Preparation of Polybutylene Oxides Bearing Terminal Ester Groups by Treatment of H[(CH_2)_40]_nSiR_3 with Acyl Halides

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Preparation of Polybutylene Oxides Bearing Terminal Ester Groups by Treatment of $H[(CH_2)_4O]_nSiR_3$ with Acyl Halides

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Treatment of $H[(CH_2)_4O]_nSiR_3$, which were prepared by the silane induced polymerization of THF with acyl halides catalyzed by $(\mu_3:\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$, provides a novel synthetic method for polybutylene oxides bearing terminal ester groups. Various acyl halides such as acetyl chloride, benzoyl bromide, adipoyl chloride, acryloyl chloride, and 2-bromoisobutyryl bromide could be used as the acyl halide component; the reactivity of acyl halides increased in the order RCOBr > RCOCl > RCOF, whereas little difference in reactivity was observed among poly-butylene oxides bearing PhMe₂Si-, Et₃Si-, and EtMe₂Si- moieties. All of the products were completely characterized by IR, ^1H, ^{13}C, H-H, and H-C COSY NMR techniques, revealing that they have one terminal butyl and one terminal acyloxy groups. In the case of the reaction with adipoyl chloride, a polymer having two $H[(CH_2)_4O]_n$ units at both ends of the adipoyl moiety was available. The methodology involving the silane-induced ring-opening polymerization followed by treatment with acyl halides was also applied to the synthesis of polycyclohexene oxide bearing 2-bromoisobutyryl bromide. The polymers bearing isobutyryloxy or acryloyloxy groups could be used as a macroinitiator or macromonomers to produce other functional polymers.

Introduction

Hydrosilylation of unsaturated molecules is catalyzed by a wide range of transition-metal salts and complexes.[1] Catalysis of hydrosilylation reactions by di- or polynuclear metal carbonyl complexes has recently received considerable attention, and use of $Co_2(CO)_8$, $Rh_4(CO)_{12}$, and Co-Rh heteronuclear clusters provides novel aspects for the hydrosilylation of alkenes, alkynes, or ketones.[2] Recently we reported that $(\mu_3:\eta^2:\eta^3:\eta^5$-acenaphthylene)$Ru_3(CO)_7$ (1) is an efficient catalyst for the hydrosilylation of unsaturated molecules, especially of ketones and aldehydes, for which the catalytic activity has been found to be superior to that of $RhCl(PPh_3)_3$ and $Ru_3(CO)_{12}$. Of particular interest is the successful silane induced ring-opening polymerization of cyclic ethers; e.g., the reactions of trialkylsilanes with an excess of THF (10-10^2 molar equivalent with respect to silanes) in the presence of a catalytic amount of 1 resulted in the production of polybutylene oxide (polyTHF) with M_n=1000-200,000 and M_w/M_n= 1.3-2.0.

The molecular weight of the polymer depended on the reaction temperature or on the charged THF/SiH ratio. NMR studies suggested that the structure of the polymer is R_3SiO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$. Deuterium labeled silanes such as $PhMe_2SiD$, gave the polymer $PhMe_2SiO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_2D$ selectively. This clearly shows that the polymerization described above involves an insertion of the $OCH_2CH_2CH_2CH_2$ unit derived from THF into the Si-H bond. Polymerization of THF was briefly mentioned by Chalk in 1970 as occurring in a $Co_2(CO)_8$-catalyzed reaction of Et_3SiH in the presence of an excess of THF; he obtained polyTHF with M_w= 50,000.[4a] Reinvestigation of the silane-induced ring-opening polymerization of THF catalyzed by $Co_2(CO)_8$ revealed that $Co_2(CO)_8$ and 1 show similar behavior in the reaction but that 1 is the more active catalyst at lower catalyst concentration. Thus, the use of 1 as a catalyst in the silane induced polymerization of THF is an interesting method for the preparation of poly-butylene oxides bearing one terminal siloxy and one terminal butyl group.

We were interested in the chemical transformation of the siloxy group in R_3SiO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ which could open

up a way to synthesize other polymers bearing a variety of functional groups. In particular, several groups have already been shown to be of potential utility in poly-butylene oxides bearing reactive ester groups at their termini.[6,7] Since poly-butylene oxides bearing terminal ester groups are generally prepared by living cationic polymerization of THF followed by end-capping with carboxylate anions, a preparative method from R_3SiO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ offers a completely different way to synthesize them.

