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# Synthesis and Stabilization of Novel Aliphatic Polycarbonate from Renewable Resource

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ABSTRACT: A novel aliphatic polycarbonate from renewable resource was prepared by copolymerization of furfuryl glycidyl ether and $CO_2$ using rare earth ternary catalyst; its number-average molecular weight ($M_n$) reached $13.3 \times 10^4$ g/mol. The furfuryl glycidyl ether and $CO_2$ copolymer (PFGEC) was easy to become yellowish at ambient atmosphere due to postpolymerization cross-linking reaction on the furan ring; the gel content was 17.2 wt % after 24 h exposure to air at room temperature. PFGEC could be stabilized by addition of antioxidant 1010 (tetrakis[methylene (3,5-di(*tert*-butyl)-4-hydroxyhydrocinnamate)]methane) in 0.5−3 wt % after copolymerization. The Diels−Alder (DA) reaction between *N*-phenylmaleimide and the pendant furan ring was also effective for the stabilization of PFGEC by reducing the amount of furan ring and introducing bulky groups into PFGEC. The cyclization degree could reach 72.1% when the molar ratio of *N*-phenylmaleimide to furan ring was 3:1, and no gel was observed after 24 h exposure to air. The glass transition temperature ($T_g$) of PFGEC was 6.8 °C, and it increased to 40.3 °C after DA reaction (molar ratio of *N*-phenylmaleimide to furan ring was 3:1). A third way was also conducted to solve the air instability of PFGEC, where tetrahydrofurfuryl glycidyl ether, a hydrogenated furfuryl glycidyl ether, was used instead of furfuryl glycidyl ether for air-stable polycarbonate, and a copolymer with $M_n$ of $7.7 \times 10^4$ g/mol and $T_g$ of −5.7 °C was synthesized.

## Introduction

Since the pioneering work from Inoue on the copolymerization of propylene oxide (PO) and carbon dioxide,[1] great progress has been achieved in the copolymerization of carbon dioxide with PO or cyclohexene oxide (CHO),[2−6] especially in catalyst design and polymerization method. Relatively less attention, however, has been paid to the choice of epoxide,[7] especially that from renewable resources, although over 60% cost of carbon dioxide−epoxide copolymer comes from epoxide produced from petroleum. Recently, the non-petroleum route became important due to increasing concern on the heavy dependence of the polymer industry on petroleum. Coates and co-workers for the first time reported a non-petroleum route for carbon dioxide copolymer,[8] where limonene oxide derived from renewable natural product cyclic monoterpene was copolymerized with $CO_2$ using $\beta$-diiminate zinc complexes.

It is well-known that furanic monomers can be prepared by hydrolysis and acid−dehydration conversion of saccharides like hemicellulose and cellulose that are abundant in bagasse and comcob.[9] Furfuryl alcohol is a hydrogenation product of furfural,[10] which could react with epichlorohydrin to form furfuryl glycidyl ether employing sodium hydroxide and *tert*-butylammonium sulfate (TBAS) as catalysts. It should be noted that epichlorohydrin could be prepared from glycerine which is a byproduct in biodiesel refinery.[11] Therefore, copolymerization of $CO_2$ and furfuryl glycidyl ether may provide a non-petroleum route for carbon dioxide copolymer.

There are many reports indicating that polymer containing furan rings has the tendency to cross-link.[12] This is also true for PFGEC, a copolymer of $CO_2$ and furfuryl glycidyl ether; it is unstable at ambient atmosphere and easily becomes yellowish. Therefore, stabilization of the copolymer was investigated, from the simple addition of antioxidants to the reduction of the furan ring through its Diels−Alder (DA) reaction with *N*-phenylmaleimide. Moreover, tetrahydrofurfuryl glycidyl ether, a hydrogenated product of furfuryl glycidyl ether, was used instead of furfuryl glycidyl ether to prepare air-stable copolymer.

