}Bu} + m\ 1,3\text{-dioxepane} \xrightarrow[0°C,\ 4\ days]{CH_2ClCH_2Cl} nBu(SiMe_2O)_{n+1}SiMe_2[O(CH_2)_4OCH_2]_mOSO_2\ C_6H_4t\text{-}Bu$$

The copolymer mixture was precipitated in methanol. This precipitate was then extracted several times with a mixture of methanol and chloroform. The purification was repeated until the integration ratio in the ^1H NMR spectrum of dioxepane to siloxane did not change. The yield was 21%. The copolymer was analyzed by SEC (Table 1).

When we tried to synthesize a copolymer containing polysiloxane of higher molecular weight (Mn=5,000), the immiscibility of polysiloxane and dioxepane was quite difficult to overcome. Even at a concentration of polysiloxane sulfonate of 0.02M, the mixture was still heterogeneous. Various solvents were tried, such as toluene, n-hexane and acetonitrile, but the results were not satisfactory.

Table 1. Molecular Weight Determinations

Compound	Mw	Mn	Mw/Mn	Wt% of dioxepane
2	1900	1583	1.2	0
6	1890	1349	1.40	0
8	1760	1165	1.51	0
copolymer	4545	2389	2.10	52%

DISCUSSION

We have successfully converted the anionic nucleophilic living end of polydimethylsiloxane to an electrophilic silylsulfonate end by either of two processes. The cleavages of hydrogen or allyl from silicon gave comparable good results.

The reaction of the -$SiMe_2H$ end group with CF_3SO_3H was rapid and high yield was obtained. However, using the relatively weaker acid, CH_3SO_3H, in this reaction was rather slow. Pd-C catalysis of the SiH cleavage was very effective. The mechanism of the Pd-C catalyst is not very clear.

The replacement reaction of allyl by a sulfonate function was quite rapid when a trace of CF_3SO_3H was used as catalyst. Without CF_3SO_3H, the reaction rate was relatively slow, despite the β-silyl effect[8,9,10] and the strong driving force of the loss of propene.

The molecular weight distributions became broader in the reactions of allyl polysiloxane or hydride-terminated polysiloxane with arylsulfonic acid. Some arylsulfonic acid cleaved the backbone of polysiloxane. Shorter reaction time may lessen this problem by adding a trace of CF_3SO_3H as catalyst, but we did not explore this reaction, because of the strong acidity of CF_3SO_3H. Polysiloxane arylsulfonate is very hygroscopic. If we failed to carefully dry or did not add hindered base, we only obtained homopolymer of DOX.

Because polysiloxane arylsulfonate is immiscible with 1,3-dioxepane in bulk as well as in concentrated solutions, our experiments were run in quite dilute conditions. The copolymer was obtained in low yield and with broad molecular weight distributions, when the low molecular weight polysiloxane sulfonate was used as macroinitiator. In our earlier report[3] on the reaction of the trimethylsilyl methanesulfonate with 1,3-dioxepane, we reported that the initiation step is slow relative to propagation, as shown by the long reaction times (3 days) and low initiator efficiency (5%). We did not obtain any copolymer when high molecular weight polysiloxane sulfonate was used as macroinitiator, due to the immiscibility of the reagents. This is an unexpected and apparently new difficulty in synthesizing block copolymers. Normally, we picture that block copolymers can combine incompatible segments. However, here we have a case where one polymer is even incompatible with the second monomer! It remains to be seen how general this situation may be.

EXPERIMENTAL

Methods - ^1H NMR spectra were recorded on a Brucker WM-250 spectrometer. Deuterochloroform and dichlorodimethylsilane were used as the solvent and internal reference. Molecular weights of polymers were measured on a Shodex GPC A 804 column calibrated with polystyrene and THF standards, chloroform as eluent and a Waters RI detector. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reagents - Methanesulfonic acid was purchased from Aldrich and purified by distillation over P_2O_5. 2,4-Di-t-butylpyridine was purchased from Aldrich and purified by distillation over CaH_2. 1,3-Dioxepane was distilled from CaH_2 and $LiAlH_4$. D_3 was purchased from Aldrich and dried over CaH_2 at about 80°C and then sublimed under vacuum.

Procedures - Experimental procedures were run under Argon atmosphere. All glasswares were dried at 300°C under vacuum. Reagents were transferred using a vacuum line, as described in our earlier report.[3]

Preparation of pentamethyldisiloxane

Me_3SiOLi (91 mmoles, prepared from 110 ml of 0.91M nBuLi and 16.24g of hexamethyldisiloxane) was slowly added to five equivalents of chlorodimethylsilane at -78°C, the reaction was stirred at room temperature overnight. The salts were filtered off and the mixture was distilled. $Me_3SiOSiMe_2H$ was obtained in 92% yield. b.p. 86-87°C. ^1H NMR: δ 0.02 (s, 9H), 0.08 (d, 6H), 4.7 (m, 1H). IR: 1257, 840, 751 (trimethylsilyl), 1060 (Si-O). Elem. Anal.: Calcl. C, 40.49%; H, 10.79%. Found: C, 40.91%, H, 10.90%.

