Preparation of Polybutylene Oxides Bearing Terminal Ester Groups by Treatment of H[(CH₂)₄O]ₙSiR₃ with Acyl Halides

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Treatment of H[(CH₂)₄O]ₙSiR₃, which were prepared by the silane induced polymerization of THF with acyl halides catalyzed by (μ₂:η⁷:η³:η⁴-acenaphthylene)Ru₃(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, ¹³C, 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[CH₂]₄Oₙ 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-bromoisoindoyl bromide. The polymers bearing isobutyroxy or acryloxy 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 dimer or polymeric metal carbonyl complexes has recently received considerable attention, and use of Co₂(CO)₈, Rh₄(CO)₁₂, and Co-Rh heteronuclear clusters provides novel aspects for the hydrosilylation of alkenes, alkynes, or ketones.²) Recently we reported that (μ₂:η⁷:η³:η⁴-acenaphthylene)Ru₃(CO)₇ (I) 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(PPPh₃)₃ and Ru₃(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 (10-10² molar equivalent with respect to silanes) in the presence of a catalytic amount of I resulted in the production of polybutylene oxide (polyTHF) with Mₙ=1000-200,000 and Mₙ/Mₚ=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 R₃SiO-[CH₂]ₘCH₂CH₂CH₂CH₂ₙ. Deuterium labeled silanes such as PhMe₂SiD, gave the polymer PhMe₂SiO-[CH₂]ₘCH₂CH₂CH₂CH₂D selectively. This clearly shows that the polymerization described above involves an insertion of the OCH₂CH₂CH₂CH₂ unit derived from THF into the Si-H bond. Polymerization of THF was briefly mentioned by Chalk in 1970 as occurring in a Co₂(CO)₈-catalyzed reaction of Et₃SiH in the presence of an excess of THF; he obtained polyTHF with Mₙ=50,000.³) Reinvestigation of the silane-induced ring-opening polymerization of THF catalyzed by Co₂(CO)₈ revealed that Co₂(CO)₈ and I show similar behavior in the reaction but that I is the more active catalyst at lower catalyst concentration. Thus, the use of I 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 R₃SiO-[CH₂]ₘCH₂CH₂CH₂CH₃, 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. 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 R₃SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ offers a completely different way to synthesize them.

Several reports concerning the transformation of a siloxy group to an ester moiety have been published in relation to transformation of organosilicon compounds and organic synthesis. 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 SnX₅, FeCl₃, ZnCl₂, and TiCl₄. 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, Oriyama, and Pawlowski. It was of interest whether a similar direct conversion could be applied to the transformation of R₃SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃. In this paper, we wish to report that a simple treatment of acyl halides with R₃SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ actually results in the complete conversion of the siloxy group to an ester group leading to an efficient preparative method for R‘COO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃.

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. We first examined the reaction of PhMe₂SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ with 2 equivalents of acetyl chloride in C₆D₆ at room temperature. The reaction was monitored by ¹H NMR spectra. After 17 hours, the signals due to the PhMe₂Si moiety of the starting material (δMe 3.01 ppm (A); δH 7.32-7.37 and 7.51-7.57 (H, I) ppm) disappeared completely, and peaks due to PhMe₂SiCl and (PhMe₂Si)₂O became visible. No other by-products were observed. The results indicated a successful transformation of PhMe₄SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ to CH₃COO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃. In a similar fashion, a solution of PhMe₂SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ [M₄(NMR)=1900, M₄(SEC)=4500, M₄/M₄-=1.4] was treated with 2 mol equivalents of acetyl chloride in C₆H₆ 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 CH₃ 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 CH₃COO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃. The ¹³C 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 νₒ, 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 PhMe₂SiO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ to CH₃COO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃ is also suggested from the average molecular weight studies. The molecular weight of CH₃COO─[(CH₂)₄O]n─CH₂CH₂CH₂CH₃, calculated from the integral ratio of B‘ to F‘ is 2400, whereas that of
PhMe₂SiO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ calculated from the ratio of A to E is 1900. SEC analysis of the acetoxymalononitrile 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. 