## Results and Discussion

**Copolymerization of FGE and $CO_2$.** The copolymerization of $CO_2$ and FGE was carried out at 80 °C under 4 MPa for 10 h using $Y(CCl_3OO)_3-ZnEt_2-$glycerine as catalyst. The catalytic activity for $CO_2$ and FGE copolymerization was 1400 g/mol Zn, and $M_n$ of PFGEC was $13.3 \times 10^4$ g/mol. In the IR spectra of PFGEC, absorption peak characteristics of carbonyl and C−O−C of the carbonate group were observed around 1750 and 1260 $cm^{-1}$, indicating the existence of the carbonate structure in the copolymer.

Figure 1 shows the $^1H$ NMR spectra of PFGEC (a) and DA reaction products (b and c); the absorption peaks at 4.4 and 5.0 ppm were assigned to $CH_2$ and CH in the carbonate unit, which was consistent with the result from IR spectra, further indicating that the copolymerization did take place.

PFGEC displayed severe color change from ivory to yellow brown once it was exposed to air, accompanied by increasing insolubility in dichloromethane. The gel content

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was 17.2 wt % when it was exposed in air for 24 h at room temperature. Therefore, it was necessary to improve the air stability of PFGEC by reducing the gel content.

Considering that the cross-linking reaction at ambient atmosphere was due to the existence of furan ring in PFGEC, which may experience radical reaction. Therefore, antioxidant 1010 (tetrakis[methylene (3,5-di(*tert*-butyl)-4-hydroxyhydrocinnamate)] methane) was added to capture the radicals. Experiments were carried out at 40 °C to accelerate the cross-linking reaction, and the results are listed in Table 1.

As can be seen from Table 1, the color changed significantly from ivory to bright yellow after 24 h, and the gel content reached 32.2 wt %, which was much higher than that placed at room temperature. The gel content increased with increasing exposure time, it reached 55.1 wt % after 168 h, and the color changed to orange. Once antioxidant 1010 was added to PFGEC, the color change was slowed down, and the gel content was dramatically reduced. When 3 wt % antioxidant was added, the copolymer became stable without any color change over 168 h. Other antioxidants such as antioxidant 264 (2,6-di-*tert*-butyl-4-methylphenol) and antioxidant 350 (*N,N,N′,N′*-tetraphenyldiaminomethane) showed similar effect in stabilizing the copolymer.

Considering the dienic character of the furan ring, PFGEC was subjected to Diels−Alder reaction as shown in Scheme 1, aiming at reducing the active furan ring moiety in the copolymer.

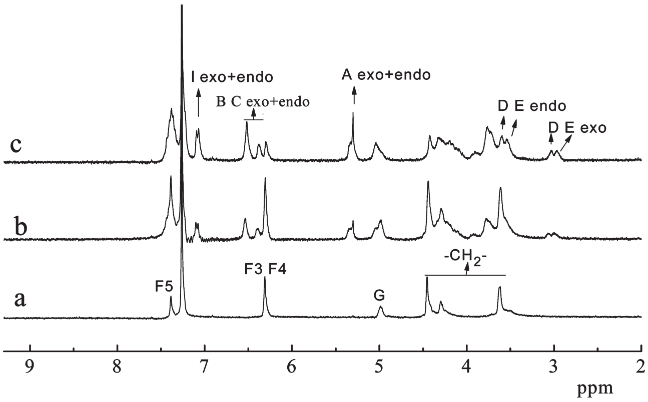


**Figure 1.** $^1$H NMR spectra of PFGEC (a); DA reaction products (b, c); the molar ratio of *N*-phenylmaleimide to the furan ring was 1:1 (b) and 3:1 (c), respectively.