Scheme 1
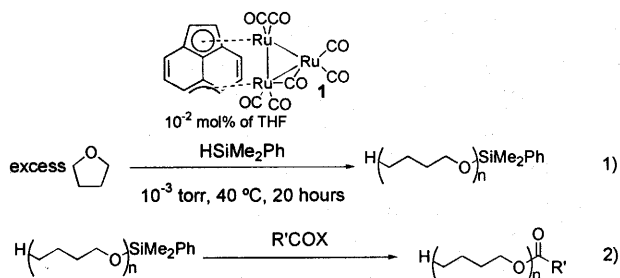
Several reports concerning the transformation of a siloxy group to an ester moiety have been published in relation to transformation of organosilicon compounds[13] and organic synthesis.[8-12] For example, conversion of silyl ethers to the corresponding acetates under mild conditions have been accomplished with acyl halides in the presence of Lewis acids such as SnX_2,[9] $FeCl_3$,[10] $ZnCl_2$,[11] and $TiCl_4$.[12] However, acylations promoted by Lewis acids are not desirable in the reaction with silylated polybutylene oxides, because the strong interactions of the poly-butylene oxide chains with Lewis acids can be expected to cause problems upon removal of the metallic species from the products. Direct conversions of silyl ethers to acetates in the absence of Lewis acids, are the reactions of acyl halides with silyl ethers, which have been reported by Daudt,[13] and Oriyama,[9] and Pawlowski.[14] It was of interest whether a similar direct conversion could be applied to the transformation of R_3SiO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$. In this paper, we wish to report that a simple treatment of acyl halides with R_3SiO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ actually results in the complete conversion of the siloxy group to an ester group leading to an efficient preparative method for $R'COO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$.

Results and Discussion

Daudt reported that treatment of several organoethoxy silanes with a 2~3 fold excess of acetyl chloride at room temperature for 4 days gave the corresponding chlorosilanes and ethylacetate.[13] We first examined the reaction of $PhMe_2SiO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ [M_n(NMR)= 2600] with 2 equivalents of acetyl chloride in C_6D_6 at room temperature. The reaction was monitored by ^1H NMR spectra. After 17 hours, the signals due to the $PhMe_2Si$ moiety of the starting material (δ_{Me} 0.31 ppm (**A**); δ_{Ph} 7.32-7.37 and 7.51-7.57 (**H, I**) ppm) disappeared completely, and peaks due to $PhMe_2SiCl$ and $(PhMe_2Si)_2O$ became visible. No other by-products were observed. The results indicated a successful transformation of $PhMe_2SiO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ to CH_3COO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$. In a similar fashion, a solution of $PhMe_2SiO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ [M_n(NMR)= 1900, M_n(SEC)= 4500, M_w/M_n= 1.4] was treated with 2 mol equivalents of acetyl chloride in C_6H_6 for 17 h at room temperature. The reaction mixture was poured into methanol, and the polymer was precipitated from the mixture at -35 °C. The precipitate (67% yield of the crude polymer) as separated by filtration from the liquid phase and analyzed by NMR. As shown in Figure 1, two broad singlets due to CH_2 groups in the polymer chain could be observed at δ 1.61 and 3.41 ppm (E' and F'). The presence of the acetyl group is evidenced by a singlet at 2.02 ppm(J'). The integrated signal intensities of B', C', D', J', and K' are 3:2:2:3:2, which indicates that the polymer contains one butyl and one acetyl group. Correlations among B', C' and D', and K' and L' were supported by a H-H COSY spectrum. These data are in accord with the structure of a polymer with the formula CH_3COO-$[(CH_2)_4O]_nCH_2CH_2CH_2CH_3$. The ^{13}C NMR spectrum and the H-C COSY spectrum of the polymer are also consistent with this assignment. The IR spectrum of the acetoxy polymer shows v_{co} absorption at 1733 cm^{-1} [cf. acetyl chloride (1807 cm^{-1}), acetic acid (1719 cm^{-1}), and butyl acetate (1743 cm^{-1})].

