# Anionic Alternating Copolymerizability of Epoxide and 3,4-Dihydrocoumarin by Imidazole

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ABSTRACT: This paper describes the alternating character in the copolymerization of glycidyl phenyl ether (GPE) and 3,4-dihydrocoumarin (DHCM) by 2-ethyl-4-methylimidazole (EMI) as an initiator. DHCM, which is an aromatic lactone that does not undergo its homopolymerization under anionic conditions, underwent the copolymerization with GPE by EMI. In the present copolymerization, formation of the GPE−DHCM alternating sequence and that of the GPE−GPE sequence competed, and the former was always the predominant one. The maximum content of the alternating sequence (90%) was achieved when the feed ratio GPE/DHCM was 1. The obtained copolymer was a polyester, for which the ester linkage was cleavable by reduction with lithium aluminum hydride. The resulting compound inherited the structure of the alternating sequence, and its high yield (90%) supported the high alternating character of the copolymerization.

## Introduction

Epoxide is one of the most important monomers for practical applications such as adhesive, sealant, and coating. One of the reasons for the broad range of applicability of epoxide is the wide variety of its polymerization systems. Copolymerizations of epoxide with other monomers are further attractive strategy to create new application fields of epoxy monomers, because proper molecular designs of the comonomers will give us opportunity to create various main chain structures which are totally different from that of the epoxy homopolymer and would bring about drastic change in the chemical and physical properties.[1−4]

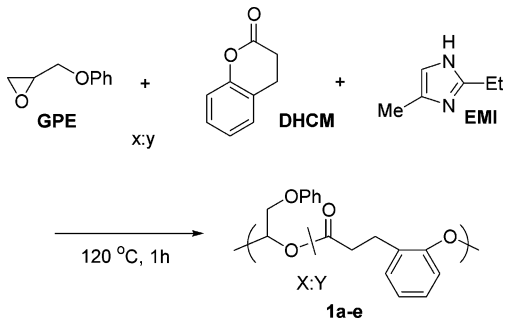
One of our research interests has been focused on development of new compounds that copolymerize with epoxide. We have reported the alternating copolymerization of epoxide and spirocyclic bislactones by potassium *tert*-butoxide as an initiator.[5] Our current specific target is the epoxy-imidazole curing system, which is based on imidazole-initiated anionic polymerization of epoxide. This curing system is widely applied to the bonding of electro devices,[6] coatings,[7] structural adhesives,[8] and fabrication of nanocomposite materials.[9] Recently, we have reported that addition of 3,4-dihydrocoumarin (DHCM), an aromatic lactone, to the system resulted in remarkable improvement of the physical properties of the corresponding cured materials, such as curing shrinkage, glass transition temperature, and adhesion strength.[10] Besides these practical aspects, we found another striking fact that DHCM did not undergo its homopolymerization by imidazole but was efficiently consumed in the epoxy−imidazole curing system.

This paper describes detailed investigation on the copolymerization behavior with clarifying the structure of the copolymer and the corresponding mechanism for its formation. The essential point discussed herein is the alternating character in the copolymerization.

## Results and Discussion

**1. Copolymerization Behavior.** Prior to the investigation on the copolymerization of GPE and DHCM (Scheme 1), the homopolymerization behaviors of these two monomers were studied. Homopolymerization of GPE by 1 mol % EMI was carried out at 120 °C in bulk, with monitoring the conversion of GPE with GC. The corresponding time−conversion relationship is shown in Figure 1a. The polymerization was quite slow, and the conversion reached only 22% for 60 min of reaction. The formed polymer **1a** was isolated by precipitation with hexane, and was analyzed by size exclusion chromatography (SEC). By this analysis, number and weight-average molecular weights ($M_n$ and $M_w$) of **1a** were estimated to be 620 and 820, respectively (Table 1, entry 1). On the other hand, DHCM did not undergo homopolymerization: A bulk mixture of DHCM and EMI (1 or 5 mol %) was heated at 120 °C; however, no reaction took place. Even though the reaction temperature was varied from 80 to 180 °C, no change was detected by $^1$H NMR analysis of the mixture. Finally, an equimolar mixture of DHCM and EMI was heated at 120 °C for 1 h; however, DHCM was robust.