In the IR spectra of the DA products, the absorption peaks characteristics of C═O stretching vibration at 1711 cm$^{-1}$ and C−N stretching vibration at 1383 cm$^{-1}$ were observed, indicating that the DA reaction took place. The $^1$H NMR spectra of the cycloaddition products are also shown in Figure 1b,c. When the molar ratio of *N*-phenylmaleimide to furan ring increased from 1:1 to 3:1, the peak characteristics of the DA products were enhanced, accompanied by the weakening of the peaks of the furan ring, indicating that the cyclization degree increased, and the amount of furan ring decreased. The characteristic absorption peaks of the exo- and endo-adducts were also observed in Figure 1b,c, where the peaks at 3.0 ppm were assigned to hydrogen atom D, E in the exo-adducts and the peaks at 3.5 ppm were assigned to hydrogen atom D, E in the endo-adducts, again indicating the occurrence of Diels−Alder reaction.

The content of carbonate unit in PFGEC (CU%) was calculated from the relative ratio of peak areas at 5.0 ppm to that at 6.4 ppm as shown in Figure 1 a, based on the following equation: CU% = $2A_{5.0}/A_{6.4}$, the CU% was approaching 99%. Therefore, the molar number of the furan ring nearly equaled to the carbonate unit in the copolymer. The cyclization degree can be calculated from $A_{7.1}/A_{5.0}$. It increased from 49.3% to 72.1% when *N*-phenylmaleimide/furan ring ratio was raised from 1:1 to 3:1.

As listed in Table 2, DA product b became more stable than the as-polymerized PFGEC. Meanwhile, products c and d can be completely dissolved in dichloromethane without any change in color even though they were exposed to ambient air for 24 h, indicating that no cross-linking reaction took place. The stability of the product was enhanced by increasing the cyclization degree, since the decrease in the furan ring could reduce the number of active hydrogen atoms causing cross-linking reaction. Moreover, the introduction of steric hindrance groups significantly weakened the cross-linking reaction. However, when more *N*-phenylmaleimide was used to raise the cyclization degree, it only showed a slight increase, instead a significant decrease in $M_n$ was observed. It dropped from 16.4 × 10$^4$ to 10.0 × 10$^4$ g/mol when the molar ratio of *N*-phenylmaleimide to the furan ring increased from 3:1 to 4:1. The reason may lie in the increasing basicity in the reaction system due to the high concentration of *N*-phenylmaleimide, which may break the carbonate bond in the main chain. The $T_g$ of the copolymer significantly changed after the DA reaction. It was 6.8 °C before the DA reaction, and it increased to 29.4 °C after the DA reaction

**Table 1. Influence of Antioxidant 1010 Amount on the Gel Content in PFGEC**[a]

| | | 24 h | | 96 h | | 168 h | |
|---|---|---|---|---|---|---|---|
| sample | antioxidant amount (wt %) | color | gel content (wt %) | color | gel content (wt %) | color | gel content (wt %) |
| 1 | 0 | bright yellow | 32.2 | yellow | 41.4 | orange | 55.1 |
| 2 | 0.5 | ivory | 0 | ivory | 8.1 | slight yellow | 9.0 |
| 3 | 1.0 | ivory | 0 | ivory | 3.3 | ivory | 3.9 |
| 4 | 3.0 | ivory | 0 | ivory | 0 | ivory | 0 |

[a] All samples were, at first, in ivory color and were placed at 40 °C for a certain period.