Complete transformation of $PhMe_2SiO$-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ to CH_3COO-$[(CH_2)_4O]_n$-$CH_2CH_2CH_2CH_3$ is also suggested from the average molecular weight studies. The molecular weight of CH_3COO-$[(CH_2)_4O]_nCH_2CH_2CH_2CH_3$ calculated from the integral ratio of B' to F' is 2400, whereas that of
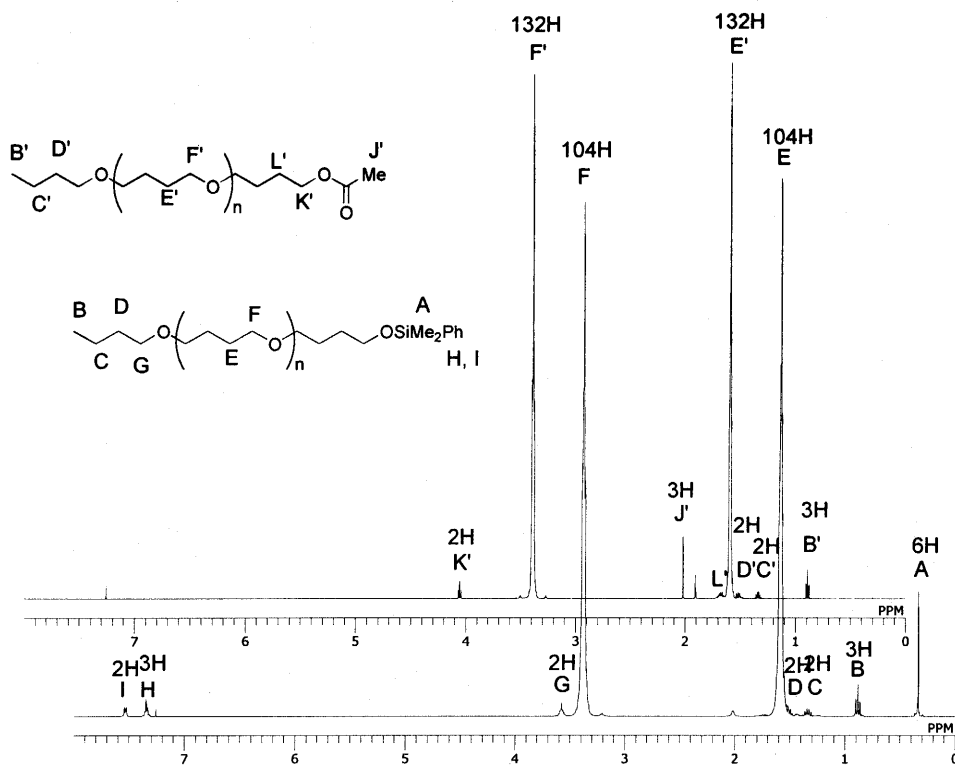
Figure 1. ^{1}H NMR spectra of $CH_3COO\text{-}[(CH_2)_4O]_nCH_2CH_2CH_2CH_3$ and $PhMe_2SiO\text{-}[(CH_2)_4O]_nCH_2CH_2CH_2CH_3$.

$PhMe_2SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ calculated from the ratio of A to E is 1900. SEC analysis of the acetoxy polymer gave M_n= 5200, M_w/M_n= 1.3, whereas that of the siloxy precursor indicated M_n(SEC)= 4500, M_w/M_n= 1.4. Molecular weights determined by SEC calibrated by polystyrene standards are reportedly half of the actual value.[15]

The reaction of other acyl halides with $R_3SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ generally gave the corresponding $R'COO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ as summarized in Table 1. Adipoyl chloride (entry 6, *vide infra*), acryloyl chloride (entry 3), 2-bromoisobutyryl bromide (entry 4) reacted smoothly at room temperature to give the product in good yields. The reaction with benzoyl chloride was slow, and only a small amount of the product was observed after 17 h (entry 2b). At 60°C, all of the starting material was consumed after 24 h; however, some amount of THF as a by-product was also formed.[16] The yield of the product was dramatically improved by using PhCOBr (entry 2d) instead of PhCOCl. In contrast, no reaction took place with PhCOF even at 80°C (entry 2a). Replacement of the siloxy group in $R_3SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ from $PhMe_2SiO$ to either Et_3SiO or $EtMe_2SiO$ did not increase

the reactivity towards benzoyl chloride. The data suggests that the reaction of $R_3SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ with acyl halides proceeds with ease even in the absence of Lewis acids. In the case of less reactive acyl halides (acyl chrolides), the use of acyl bromides is effective. This transformation can also be applied to the conversion of polycyclohexene oxide silyl ether to the corresponding ester. Here, it is a secondary siloxy group that reacts which is expected to be less reactive towards acyl halides because of steric reasons. Thus, polycyclohexene oxide $PhMe_2Si$- ether $[M_n(SEC) = 8300, M_w/M_n = 2.0]$, which was prepared by 1-catalyzed silane induced polymerization of cyclohexene oxide, was treated with 2 equivalents of 2-bromoisobutyryl bromide at room temperature for 22 h to afford the corresponding ester in 71% yield $[M_n(SEC) = 9200, M_w/M_n = 1.9]$.