**Scheme 1**




In contrast to these homopolymerization behaviors, these two monomers exhibited much higher reactivity in the copolymerization. The conditions were same as those for the homopolymerization of GPE (at 120 °C, $[EMI]_0 = 0.01([GPE]_0+[DHCM]_0)$). In our previous report, the copolymerization was performed at 100 °C using 5 mol % EMI.[10] However, due to the high initial concentration of EMI, significant heat evolution occurred to promote the copolymerization without reproducibility. To prevent such excessive heat evolution and ensure the reproducibility in experiment, the initial amount of EMI was reduced to 1 mol %, and accordingly, the

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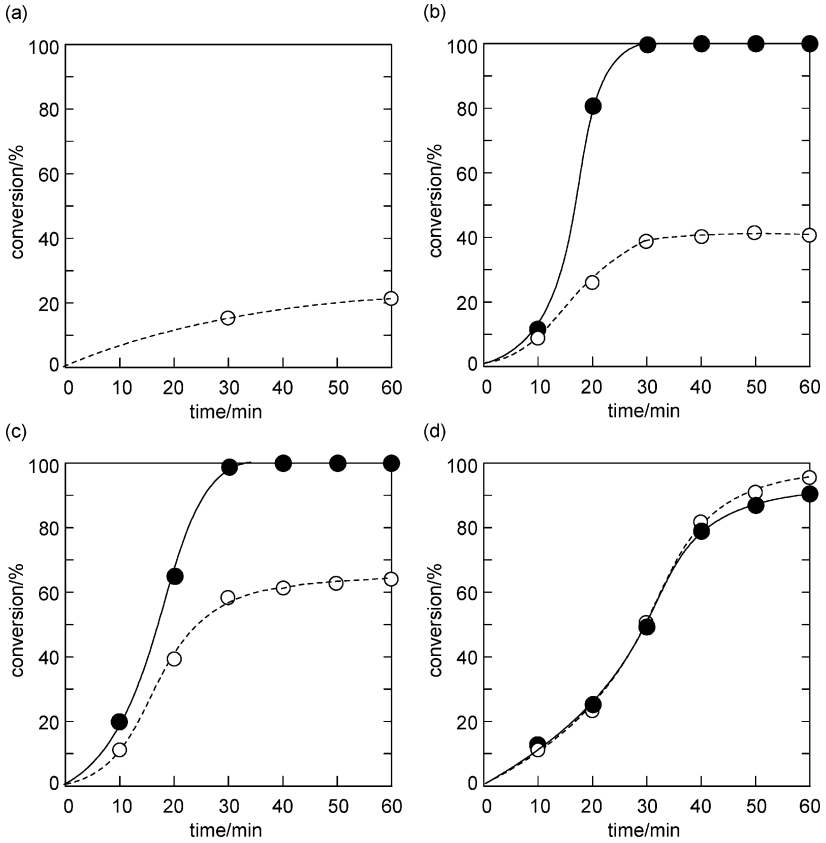



**Figure 1.** Time−conversion plots for (a) the homopolymerization of GPE, and the copolymerizations with (b) feed ratio $[GPE]_0$:$[DHCM]_0$ = 85:15, (c) feed ratio $[GPE]_0$:$[DHCM]_0$ = 70:30, and (d) feed ratio $[GPE]_0$:$[DHCM]_0$ = 50:50.

**Table 1. Copolymerization of GPE and DHCM**

| run | feed ratio GPE:DHCM | conversion/%[a] GPE | conversion/%[a] DHCM | polymer | yield/%[b] | composition[c] GPE:DHCM | $M_n$[d] | $M_w$[d] |
|---|---|---|---|---|---|---|---|---|
| 1 | 100:0 | 23 | | **1a** | 22 | 100:0 | 720 | 970 |
| 2 | 85:15 | 43 | >99 | **1b** | 52 | 78:22 | 960 | 1280 |
| 3 | 70:30 | 64 | >99 | **1c** | 77 | 63:37 | 1170 | 1780 |
| 4 | 50:50 | 95 | 90 | **1d** | 96 | 51:49 | 1380 | 2060 |
| 5 | 30:70 | >99 | 43 | **1e** | 38 | 49:51 | 1220 | 1620 |
| 6 | 0:100 | | 0 | no polymerization | | | | |

[a] Determined by GC. [b] Because of high viscosity of the polymer, a small amount of the solvent was not completely removed. [c] Evaluated by $^1$H NMR analysis. [d] Estimated by SEC (eluent: THF, Pst-standards).