**Scheme 1. DA Reaction of PFGEC and *N*-Phenylmaleimide**

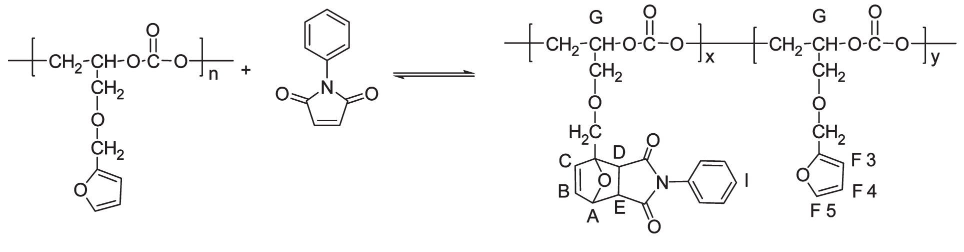
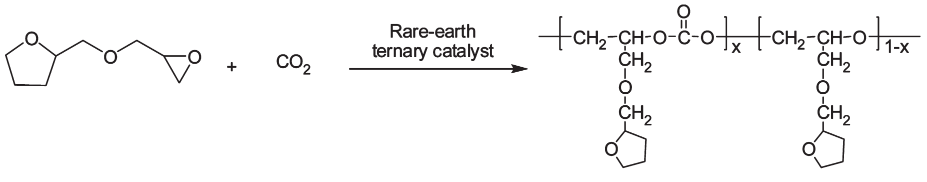


Table 2. Main Properties of the DA Products

| | | cyclization degree (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *N*-phenyl maleimide/furan ring (mol/mol) | $^1$H NMR[a] | EA[b] | $M_n$[c] × $10^{-4}$ (g/mol) | PDI $M_n/M_w$[c] | $T_g$[d] (°C) | color[e] | gel content[e] (%) |
| a | 0 | 0 | 0 | 13.3 | 3.24 | 6.8 | slight yellow | 17.2 |
| b | 1/1 | 49.3 | 47.9 | 15.4 | 3.79 | 29.4 | white | 5.8 |
| c | 3/1 | 72.1 | 68.9 | 16.4 | 3.82 | 40.3 | white | 0 |
| d | 4/1 | 74.3 | 70.1 | 10.0 | 4.92 | 39.2 | white | 0 |

[a] Determined by $^1$H NMR analysis. [b] Determined by elemental analysis. [c] Determined by GPC. [d] Determined by DSC. [e] Exposed at ambient atmosphere for 24 h.

Scheme 2. Copolymerization of TFGE and $CO_2$ for PTFGEC



TFGE PTFGEC

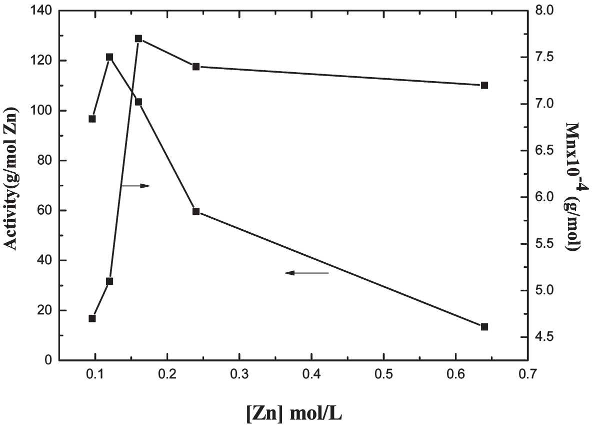


**Figure 2.** Influence of the catalyst concentration on the copolymerization of TFGE and $CO_2$. Reaction conditions: $P_{CO_2}$:4 MPa; reaction time: 10 h; temperature: 65 °C; 1,3-dioxolane: 5 mL; TFGE: 10 mL.

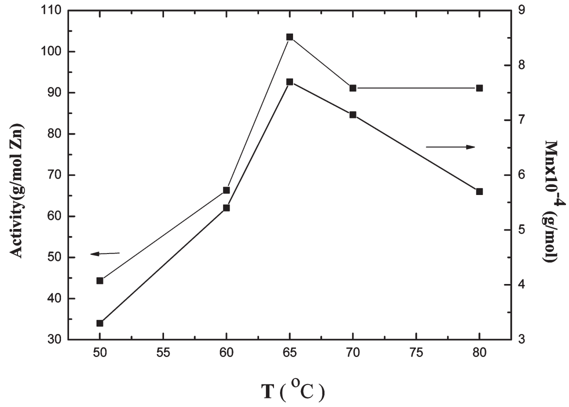


**Figure 3.** Influence of reaction temperature on copolymerization of TFGE and $CO_2$. Reaction conditions: $P_{CO_2}$: 4 MPa; reaction time: 10 h; $ZnEt_2$: 0.25 mL; 1,3-dioxolane: 5 mL; TFGE: 10 mL.