It is expected that application of this transformation to the preparation of polyalkylene oxides bearing esters could bring about some new aspects in the chemistry of functionalized polymers. Thus, the reaction of $R_3SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ with adipoyl chloride resulted in an adipate bearing two $O\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ groups. For

Table 1. Reaction of $PhMe_2SiO-[(CH_2)_4O]_nCH_2CH_2CH_2CH_3$ with acyl halides

Entry	Polymer-SiR3	Mn (NMR) (g/mol)	Mn (SEC) (g/mol)	Mw/Mn	R'COX	solvent	temp. (°C)	time (hours)	conversion (%)	yield (%)	Mn (NMR) (g/mol)	Mn (SEC) (g/mol)	Mw/Mn
1	THF-SiMe2Ph	1900	4500	1.4	MeCOCl	C6H6	r.t.	17	100	67	2400	5200	1.3
2a	THF-SiMe2Ph	1900	4500	1.4	PhCOF	C6D6	80	62	0	0	-	-	-
2b	THF-SiMe2Ph	1900	4500	1.4	PhCOCl	C6D6	40	68	39	57	-	-	-
2c	THF-SiMe2Ph	1900	4500	1.4	PhCOCl	C6D6	60	24	100	65	2400	3500	1.3
2d	THF-SiMe2Ph	2200	6400	1.5	PhCOBr	C6D6	r.t.	24	100	72	2600	5700	1.4
3	THF-SiMe2Ph	1900	4500	1.4	CH2=CHCOCl	C6H6	r.t.	25	100	77	2300	5400	1.3
4	THF-SiMe2Ph	2200	6400	1.5	BrMe2CCOBr	C6H6	r.t.	47	100	86	3000	4700	1.5
5	CychexOx-SiMe2Ph	5000	8300	2.0	BrMe2CCOBr	C6H6	r.t.	22	-	71	-	9200	1.9
6*	THF-SiMe2Ph	1900	4500	1.4	ClCO(CH2)4COCl	C6D6	r.t.	47	>95	78	4400	7100	1.5

* THF-SiMe2Ph: ClCCO(CH2)4COCl= 2:1
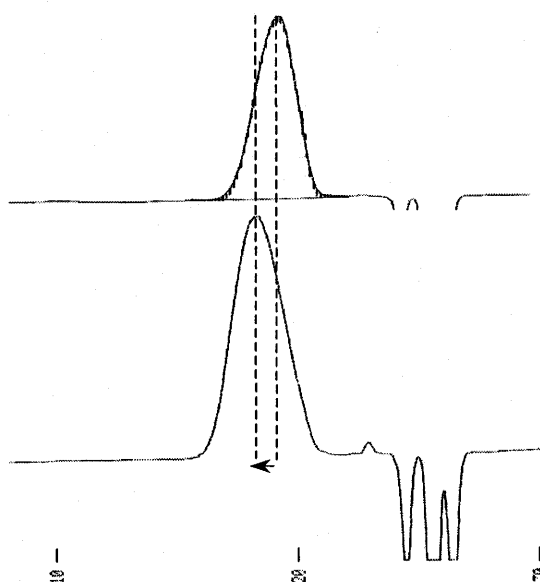
Figure 2. SEC charts of $PhMe_2PhSiO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$ (upper) and $CH_3CH_2CH_2CH_2-[O(CH_2)_4]_n-OCO(CH_2)_4CO[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$ (lower).