polymerization temperature was raised to 120 °C to compensate the reduced reactivity of the system caused by utilization of the reduced amount of EMI. When the copolymerization was carried out with a feed ratio $[GPE]_0$:$[DHCM]_0$ = 85:15, conversion of GPE reached 43% for 60 min, while DHCM was completely consumed within 30 min (Figure 1b). Increasing the DHCM content to 30% and 50% resulted in remarkable increase in the GPE conversion (Figure 1c,d), and accordingly, the molecular weight of the formed polymer increased (Table 1, entries 2−4). When the feed ratio was 50:50, GPE and DHCM were consumed almost in the same rate suggesting alternating character of the copolymerization. This character was also suggested by the fact that the content of DHCM-unit in the copolymer was always higher than that expected from the feed ratio (except entry 5). In entry 5, copolymerization was carried out with a feed ratio [GPE]:[DHCM] = 30:70. In this case, GPE was totally consumed and the same amount of DHCM was also consumed by its copolymerization with GPE. The rest of DHCM remained unconsumed due to the lack of homopolymerization ability, in other word, lack of ability to give the DHCM−DHCM sequence.

**2. Spectroscopic Analyses of the Copolymers.** In the copolymerization, incorporation of the DHCM-derived unit into the main chain by successful copolymerization was confirmed by IR absorption at 1735 $cm^{-1}$ and $^{13}$C NMR signal at 172 ppm of the copolymers.

Further detailed structural analyses of the obtained polymers **1a**−**d** were examined using their $^1$H NMR spectra (Figure 2). In comparison to the $^1$H NMR spectrum for the homopolymer **1a** (Figure 2a), those for the copolymers indicated characteristic signals at 2.6 and 2.9 ppm (Figure 1b−d), which were attributable to the two methylene groups derived from DHCM. In addition, the spectra for the copolymers indicated two signals at 5.3 and 5.5 ppm. On the basis of these chemical shifts, it was speculated that these signals would be assigned to methine protons, which were located on carbon attached to acyloxy group. Such methine protons would be exist in the possible sequences, DHCM−GPE−DHCM (sequence A having methine proton $H^a$) and GPE−GPE−DHCM (sequence B having methine proton $H^b$) (see the formula in Figure 2). Formation of DHCM−DHCM sequence would be not allowed because DHCM did not undergo its homopolymerization. $H^a$ appeared