The Reaction of Pentamethyldisiloxane with Methanesulfonic Acid

Pentamethyldisiloxane (1.13g, 7.6 mmol) was combined with 0.73g (7.6 mmol) CH_3SO_3H in 100 ml toluene at 0°C, 2% of Pd-C was added very slowly to this solution. The mixture was stirred at 0°C for 24 hrs. Pd-C was filtered off and the residue was distilled. $Me_3SiOSiMe_2OSO_2CH_3$ was obtained in 85% yield, b.p. 97-99°C/0.1 torr. ^1H NMR: δ 0.03 (s, 9H), 0.35 (s, 6H), 2.8 (s, 3H). IR: 1390, 1170 (sulfonate), 1260, 750, 780 and 725 cm^{-1}. Elem. Anal.: Calcd for $C_6H_{18}O_4SSi_2$ C: 29.74%; H, 7.43%. Found: C, 29.81%; H, 7.62%. Higher reaction temperature decreased the yield dramatically.

Preparation of allylpentamethyldisiloxane

Me_3SiOLi (0.03 mol) was added to five equivalents of allyl chlorosilane in 200 ml of THF at -78°C. The mixture was stirred overnight from -78°C to 0°C. The salts were filtered off, the solution was distilled. $Me_3SiOSiMe_2CH_2CH{=}CH_2$ was obtained at b.p. 95-96°C/55 torr. Yield 88%. ^1H NMR: δ0.02 (s,9H), 0.03 (s, 6H), 1.25 (d,2H), 3.9 (m, 2H) and 4.7 (m, 117). IR: 1630 (allyl), 1250, 1060, 750, 752 cm^{-1}. Elem. Anal.: calcd. C, 51.01%, H, 10.62%. Found: C, 50.82%, H, 10.83%.

Reaction of allylpentamethyldisiloxane with alkyl or aryl sulfonic acid

CH_3SO_3H (0.25g, 2.68 mmol) was added to 0.360 g (2.68 mmol) of allyl pentamethyldisiloxane in 150 ml of toluene at 0°C. The mixture was stirred at 26°C for 1 day. The yield was 85%.

When p-toluenesulfonic acid (0.462 g, 2.68 mmol) was used instead of CH_3SO_3H, the miscibility was significantly enhanced and the yield was 86%. When 0.570 g (2.68 mmol) of t-butylbenzenesulfonic acid was used, the yield went up to 89% using the same conditions.

Synthesis of oligomeric functionalized polysiloxane synthesis of lithium polysilanolate 1

Lithium polysilaolate was made according to the method of Cameron et. al.[7] n-Butyl lithium (1.6M, 3 ml) was added to cyclotrisiloxane (3 g) which has been dissolved in THF (1 ml) and n-hexane (3 ml) at -78°C, the mixture was stirred at 0°C for 2 days.

Synthesis of polysiloxane arylsulfonate 5

Via hydropolysiloxane 3

Five equivalents of chlorodimethylsilane were added to lithium polysilanolate at -78°C; the reaction was then stirred at room temperature overnight. The salt was filtered off and low boiling material was evaporated. The residue was identified to be 3. ^{1}H NMR: δ 4.7 (m, 1H), 1.2 (m, 4H), 0.9 (t, 3H) and 0.07 (broad, 132 H). The yield was 87%. p-Toluenesulfonic acid (0.27g, 2 mmol) in toluene (10 ml) was added to the flask containing the toluene solution of 3. After stirring and cooling to -15°C, 5% Pd-C (0.07 g) was added to this solution, the mixture was stirred continuously for one day. The catalyst was filtered off. Low boiling point materials were evaporated, the residue was identified by ^{1}H NMR as 5. Yield was 93%. ^{1}H NMR: δ 7.4 (m, 5H), 1.2 (m, 4H) 0.9 (t, 3H) and 0.07 (broad, 132 H).

Via allylpolysiloxane 7

Three equivalents of allylchlorodimethylsilane (2 ml) were added to lithium polysilanolate at -78°C and stirred at room temperature overnight. The salts were filtered off and the low boiling material was evaporated. The residue was identified by ^{1}H NMR to be 7. ^{1}H NMR: δ 5.7 (m, 1H), 4.8 (m, 2H), 1.5 (d, 2H), 1.2 (m, 4H), 0.8 (m, 3H) and 0.05 (broad, 120 H). The yield was 86%. This residue 7 (1.36 g, 2 mmol) was added to t-butylbenzenesulfonic acid (0.43 g, 2 mmol) in dichloroethane (10 ml) at room temperature for 2 days. The yield of 5 was 90%.

Synthesis of block copolymer

Polysiloxane toluenesulfonate 3 (3.3g) was combined with 0.1 g of 2,6-di-t-butylpyridine in 50 ml of dichloroethane. 1,3-Dioxepane (0.5g) was added to this solution at 0°C. The mixture was stirred at 0°C for 4 days, and quenched with pyridine and precipitated in methanol. This precipitated material was extracted several times with a mixture of methanol and chloroform. Purification was repeated until the integration ratio of dioxepane to siloxane did not change in the ^{1}H NMR spectrum. The yield was 21%. The copolymer was identified by SEC, Mn=2380, Mw=4545, Mw/Mn=2.1.

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