achievement of this reaction, exactly two equivalents of $R_3SiO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$ must be allowed to react with adipoyl chloride; use of excess adipoyl chloride leads to formation of a half-ester, whereas application of excess of $R_3SiO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$ causes difficulty in separation of the product from the reaction mixture. In a 5 mm ϕ NMR tube, a mixture of $PhMe_2SiO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$ [M_n(NMR)= 1900, M_n(SEC)= 4500, M_w/M_n= 1.4] and adipoyl chloride (1 eq. to the calculated amount of silyl group) was dissolved in C_6D_6. After 48 hours at room temperature, the signals due to the methyl protons of the

silyl ether disappeared and the quantitative introduction of the ester moiety (>95% functionalization) was evidenced by quantitative appearance of the signal due to the COOCH_2 moiety of the product. The crude polymer obtained [M_n(NMR)= 3200, M_n(SEC)= 6400, M_w/M_n= 1.7] was purified by precipitation from diethyl ether and hexane at −35 °C (78% yield of the crude polymer). IR, ^1H, ^{13}C, H-H COSY, and H-C COSY NMR spectra of the purified polymer were in accord with the structure, $CH_3CH_2CH_2CH_2-[O(CH_2)_4]_n-O-CO(CH_2)_4CO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$. The molecular weights as determined by NMR and SEC were 4400 and 7100, respectively, this being roughly twice as much as the molecular weight of the siloxy precursor. This result clearly suggests that the use of a bifunctional acyl halide as a linear polymer having molecular weight twice as much as the siloxy precursor. In other words, polymers bearing various structures could be prepared by the appropriate choice of multifunctional acyl halides. Successful formation of the adipate showed another important finding in our silane-induced polymerization of THF. We could concluded from NMR spectroscopic measurement that the polymer formed by the 1-catalyzed polymerization has one siloxy and one butyl terminal. This structure was unequivocally supported by formation of $CH_3CH_2CH_2CH_2-[O(CH_2)_4]_n-O-CO(CH_2)_4CO-[(CH_2)_4O]_n-CH_2CH_2CH_2CH_3$.
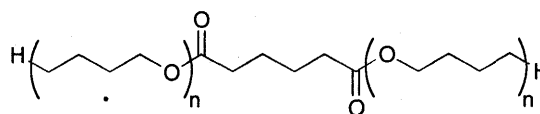

Figure 3.

Therefore, the transformation described in this paper made it possible to synthesize poly-butylene

oxides or polycyclohexene oxides bearing one reactive ester group. The preparation and polymerization of polyethylene oxide or polybutylene oxide macromonomers bearing a double bond at the polymer terminus have been reported by Ito, Dreyfuss, Rempp, Sierra-Vargas, Kreβ, and Goethals.[7] So far, a number of macromonomers have been available as potential building blocks to design a variety of well-defined, branched homo- and copolymers including comb, star, brush, and graft types. Polybutylene oxides bearing a bromoacetyl or a 2-bromoisobutyryl group at the polymer terminal have recently been investigated as macroinitiators for block copolymerization of THF and MMA.[6] In these studies, the authors prepared macromonomers or macroinitiators by conventional living polymerization/end-capping methods. Our reaction is an alternative synthetic route to these reactive polymers. As an example showing that our method can actually be used as a macroinitiator, block copolymerization of polyTHF-CBr(Me)$_2$ with MMA promoted by CuBr[6a] as reported by Matyjaszewski was examined. As described in the experimental section in detail, the copolymer was obtained in 98% yield, and the ^{1}H NMR of the copolymer revealed that the product contains polyTHF and polyMMA segments. Although copolymerization of polycyclohexene oxide-CBr(Me)$_2$ [M_n(SEC)= 9100, M_w/M_n= 1.9] with MMA has not been reported in the literature, the reaction also proceeded to give the corresponding copolymer [M_n(SEC)= 58000, M_w/M_n= 2.0].[6a]
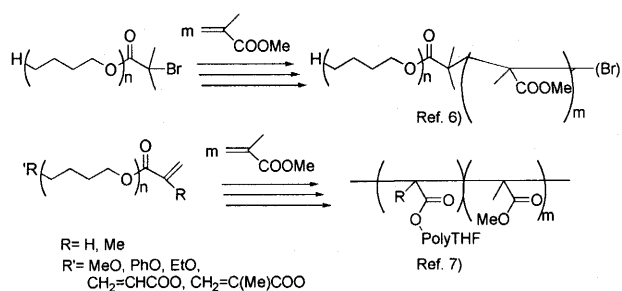
Scheme 2.
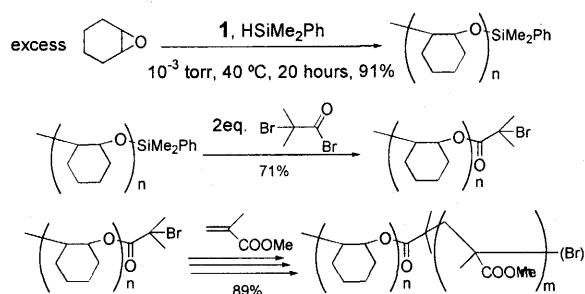
Scheme 3.