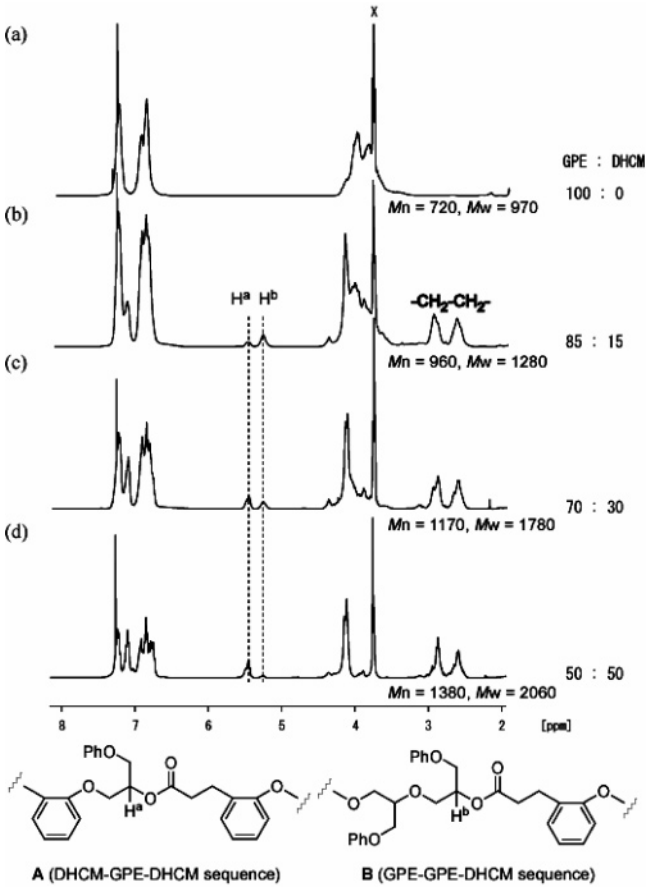



**Figure 2.** $^1$H NMR spectra of the obtained polymers: (a) **1a**, (b) **1b**, (c) **1c**, and (d) **1d**.

in slightly lower magnetic field than $H^b$ presumably due to the presence of the DHCM-derived aryl ether linkage in the main chain of the sequence A, which would be more electron negative than the GPE-derived alkyl ester linkage in that of the sequence B. The intensity ratio between the two signals for $H^a$ and $H^b$ depended on the monomer feed ratio for the copolymerization. The larger the relative amount of DHCM was, the stronger the relative intensity of $H^a$ to $H^b$ became. This means that the increase in the relative amount of DHCM would suppress the formation of GPE−GPE sequence and enhance the formation of the sequence A, the alternating sequence of the two monomers.

**3. Reductive Cleavage of the Copolymers.** As was confirmed by the spectroscopic analyses, the copolymers were polyesters, of which ester linkage could be easily cleaved by various methods such as hydrolysis and reduction, to give the corresponding fragments that would inherit the sequences in the copolymers. We examined reductive cleavage of the copolymers **1b**−**d** with $LiAlH_4$ (Scheme 2). Reduction of the copolymer **1b** (composition: GPE:DHCM = 85:15) resulted in complete cleavage of the ester linkage in the main chain (Table 2, entry 1). The resulting mixture contained diols **2**, **3**, which were isolated by preparative HPLC in 24% and 36% yield, respectively. $^1$H− and $^{13}$C NMR analyses of the diols confirmed that **2** and **3** were derived from the (GPE)−*DHCM*−*GPE*−(DHCM) sequence and the (GPE)−*DHCM*−*GPE*−*GPE*−(DHCM) sequence, respectively. The other products were oligomers, which were derived from longer GPE sequences. As the DHCM content of the copolymer increased, yield of **2** increased and that of **3** decreased (Table 2, entries 2 and 3): Reduction of **1d** gave **2** in 90% yield, confirming that the

**Scheme 2**

Predominant sequences in the copolymers **1b-d**

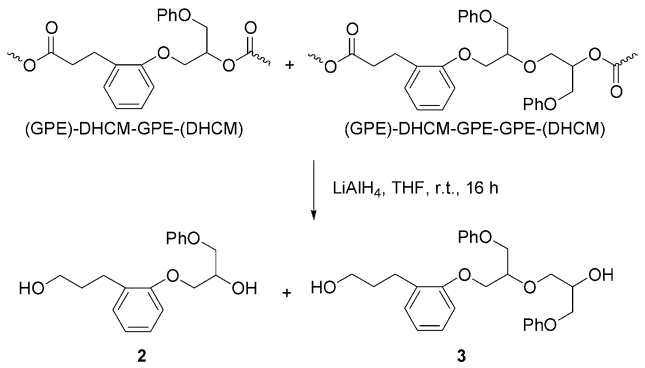



**Table 2. Reductive Degradation of the Copolymers with $LiAlH_4$**

| run | copolymers | yield of **2**/% | yield of **3**/% |
|---|---|---|---|
| 1 | **1b** | 24 | 36 |
| 2 | **1c** | 64 | 21 |
| 3 | **1d** | 90 | ∼0 |

copolymerization was not a statistic one but an alternating one, which gave the (GPE)−*DHCM*−*GPE*−(DHCM) sequence in high probability.

**4. Mechanism for the 1:1 Alternating Tendency.** Scheme 3 shows possible reaction pathways involved in the copolymerization. As was demonstrated by the attempt of the equimolar reaction of DHCM and EMI, EMI does not react with DHCM, and thus this reaction would not be involved in the initiation step. Therefore, EMI should react with GPE first. It has been reported that a 1:2 EMI−GPE adduct would be the initiating species in the homopolymerization of GPE using EMI:[11] Nucleophilic attack of EMI to GPE would give the corresponding 1:1 EMI−GPE adduct, which would react with another GPE successively to give the corresponding 1:2 EMI−GPE adduct. This adduct has a zwitterionic structure, of which alkoxide would be the initiator for the copolymerization.