with the molar ratio of *N*-phenylmaleimide to the furan ring at 1:1; it became 40.3 °C when the molar ratio of *N*-phenylmaleimide to the furan ring was at 3:1, mainly due to the incorporation of polar groups after the DA reaction.

**Copolymerization of TFGE and $CO_2$.** In order to directly prepare air-stable copolymer, tetrahydrofurfuryl glycidyl ether (TFGE), a hydrogenated furfuryl glycidyl ether, was used as a new monomer, and aliphatic polycarbonate with pendant tetrahydrofurfuryl methyl ether (PTFGEC) was synthesized by copolymerization of $CO_2$ and TFGE using the $Y(CCl_3OO)_3-ZnEt_2-$glycerine coordination catalyst. In the IR spectrum of monomer TFGE, the absorption peaks at 1077 and 850 cm$^{-1}$ characteristics of C−O bond and monosubstituted ethylene oxide, respectively, were observed. In the $^1$H NMR spectrum of TFGE, the absorption peaks at 2.6, 2.7, and 3.2 ppm were assigned to $CH_2$ and CH in the monosubstituted ethylene oxide unit. The peaks between 3.4 and 3.7 ppm were characteristics of $CH_2$ and CH adjacent to the oxygen atom. The absorption peaks at 1.1 and 1.8 ppm were the absorption peaks of the hydrogen atoms in positions C3 and C4 in tetrahydrofuran, which was consistent with the TFGE structure. The absorption peaks characteristics of the carbonate unit in PTFGEC were observed, both from 1750 and 1260 cm$^{-1}$ in the FTIR spectrum and from 4.4 and 5.0 ppm in the $^1$H NMR spectrum, indicating that the copolymerization reaction as shown in Scheme 2 did occur. It should be noted that the copolymer was stable without any color change when it was exposed to air.

Figure 2 shows the influence of catalyst concentration on the copolymerization of TFGE and $CO_2$. At first, the catalytic activity and $M_n$ of PTFGEC increased with increasing catalyst concentration; however, both of them decreased with increasing catalyst concentration over 0.16 mol/L, probably due to degradation under a higher catalyst concentration. It should be noted that even under the same catalyst system the catalytic activity for PTFGEC was much lower than that for poly(propylene carbonate), mainly because of the steric hindrance of the bulky side chain.

The influence of polymerization temperature on the copolymerization of TFGE and $CO_2$ was studied and is shown in Figure 3. Both catalytic activity and $M_n$ reached maximum at 65 °C. Higher reaction temperature may cause depolymerization and degradation of PTFGEC, leading to a decrease in catalytic activity and $M_n$.

The catalytic activity increased with an increase in reaction time. $M_n$ of the copolymer reached a maximum after 10 h, while it decreased with a further increase in reaction time. The drop of $M_n$ after more than 10 h was probably due to the copolymer degradation in the presence of catalyst as reported by Kuran.[13] The influence of reaction pressure on

**Table 3. Influence of Reaction Time and Pressure on Copolymerization**[a]

| sample | time (h) | pressure (MPa) | activity (g polymer/ mol Zn) | carbonate linkages (%)[b] | $M_n^c \times 10^{-4}$ (g/mol) | PDI[c] ($M_w/M_n$) |
|---|---|---|---|---|---|---|
| 1 | 8 | 4.0 | 91.1 | 92.1 | 5.3 | 2.28 |
| 2 | 10 | 4.0 | 103.5 | 92.3 | 7.7 | 2.27 |
| 3 | 18 | 4.0 | 155.7 | 92.6 | 4.6 | 2.89 |
| 4 | 32 | 4.0 | 360.7 | 91.7 | 2.3 | 3.63 |
| 5 | 10 | 3.0 | 99.4 | 90.3 | 3.4 | 2.16 |
| 6 | 10 | 2.0 | 93.7 | 83.2 | 1.5 | 1.94 |