Conclusion

As described above, we have developed new preparative methods for poly-butylene oxides and polycyclohexene oxides bearing various ester functions at the polymer terminus by the reaction of $R_3SiO\text{-}[(CH_2)_4O]_n\text{-}CH_2CH_2CH_2CH_3$ with acyl halides. Various acyl halides including a bifunctional acyl halide can be used for the transformation; in particular, acyl bromides have been seen to be effective when the rate of the reaction is low with acyl chlorides. Complete conversion of the siloxy moiety of the precursor to the ester group of the product was accomplished; this was unequivocally proven by spectroscopy and SEC analyses. The transformation can be applied to the preparation of reactive polymers including macromonomers and macroinitiators. The reaction with bifunctional acyl halides suggests potential utility of this synthetic method for the production of polymers having a wide variety of structures by the appropriate choice of multifunctional acyl halides.

Experimental Section

General considerations. All manipulations were carried out using standard Schlenk techniques under an argon atmosphere. NMR spectra (400, 600 MHz) were measured in CDCl$_3$ unless otherwise noted; δ values are given in ppm and coupling constants (J) in Hz. Assignments of the NMR signals were made with the aid of 2D techniques. C$_6$H$_6$ and C$_6$D$_6$ were distilled from sodium benzophenone ketyl just before use. Size exclusion chromatography (SEC) analysis of the polymers was carried out using a Jasco HPLC system in THF calibrated by standard samples of polystyrene.

Reaction of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ with acetyl chloride. To a solution of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ [M_n(NMR)= 1900, M_n(SEC)= 4500, M_w/M_n= 1.4] (0.244g, 0.13 mmol) dissolved in C$_6$H$_6$ (1.6 mL) was added acetyl chloride (20 μL, 0.28 mmol), and the mixture was stirred at room temperature for 17 hours. The reaction mixture was poured into methanol (100 mL) and was purified by precipitation at –35 °C. The precipitate (0.166g that 67% yield of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. The integral ratio (Me of the butyl terminal vs. CH$_2$OAc) gave an average molecular weight of 2400. The SEC analysis showed M_n= 5200, M_w/M_n= 1.3.

^{1}H(CDCl$_3$): δ 0.89 (t, J= 7.4 Hz, 3H, CH$_3$), 1.34 (m, 2H,

CH$_2$), 1.51 (m, 2H, CH$_2$), 1.61 (bs, CH$_2$ in polymer chain), 1.67 (m, 2H, COOCH$_2$CH_2), 2.02 (s, 3H, COCH$_3$), 3.41 (bs, OCH$_2$ in polymer chain), 4.05 (t, $J=$ 6.5 Hz, 2H, COOCH$_2$), ^{13}C(CDCl$_3$): δ 13.9 (CH$_3$), 19.3 (CH$_2$), 20.9 (COCH$_3$), 25.4, 26.5 (CH$_2$ in polymer chain), 31.8 (CH$_2$), 64.3 (COOCH$_2$), 70.5 (OCH$_2$ in polymer chain), 171.1 (CO). IR(CH$_2$Cl$_2$): 1733cm^{-1}.

Reaction of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ with adipoyl chloride. In a 5 mm φ NMR tube, a mixture of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ [M_n(NMR)= 1900, M_n(SEC)= 4500, $M_w/M_n=$ 1.4] (0.127g, 0.07mmol), adipoyl chloride (5µL, 0.034 mmol) was dissolved in C$_6$D$_6$ (0.7 mL). The NMR sample was carefully degassed several times and sealed in vacuo. Reaction profiles were monitored by ^{1}H NMR. After 48 hours at room temperature, the reaction mixture was poured into methanol (30 mL). The crude polymer precipitate was dissolved in diethyl ether (0.4 mL) and was purified by precipitation by adding hexane (100mL) at –35 °C. The precipitate (0.049g, *i.e.* 78% yield of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. The integral ratio (*Me* of the butyl terminal vs. CH_2OAdipoyl) gave an average molecular weight of 4400. The SEC analysis showed $M_n=$ 7100, $M_w/M_n=$ 1.5.