In the propagation step, the intrinsic nature of the alkoxide would force it to choose DHCM rather than GPE as a preferable monomer, leading to the formation of the corresponding phenoxide (**II**) (=step A). Selectivity in this step, i.e., which monomer is chosen, would depend on the initial feed ratio $[GPE]_0$:$[DHCM]_0$. Under the GPE-rich conditions, the alkoxide

**Scheme 3**

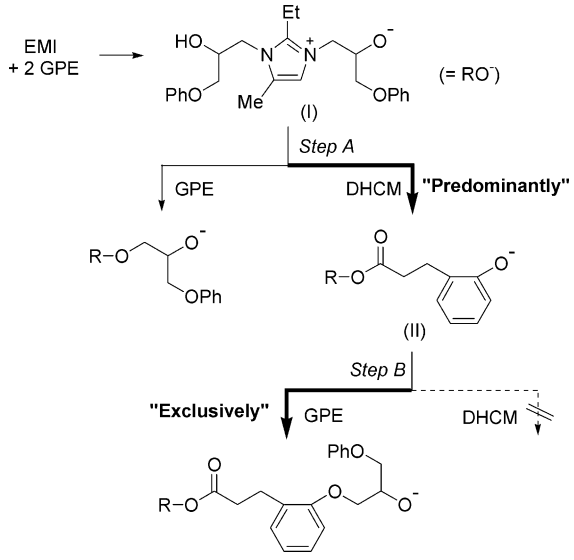
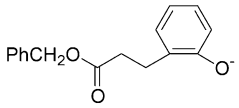
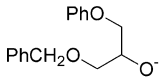
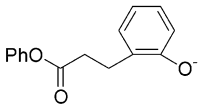
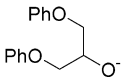


**Table 3. Semiempirical Molecular Orbital Calculations (PM3) for Model Reactions for the Propagation Reactions of the Copolymerization**

| entry | reactants | $H_{reactants}$ (kJ/mol)[a] | product | $H_{product}$ (kJ/mol)[b] | $\Delta H$ (kJ/mol)[c] |
|---|---|---|---|---|---|
| 1 | $PhCH_2O^-$ + DHCM | -341.6 |  | -497.4 | -156 |
| 2 | $PhCH_2O^-$ + GPE | -151.2 |  | -294.9 | -144 |
| 3 | $PhO^-$ + DHCM | -441.6 |  | -470.6 | -29.0 |
| 4 | $PhO^-$ + GPE | -251.2 |  | -319.5 | -68.3 |

[a] $H_{reactants}$ is the sum of the heat of formation of the starting materials. [b] $H_{product}$ is the heat of formation of the product. [c] $\Delta H = H_{product} - H_{reactants}$.

would be allowed to choose GPE as a reaction counterpart of it. This explanation was supported by our computational calculations (vide infra). Step A would be followed by step B, which is a nucleophilic reaction of the phenoxide (**II**) with GPE. In this step, **II** does not react with DHCM at all, and exclusively reacts with GPE to give the corresponding alkoxide. Repetition of step A with predominant choice of DHCM and step B with the exclusive choice of GPE affords the copolymer, which is rich in the GPE−DHCM alternating sequence.

As was discussed above, DHCM is a unique lactone, which exhibits no homopolymerization ability but undergoes the copolymerization with GPE efficiently. This unique reactivity should be arisen by the structural feature of DHCM: DHCM is a sort of masked phenols, which produces a phenoxide-type propagating species by its nucleophilic ring-opening reaction. Generally, phenoxide is a good leaving group for nucleophilic substitution reaction, permitting DHCM to exhibit a high reactivity toward alkoxide-type propagating species. On the other hand, in the reaction of phenoxide with ester of phenol, there is no advantage in terms of enthalpy in general, because this reaction gives a combination of phenoxide and ester of phenol again. This general consideration allows us to estimate that the phenoxide in the propagating chain end would not react with DHCM efficiently. In fact, phenol did not react with DHCM in the presence of EMI, while benzyl alcohol reacted with DHCM to give the corresponding adduct **4** (see the Supporting Information).

**5. Computational Calculations.** In order to help our understanding of the experimental results, semiempirical molecular orbital calculations for some model reactions for the propagating steps were performed. As models for the propagating chain ends in the copolymerization, phenoxide and benzylalkoxide were chosen. These two anionic species were combined with GPE and DHCM as reactants into four sets of reactions. For each of these reactions, the sums of the heats of formation of the reactants ($=H_{reactants}$) and that of the product ($=H_{product}$) were calculated. From these values, the enthalpy change that accompanies the reaction, $\Delta H$ ( $= H_{product} - H_{reactants}$), was obtained. The obtained $H_{reactants}$, $H_{product}$, and $\Delta H$ values are listed in Table 3. In all cases, the $\Delta H$ values were evaluated as negative values; i.e., they should be exothermic ones.