[a] Reaction conditions: temperature: 65 °C; 1,3-dioxolane: 5 mL; TFGE: 10 mL; $ZnEt_2$: 0.25 mL. [b] Determined by $^1H$ NMR spectroscopy. CU% = $A_{5.0}/A_{4.0}$. [c] Determined by GPC.

the carbonate linkage of PTFGEC is summarized in Table 3. Similar to the copolymerization of propylene oxide and $CO_2$, the carbonate linkage in PTFGEC decreased with decreasing pressure. It was 92.3% at 4 MPa and dropped to 90.3% at 3 MPa, and it became 83.2% at 2 MPa. The $T_g$ of PTFGEC was −5.7 °C, which was lower than that of PFGEC, since the tetrahydrofuran side chain in PTFGEC was more flexible than furan side chain in PFGEC, leading to decrease of $T_g$.

## Conclusion

Novel carbon dioxide copolymer was synthesized from renewable resource, where the copolymerization of FGE and $CO_2$ was realized through rare earth ternary coordination catalyst. The obtained copolymer was not air stable due to cross-linking reaction, but it can be stabilized by adding antioxidant or using Diels−Alder (DA) reaction. Moreover, air-stable PTFGEC was prepared through copolymerization of TFGE and $CO_2$, with $M_n$ of $7.7 \times 10^4$ g/mol and $T_g$ of −5.7 °C.

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**Supporting Information Available:** Experimental section, IR spectra of PFGEC and DA reaction products, IR spectra of the TFGE and PTFGEC, $^1H$ NMR spectra of the TFGE and PTFGEC. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) (a) Inoue, S.; Koinuma, H.; Tsuruta, T. *J. Polym. Sci., Part B: Polym. Lett.* **1969**, *7*, 287–292. (b) Inoue, S.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1969**, *130*, 210–220. (c) Inoue, S.; Koinuma, H.; Yokoo, Y.; Tsuruta, T. *Makromol. Chem.* **1971**, *143*, 97–104. (d) Inoue, S.; Kobayashi, M.; Koinuma, H.; Tsuruta, T. *Makromol. Chem.* **1972**, *155*, 61–73. (e) Kuran, W.; Pasynkiewicz, S.; Skupinska, J.; Rokicki, A. *Makromol. Chem.* **1976**, *177*, 11–20. (f) Hirano, T.; Inoue, S.; Tsuruta, T. *Makromol. Chem.* **1976**, *177*, 3237–3243. (g) Takeda, N.; Inoue, S. *Makromol. Chem.* **1978**, *179*, 1377–1381.

(2) For reviews, see: (a) Inoue, S. *Makromol. Chem. A* **1979**, *13*, 651–664. (b) Rokicki, A.; Kuran, W. *J. Macromol. Sci., Rev. Macromol. Chem.* **1981**, *21*, 135–196. (c) Darensbourg, D. J.; Holtcamp, M. W. *Coord. Chem. Rev.* **1996**, *153*, 155–174. (d) Super, M.; Beckman, E. J. *Macromol. Symp.* **1998**, *127*, 89–108. (e) Coates, G. W.; Moore, D. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6618–6639. (f) Sugimoto, H.; Inoue, S. *Pure Appl. Chem.* **2006**, *78*, 1823–1834.