^{1}H(CDCl$_3$): δ 0.89 (t, $J=$ 7.4 Hz, 6H), 1.34 (m, 4H), 1.51 (m, 4H), 1.61 (bs, adipoylCH$_2$, CH$_2$ in polymer chain), 2.31 (bt, $J=$ 6.5 Hz, 4H, adipoylCH$_2$CO), 3.41 (bs, OCH$_2$ in polymer chain), 4.09 (t, $J=$ 6.5 Hz, 4H), ^{13}C(CDCl$_3$): δ 13.9 (CH$_3$), 19.3 (CH$_2$), 24.3, 25.4 (adipoylCH$_2$), 26.2, 26.3, 26.5 (CH$_2$ in polymer chain), 31.8 (CH$_2$), 33.8 (adipoylCH$_2$CO), 64.1 (COOCH$_2$), 70.1, 70.6 (OCH$_2$ in polymer chain), 173.3 (CO). IR(CH$_2$Cl$_2$): 1729cm^{-1}.

Reaction of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ with 2-bromoisobutyryl bromide. To a solution of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ [M_n(NMR)= 2200, M_n(SEC)= 6400, $M_w/M_n=$ 1.5] (1.10g, 0.5 mmol) dissolved in C$_6$H$_6$ (7.0 mL) was added 2-bromoisobutyryl bromide (125 µL, 1 mmol), and the mixture was stirred at room temperature for 14 hours. The reaction mixture was poured into methanol (60 mL). The crude polymer precipitated was dissolved in diethyl ether (0.4 mL) and was purified by precipitation by adding hexane (200 mL) at –35 °C. The precipitate (0.93g *i.e.* 86% yield of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. The integral ratio

of the polymer (*Me* of the butyl terminal vs. CH_2OCOMe$_2$Br) gave an average molecular weight of 3000. The SEC analysis showed $M_n=$ 4400, $M_w/M_n=$ 1.5.

^{1}H(CDCl$_3$): δ 0.89 (t, $J=$ 7.4 Hz, 3H, CH$_3$), 1.34 (m, 2H, CH$_2$), 1.51 (m, 2H, CH$_2$), 1.61 (bs, CH$_2$ in polymer chain), 1.90 (s, 6H), 3.41 (bs, OCH$_2$ in polymer chain), 4.16 (t, $J=$ 6.5 Hz, 2H, COOCH$_2$), ^{13}C(CDCl$_3$): δ 13.9 (CH$_3$), 19.3(CH$_2$), 25.3, 26.1, 26.5 (CH$_2$ in polymer chain), 30.7 (isobutyryl Me), 31.8 (CH$_2$), 55.8 (isobutyryl C), 65.8 (COOCH$_2$), 70.5 (OCH$_2$ in polymer chain), 171.6 (CO). IR(CH$_2$Cl$_2$): 1730cm^{-1}.

Reaction of polycyclohexene oxide-OSiMe$_2$Ph with 2-bromoisobutyryl bromide. To a solution of polycyclohexene oxide-OSiMe$_2$Ph [M_n(NMR)= 5000, M_n(SEC)= 8300, $M_w/M_n=$ 2.0] (0.102g, 0.02 mmol) dissolved in C$_6$H$_6$ (0.6 mL) was added 2-bromoisobutyryl bromide (6 µL, 0.05 mmol), and the mixture was stirred at room temperature for 22 hours. The reaction mixture was poured into methanol (25 mL). The crude polymer precipitated was dissolved in CHCl$_3$ (1.2 mL) and was purified by precipitation by adding methanol (50 mL) at room temperature. The precipitate (0.081g *i.e.* 71% yield of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. PhMe$_2$SiO group was disappeared in NMR sprectrum. The SEC analysis showed $M_n=$ 9100, $M_w/M_n=$ 1.9.

^{1}H(CDCl$_3$): δ 1.0-2.2 (polymer), 3.2-3.8 (polymer), ^{13}C(CDCl$_3$): δ 14.1, 21-24 (polymer), 2.75-31.0 (polymer), 31.5, 56.5, 75-79 (polymer), 170.8 (CO). IR(CH$_2$Cl$_2$): 1733cm^{-1}.