$\Delta H$ for the reaction of benzylalkoxide and DHCM was −156 kJ/mol (entry 1), while that for the reaction of benzylalkoxide and GPE was −144 kJ/mol (entry 2), suggesting that both of these two reactions could proceed smoothly and compete with each other, but the former reaction would proceed rather faster. These virtual reactions simulates step A in Scheme 3, and the calculation results are in good accordance with our consideration that the alkoxide-type propagating species would react with DHCM predominantly but not exclusively as was discussed in the former section.

On the other hand, $|\Delta H|$ for the reaction of phenoxide and DHCM was 29.0 kJ/mol (entry 3), supporting the experimental results that DHCM did not reacted with phenol in the presence of EMI. In addition, this value was smaller than the $|\Delta H|$ value of 68.3 kJ/mol for the reaction of phenoxide and GPE (entry 4), and this significant difference in the $|\Delta H|$ values (68.3 − 29.0 = 39.3 kJ/mol) supported our consideration that the phenoxide-type chain end would react with GPE exclusively as shown in step B in Scheme 3.

## Summary

The imidazole-initiated copolymerization of GPE and DHCM was studied in detail. The propagating species were alkoxide-type and phenoxide-type, which were formed by the nucleophilic ring opening reactions of GPE and DHCM, respectively. The former one reacted with DHCM predominantly while the latter reacted with GPE exclusively, leading to formation of the GPE−DHCM alternating sequence with high probability. The present results gave fundamental knowledge for our ongoing works, such as (1) further improvement of the selectivity in monomer discrimination in the propagating reaction, (2) designing new DHCM derivatives, and (3) development of new curable systems for high performance adhesives and coating materials.

## Experimental Section

**Materials.** All reagents and solvents were used as received. Benzyl alcohol was obtained from Kishida Chemical Co. Ltd. Glycidyl phenyl ether (GPE), 3,4-dihydrocoumarin (DHCM), 2-ethyl-4-methylimidazole (EMI), phosphate buffer powder (pH = 7.4), phenol, $LiAlH_4$, and the other solvents were purchased from Wako Pure Chemical Industries.

**Measurements.** NMR spectra (400 MHz for $^1H$, $\delta_{CHCl_3} = 7.26$ ppm; 100.6 MHz for $^{13}C$, $\delta_{CHCl_3} = 77.00$ ppm; 79.5 MHz for $^{29}Si$,

$\delta_{TMS} = 0.00$ ppm) were obtained on a Varian NMR spectrometer model Unity INOVA. Chemical shift $\delta$ and coupling constant $J$ are given in ppm and Hz, respectively. IR spectra were obtained on a JASCO FT/IR-460 plus. MS spectra were measured on a Bruker BioAPEX70e. Number-average molecular weight ($M_n$) and weight-average molecular weight ($M_w$) were estimated from size exclusion chromatography (SEC), performed on a Tosoh chromatograph model HLC-8120GPC equipped with Tosoh TSK gel-Super HM-H styrogel columns (6.0 mm $\phi \times$ 15 cm), using THF as an eluent at a flow rate of 0.6 mL/min after calibration with polystyrene standards. Preparative SEC was performed on a Japan Analytical Industry (JAI) LC-908 system equipped with a combination of JAIGEL-1H and 2H styrogel columns (20 mm o.d. $\times$ 60 cm), using chloroform as an eluent with a flow rate of 3.0 mL/min. Consumption of monomers during the polymerization process was monitored by Shimadzu gas chromatograph model GC-18A equipped with J&W Scientific DB-WAXETR 125−7332 (0.53 mm $\times$ 30 m) capillary column.