(3) For examples of zinc-based catalysts, see: (a) Ree, M.; Bae, J. Y.; Jung, J. H.; Shin, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1863–1876. (b) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28*, 7577–7579. (c) Super, M.; Berluche, E.; Costello, C.; Beckman, E. *Macromolecules* **1997**, *30*, 368–372. (d) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019. (e) Darensbourg, D. J.; Holtkamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1999**, *121*, 107–116. (f) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (g) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 14284–14285. (h) Nakano, K.; Nozaki, K.; Hiyama, T. *J. Am. Chem. Soc.* **2003**, *125*, 5501–5510. (i) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924. (j) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S. I.; Yun, H. S.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037. (k) van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2005**, *38*, 7306–7313.

(4) For examples of Al-based catalysts, see: (a) Aida, T.; Inoue, S. *Macromolecules* **1982**, *15*, 682–684. (b) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8–13. (c) Chisholm, M. H.; Zhou, Z. *J. Am. Chem. Soc.* **2004**, *126*, 11030–11039.

(5) For examples of Co, Cr, and Cd-based catalysts, see: (a) Kruper, W. J.; Dellar, D. V. *J. Org. Chem.* **1995**, *60*, 725–727. (b) Darensbourg, D. J.; Niezgoda, S. A.; Draper, J. D.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 4690–4698. (c) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144–148. (d) Cohen, C. T.; Chu, T.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 10869–10878. (e) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005**, *127*, 14026–14038. (f) Peretti, K. L.; Ajiro, H.; Cohen, C. T.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127*, 11566–11567.

(6) For examples of other metal-based catalysts: (a) Chen, X. H.; Shen, Z. Q.; Zhang, Y. F. *Macromolecules* **1991**, *24*, 5305–5308. (b) Tan, C.-S.; Hsu, T.-J. *Macromolecules* **1997**, *30*, 3147–3150. (c) Darensbourg, D. J.; Wildeson, J. R.; Yarbough, J. C.; Riebenspies, J. H. *J. Am. Chem. Soc.* **2000**, *122*, 12487–12496. (d) Cui, D.; Nishiura, M.; Hou, Z. *Macromolecules* **2005**, *38*, 4089–4095. (e) Robertson, N. J.; Qin, Z. Q.; Dallinger, G. C.; Lobkovsky, E. B.; Lee, S.; Coates, G. W. *Dalton Trans.* **2006**, *45*, 5390–5395. (f) Xiao, Y.; Wang, Z.; Ding, K. *Macromolecules* **2006**, *39*, 128–137.

(7) (a) Hirano, T.; Inoue, S.; Tsuruta, T. *Makromol. Chem.* **1975**, *176*, 1913–1917. (b) Hirano, T.; Inoue, S.; Tsuruta, T. *Makromol. Chem.* **1976**, *177*, 3245–3253. (c) Shen, Z.; Chen, X.; Zhang, Y. *Macromol. Chem. Phys.* **1994**, *195*, 2003–2011. (d) Lukaszczyk, J.; Jaszcz, K.; Kuran, W.; Listos, T. *Macromol. Rapid Commun.* **2000**, *21*, 754–757. (e) Tan, C.-S.; Juan, C.-C.; Kuo, T.-W. *Polymer* **2004**, *45*, 1805–1814. (f) Darensbourg, D. J.; Moncada, A. I. *Macromolecules* **2009**, *42*, 4063–4070.

(8) Byrne, C. M.; Allen, S. D.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2004**, *126*, 11404–11405.

(9) Gandini, A.; Belgacem, M. N. *Prog. Polym. Sci.* **1997**, *22*, 1203–1379.

(10) Moreau, C.; Belgacem, M. N.; Gandini, A. *Top. Catal.* **2004**, *27*, 11–30.

(11) McCoy, M. *Chem. Eng. News* **2006**, *84*, 7.

(12) Gandini, A. *Adv. Polym. Sci.* **1977**, *25*, 47–96.

(13) Kuran, W.; Gorecki, P. *Makromol. Chem.* **1983**, *184*, 907–912.