Reaction of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ with acryloyl chloride. To a solution of PhMe$_2$SiO-[(CH$_2$)$_4$O]$_n$-CH$_2$CH$_2$CH$_2$CH$_3$ [M_n(NMR)= 1900, M_n(SEC)= 4500, $M_w/M_n=$ 1.4] (0.225g, 0.12 mmol) dissolved in C$_6$H$_6$ (1.5 mL) was added acryloyl chloride (20 µL, 0.025 mmol), and the mixture was stirred at room temperature for 25 hours. The reaction mixture was poured into methanol (100 mL). The crude polymer precipitated was dissolved in diethyl ether and was purified by precipitation by adding hexane at –35 °C. The precipitate (0.18g *i.e.* 77% yield of the crude polymer) was separated by filtration from the liquid phase and subjected to NMR and SEC analysis. The integral ratio of the polymer (*Me* of the butyl terminal vs. CH_2OAcryloyl) gave an average molecular weight of 2300. The SEC analysis showed $M_n=$ 5500, $M_w/M_n=$ 1.3.

^{1}H(CDCl$_3$): δ 0.89 (t, $J=$ 7.4 Hz, 3H), 1.34 (m, 2H),

1.51 (m, 2H), 1.61 (bs, CH$_2$ in polymer chain), 3.41 (bs, OCH$_2$ in polymer chain), 4.15 (t, J= 6.5 Hz, 2H), 5.81 (dd, J= 1.5 Hz, 10.5 Hz, 1H, CH$_2$=), 6.10 (dd, J= 10.5 Hz, 17.3 Hz, 1H, =CHCO), 6.32 (dd, J= 1.5 Hz, 17.3 Hz 1H, CH$_2$=). ^{13}C(CDCl$_3$): δ 13.9 (CH$_3$), 19.3 (CH$_2$), 25.5, 26.4, 26.5 (CH$_2$ in polymer chain), 31.8 (CH$_2$), 64.3 (COOCH$_2$), 70.5 (OCH$_2$ in polymer chain), 128.5 (=CHCO), 130.5 (CH$_2$=), 166.2 (CO). IR(CH$_2$Cl$_2$): 1718cm^{-1}.

Block copolymerization of CH$_3$CH$_2$CH$_2$CH$_2$-[O(CH$_2$)$_4$]$_n$-OCO-CBr(Me$_3$)$_2$ with methyl methacrylate (MMA) [MMA: macroinitiator: CuBr: C$_7$-bipy= 134: 1: 0.94: 2.1:]. The reaction was carried out accroding to the literature method.[6a] A mixture of PolyTHF-CBr(Me$_3$)$_2$ [M_n(NMR)= 3000, M_n(SEC)= 4400, M_w/M_n= 1.5] (0.105g, 0.035 mmol), CuBr (4.7 mg, 0.03 mmol), 4,4'-diheptyl-2,2'-bipyridine (26.4 mg, 0.075 mmol), MMA (0.5 mL, 4.7 mmol), and toluene (0.5 mL) was placed in a glass tube. The mixture was degassed several times, sealed in vacuo, and heated at 90 °C for 22 hours. The reaction mixture was dissolved in THF, and passed through an alumina column to remove copper species to give 0.56g of copolymer (98%). The SEC analysis of the crude polymer showed Mn= 16000 (calcd. M_n= 17800), M_w/M_n= 1.4. After precipitation from THF-methanol, SEC analysis showed M_n= 23,000, M_w/M_n= 1.1 [cf. K. Matyjaszewski[6a], M_n(Polybutylene oxide)= 15,400, M_n(block copolymer)= 56,700, M_n(calc)= 35,000].

Block copolymerization of polycyclohexene oxide-CBr(Me$_3$)$_2$ with methyl methacrylate (MMA) [MMA: [pCychexOx-Br]: CuBr: C$_7$-bipy= 459: 1: 1.3: 2]. A mixture of polycyclohexene oxide-CBr(Me$_3$)$_2$ [M_n(NMR)= 5000, M_n(SEC)= 9200, M_w/M_n= 1.9] (0.0511g, 0.01 mmol), CuBr (1.9 mg, 0.013 mmol), 4,4'-diheptyl-2,2'-bipyridine (7.0 mg, 0.020 mmol), MMA (0.5 mL, 4.7 mmol), and toluene (0.5 mL) were placed in a glass tube. The mixture was degassed several times, sealed in vacuo, and polymerized at 90 °C for 22 hours. The reaction mixture was dissolved in THF, and passed through an alumina column to remove copper speciesx to give 0.48g of copolymer (89%). The SEC analysis showed M_n= 58,000 (calcd. M_n= 50,000), M_w/M_n= 2.0. After precipitation from THF-methanol, SEC analysis showed M_n= 58,000, M_w/M_n= 2.0.

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