**Copolymerization of GPE and DHCM in the Presence of EMI.** Typical procedure: To a mixture of GPE (1.01 g, 6.70 mmol) and DHCM (0.995 g, 6.72 mmol) was added EMI (20.2 mg, 0.183 mmol). The resulting mixture was stirred at 120 °C for 1 h. After the reaction, the crude product was dissolved in tetrahydrofuran (THF) (10 mL), and the solution was poured into hexane (300 mL) to precipitate the obtained polymer. The polymer (**1d**: 1.93 g, $M_n = 1380$, $M_w = 2060$) purified by reprecipitation was obtained in 96% yield. $^1$H NMR (in $CDCl_3$, at 20 °C): 7.30−7.19 (br, 2H), 7.12−7.08 (br, 2H), 6.94−6.73 (br, 5H), 5.52−5.41 and 5.28−5.20 (br, 1H), 4.19−4.08 (br, 5H), 2.92−2.83 (br, 2H), 2.69−2.49 (br, 2H). $^{13}$C NMR (in $CDCl_3$, at 20 °C): 172.2, 158.1, 155.9, 130.0, 129.3, 128.4, 127.5, 121.0, 120.8, 114.4, 111.2, 70.2, 65.8, 33.8, 25.9. IR (KBr): 1735 (−C(=O)−O−), 1241 (Ph−O−$CH_2$), 753 (*o*-Ph), 692 (Ph) cm$^{-1}$.

The kinetics for the copolymerization was studies by performing the same experiment in another batch, in the presence of butyl phenyl ether as an internal standard (91.4 mg, 0.608 mmol). Every 10 min, a small amount of the reaction mixture (less than 5 mg) was taken and dissolved in chloroform. The solution was analyzed with GC to determine the conversions of GPE and DHCM.

**Reductive Cleavage of the Copolymers with $LiAlH_4$.** Typical procedure: To a suspension of $LiAlH_4$ (0.445 g, 11.6 mmol) in THF (10 mL) was added a solution of **1b** (0.402 g) in THF (20 mL) at 0 °C, and the resulting mixture was stirred at room temperature. After 16 h, the solution was carefully poured into a phosphate buffer solution (400 mL, pH = 7.4) at 0 °C. The mixture was extracted with ethyl acetate (500 mL), and the organic layer was washed by distilled water, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was fractionated with preparative SEC to give **2** (0.0725 g, 0.240 mmol; 24%) and **3** (0.1408 g, 0.311 mmol; 36%). **2**: colorless oil; $^1$H NMR ($CDCl_3$, 20 °C) 7.31−7.26 (m, 2H), 7.20−7.15 (m, 2H), 6.99−6.85 (m, 5H), 4.44−4.37 (m, 1H), 4.22−4.11 (m, 4H), 3.92 (br, 1H), 3.59, (t, 2H, $J = 5.6$ Hz), 2.85−2.73 (m, 2H), 2.28 (br, 1H), 1.81 (quintet, 2H, $J = 5.6$ Hz); $^{13}$C NMR (in $CDCl_3$, at 20 °C) 158.3, 156.3, 130.4, 130.1, 129.4, 127.0, 121.0, 120.2, 114.4, 111.1, 68.9, 68.6, 68.5, 60.9, 33.3, 25.5; IR (neat) 3365, 1240, 753, 692 cm$^{-1}$. EI−MS (*m/e*) [M]$^+$: 302.1521 (calcd 302.1518). **3**: colorless oil; $^1$H NMR ($CDCl_3$, 20 °C) 7.30−7.23 (m, 4H), 7.17−7.13 (m, 2H), 6.98−6.84 (m, 8H), 4.38−3.71 (m, 11H), 3.55−3.43 (m, 2H), 3.16 (br, 1H), 2.88−2.81 and 2.74−2.67 (two br, 2H), 1.93−1.82 (br, 2H) and 1.79−1.67 (br, 2H); $^{13}$C NMR (in $CDCl_3$, at 20 °C) 158.5, 158.2, 156.2, 130.6, 129.9, 129.5, 129.5, 129.5, 129.4, 127.2, 121.5, 121.3, 121.2, 121.0, 120.9, 114.5, 111.1, 77.3, 72.8, 72.1, 69.1, 68.5, 68.1, 67.4, 66.7, 66.5, 60.7, 33.3, 25.1; IR (neat) 3418, 1242, 753, 691 cm$^{-1}$. EI−MS (*m/e*) [M]$^+$: 452.2216 (calcd 452.2199).

**Computational Calculations.** Semiempirical molecular orbital calculations were performed based on Parametrization Method 3 (PM3) using the Spartan '06 calculation program package.

**Acknowledgment.** This work was financially supported from Henkel KGaA in Germany.

**Supporting Information Available:** Figures showing the $^1$H NMR spectra of **2** and **3**, text and schemes giving the procedure for the EMI-catalyzed reaction of DHCM and benzyl alcohol, and a figure showing the $^1$H NMR spectrum of the resulting adduct **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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