The reaction of other acyl halides with R₃SiO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ generally gave the corresponding R’COO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ 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. 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 R₃SiO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ from PhMe₂SiO to either Et₃SiO or EtMe₂SiO did not increase the reactivity towards benzyol chloride. The data suggests that the reaction of R₃SiO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ with acyl halides proceeds with ease even in the absence of Lewis acids. In the case of less reactive acyl halides (acyl chlorides), the use of acyl bromides is effective. This transformation can also be applied to the conversion of policyclohexene 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, policyclohexene oxide PhMe₂Si-ether [M₆(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 [M₆(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 R₃SiO-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ with adipoyl chloride resulted in an adipate bearing two O-[(CH₂)₄O]ₙCH₂CH₂CH₂CH₃ groups.
Table 1. Reaction of PhMe2SiO-{[(CH2)2]n}CH2CH2CH3 with acyl halides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer-SiR3</th>
<th>Mn (NMR) (g/mol)</th>
<th>Mn (SEC) (g/mol)</th>
<th>R'COX</th>
<th>solvent temp. (°C)</th>
<th>time (hours)</th>
<th>conversion (%)</th>
<th>yield (%)</th>
<th>Mn (NMR) (g/mol)</th>
<th>Mn (SEC) (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>MeCOCl</td>
<td>r.t.</td>
<td>17</td>
<td>100</td>
<td>67</td>
<td>2400</td>
</tr>
<tr>
<td>2a</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>PhCOF</td>
<td>80</td>
<td>62</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2b</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>PhCOCl</td>
<td>40</td>
<td>68</td>
<td>39</td>
<td>67</td>
<td>-</td>
</tr>
<tr>
<td>2c</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>PhCOCl</td>
<td>60</td>
<td>24</td>
<td>100</td>
<td>65</td>
<td>2400</td>
</tr>
<tr>
<td>2d</td>
<td>THF-SiMe2Ph</td>
<td>2200</td>
<td>6400</td>
<td>1.5</td>
<td>PhCOBr</td>
<td>r.t.</td>
<td>24</td>
<td>100</td>
<td>72</td>
<td>2500</td>
</tr>
<tr>
<td>3</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>CH3=CHCOCl</td>
<td>r.t.</td>
<td>25</td>
<td>100</td>
<td>77</td>
<td>2300</td>
</tr>
<tr>
<td>4</td>
<td>THF-SiMe2Ph</td>
<td>2200</td>
<td>6400</td>
<td>1.5</td>
<td>BrMe2CCOBr</td>
<td>r.t.</td>
<td>47</td>
<td>100</td>
<td>86</td>
<td>3000</td>
</tr>
<tr>
<td>5</td>
<td>Cyexolar-SiMe2Ph</td>
<td>5000</td>
<td>8300</td>
<td>2.0</td>
<td>BrMe2CCOBr</td>
<td>r.t.</td>
<td>22</td>
<td>&gt;95</td>
<td>78</td>
<td>4400</td>
</tr>
<tr>
<td>6</td>
<td>THF-SiMe2Ph</td>
<td>1900</td>
<td>4500</td>
<td>1.4</td>
<td>CICO(CH2)COCl</td>
<td>C8D8</td>
<td>r.t.</td>
<td>&gt;95</td>
<td>78</td>
<td>4400</td>
</tr>
</tbody>
</table>

* THF-SiMe2Ph: CICO(CH2)COCl = 2:1

Figure 2. SEC charts of PhMe2SiO-{[(CH2)2]n}CH2CH2CH3 (upper) and CH2CH2CH2CH2-[O(CH2)2]n-O-CO(CH2)CO-[CH2]nO CH2CH2CH2CH3 (lower).

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, Rempf, Sierra-Vargas, Kreß, 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.\(^5\) 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\(^6\) 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)\(_2\) with MMA has not been reported in the literature, the reaction also proceeded to give the corresponding copolymer \([M_n(SEC)= 58000, M_d/M_n = 2.0]\).\(^6\)

\[
\begin{align*}
\text{Scheme 3.} \\
\text{excess} & \quad 10^3 \text{torr, } 40 ^\circ \text{C, 20 hours, 91}\% \\
\text{1 eq} & \quad \text{br} \quad \text{71}\% \\
\text{2 eq} & \quad \text{br} \quad \text{89}\% \\
\text{SiMe}^2Ph & \quad \text{COOMe} \\
\text{SiMe}^2Ph & \quad \text{COOMe} \\
\end{align*}
\]

\[\begin{align*}
R & = \text{H, Me} \\
R & = \text{MeO, PhO, EtO, CH}_2\text{CHCOOH, CH}_2\text{CH}_2\text{CMe(Me)COO} \\
\end{align*}\]

\[
\begin{align*}
\text{Scheme 2.} \\
\text{excess} & \quad 1, \text{HSiMe}^2\text{Ph} \\
\text{2eq} & \quad \text{br} \quad \text{89}\% \\
\text{SiMe}^2\text{Ph} & \quad \text{COOMe} \\
\text{SiMe}^2\text{Ph} & \quad \text{COOMe} \\
\end{align*}
\]

\[\begin{align*}
R & = \text{H, Me} \\
R & = \text{MeO, PhO, EtO, CH}_2\text{CHCOOH, CH}_2\text{CH}_2\text{CMe(Me)COO} \\
\end{align*}\]

Conclusion

As described above, we have developed new preparative methods for polybutylene oxides and polycyclohexene oxides bearing various ester functions at the polymer terminus by reaction of R\(_3\)SiO-[(CH\(_2\))\(_n\)]-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\) 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 silylo 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; \(\delta\) 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\(_{17}\)H\(_6\) and C\(_{18}\)D\(_6\) were distilled from sodium benzenophenone 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\(_2\))\(_n\)]-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\) with acetyl chloride. To a solution of PhMe\(_2\)SiO-[(CH\(_2\))\(_n\)]-CH\(_2\)CH\(_2\)CH\(_2\)CH\(_3\) \([M_n(SEC)= 1900, M_d(SEC)= 4500, M_d/M_n = 1.4]\) (0.244g, 0.13 mmol) dissolved in C\(_{6}\)H\(_6\) (1.6 mL) was added acetyl chloride (20 \(\mu\)L, 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 \(-35 ^\circ \text{C}\). 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 \((M_e\text{ of the butyl terminal vs. } \text{CH}_2\text{OAc})\) gave an average molecular weight of 2400. The SEC analysis showed \(M_n= 5200, M_d/M_n = 1.3\).

\[^1\text{H(CDCI}_3]\): \(\delta 0.89\) (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$_3$), 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(CDC$_3$): 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$_3$), 64.3 (COOCH$_2$), 70.5 (OCH$_2$ in polymer chain), 171.1 (CO), IR(CH$_2$Cl$_2$): 1733 cm$^{-1}$.

**Reaction of PhMe$_2$SiO-$[$(CH$_2$)$_4$]$_n$-$CH_2$CH$_2$CH$_2$CH$_3$ with adipoyl chloride.** In a 5 mm $^3$ NMR tube, a mixture of PhMe$_2$SiO-$[$(CH$_2$)$_4$]$_n$-$CH_2$CH$_2$CH$_2$CH$_3$ [M$_d$(NMR)= 1900, M$_d$(SEC)= 4500, M$_r$/M$_w$ = 1.4] (0.127g, 0.07mmol), adipoyl chloride (5[$\mu$L, 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 from the liquid phase and subjected to NMR and SEC analysis. The integral ratio (Me of the butyl terminal vs. CH$_2$OAdipoyl) gave an average molecular weight of 4400. The SEC analysis showed M$_w$ = 7100, M$_r$/M$_w$ = 1.5.

$^1$H(CDC$_3$): 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(CDC$_3$): 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$_2$): 1729 cm$^{-1}$.

**Reaction of PhMe$_2$SiO-$[$(CH$_2$)$_4$]$_n$-$CH_2$CH$_2$CH$_2$CH$_3$ with 2-bromoisobutyryl bromide.** To a solution of PhMe$_2$SiO-$[$(CH$_2$)$_4$]$_n$-$CH_2$CH$_2$CH$_2$CH$_3$ [M$_d$(NMR)= 2200, M$_d$(SEC)= 6400, M$_r$/M$_w$ = 1.5] (1.10g, 0.5 mmol) dissolved in C$_6$H$_6$ (7.0 mL) was added 2-bromoisobutyryl bromide (125 [$\mu$L, 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 precipitate was dissolved in diethyl ether (0.4 mL) and was purified by precipitation from the liquid phase (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$_2$OAcryloyl) gave an average molecular weight of 2300. The SEC analysis showed M$_w$ = 5500, M$_r$/M$_w$ = 1.3.

$^1$H(CDC$_3$): δ 0.89 (t, J = 7.4 Hz, 3H), 1.34 (m, 2H),...
1.51 (m, 2H), 1.61 (bs, CH₂ in polymer chain), 3.41 (bs, OCH₂ in polymer chain), 4.15 (t, J = 6.5 Hz, 2H), 5.81 (dd, J = 1.5 Hz, 10.5 Hz, 1H, CH₂=), 6.10 (dd, J = 10.5 Hz, 17.3 Hz, 1H, =CHCO), 6.32 (dd, J = 1.5 Hz, 17.3 Hz 1H, CH₂=). 

Block copolymerization of CH₂=CH₂CH₃CH₂-[O(CH₃)₂]₄-OOC-CBr(Me)₂ with methyl methacrylate (MMA) [MMA: macroinitiator: CuBr: C₆H₅-bipy= 134: 1: 0.94: 2.1:1]. The reaction was carried out according to the literature method. A mixture of PolyTHF-CBr(Me)₂ [M₆(NMR)= 3000, M₆(S)EC= 4400, M₆/M₅= 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. M₆= 17800), M₅/M₆ = 1.4. After precipitation from THF-methanol, SEC analysis showed M₆ = 23,000, M₅/M₆ = 1.1 [cf. K. Matyaszaszkiewicz, 6a] M₅(Polybutylene oxide) = 15,400, M₆(block copolymer) = 56,700, M₆(calc)= 35,000.

Block copolymerization of polycyclohexene oxide-CBr(Me)₂ with methyl methacrylate (MMA) [MMA: [pyCyclExOx-Br]: CuBr: C₆H₅-bipy= 459: 1: 1.3: 2]. A mixture of polycyclohexene oxide-CBr(Me)₂ [M₆(NMR)= 5000, M₆(S)EC= 9200, M₅/M₆= 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 species to give 0.48g of copolymer (89%). The SEC analysis showed M₆ = 58,000 (calcd. M₆= 50,000), M₅/M₆= 2.0. After precipitation from THF-methanol, SEC analysis showed M₆ = 58,000, M₅/M₆= 2.0.

References and Notes
16) Liberation of THF suggests decomposition of the product, and in fact, the polymer formed at 60°C had a lower molecular weight than that formed with PhCOBr at room temperature.

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