Macromolecules **2007,** *40,* 7739−7741 **7739**

Linear Low-Density Polyoxymethylene versus Linear Low-Density Polyethylene

Andrea D. Ilg, Craig J. Price, and Stephen A. Miller*,†

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received September 13, 2007
Revised Manuscript Received September 17, 2007

The controlled introduction of branches into high-density polyethylene (HDPE) via copolymerization strategies has given rise to a family of linear low-density polyethylenes (LLDPE, Figure 1) with very tunable properties for a wide variety of applications.[1] LLDPE is projected to remain the fastest growing polyolefin with consumption doubling from 2006 (17 billion kg/year) to 2020 (34 billion kg/year) while expanding from 17% to 19% of the polyolefin market.[2]

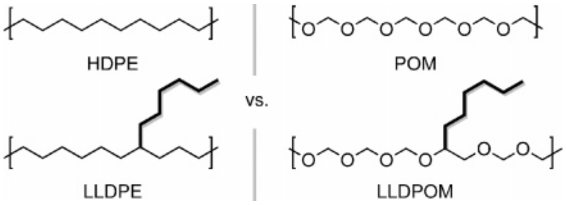


Figure 1. The branching effect on HDPE is well investigated, but very little is known about the branching effect on polyoxymethylene (POM).

Polyoxymethylene (POM) is an engineering plastic (0.5 billion kg/year) routinely used as a metal substitute in medical devices, appliances, hardware, electronic components, and zippers.[3] In stark contrast to the successful adaptation of HDPE to afford LLDPE, no branched variants of POM have received commercial attention. Such linear low-density polyoxymethylenes (LLDPOM)[4] are essentially unknown, but we hypothesized that their thermal and mechanical properties should be readily tuned by controlling branch content—vis-à-vis LLDPE.

Moreover, although POM currently derives from fossil fuel methanol, POM and LLDPOM are poised to become increasingly attractive because methanol can be synthesized from renewable (hydrogen) and biorenewable (carbon dioxide, wood, agricultural waste) feedstocks, and these polyacetal polymers are amenable to chemical recycling, affording the original formaldehyde monomer (Scheme 1). A methanol economy has received serious consideration as a sustainable, bio-based successor to the fossil fuel economy.[5] To the extent that the methanol economy enjoys future success, polymers derived from this C1 feedstock will become economically privileged.

Scheme 1. Chemical Lifecycle of Polyoxymethylene (POM)

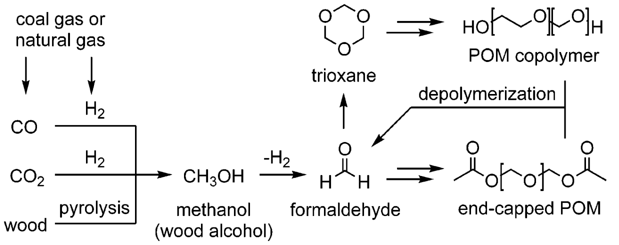
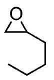
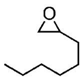
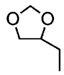
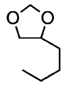
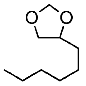


Table 1. Trioxane/Comonomer Copolymerization Results[a]

comonomer	feed (mol%)	incorp. (mol%)[b]	rel. rate[c]	incorp. (mol%)[d]	yield (g)	T_m (°C)
propylene oxide	3.0	4.4	1.48	5.5	3.23	165.8
	7.4	8.9	1.20	11.3	4.39	163.4
	10.0	8.8	0.88	12.3	4.79	163.0
	15.0	15.8	1.05	16.9	4.23	158.8
	20.0	16.4	0.82	18.0	4.08	156.6
	25.0	17.9	0.72	21.1	3.55	154.6
1-butene oxide	3.0	4.2	1.40	6.7	3.89	167.1
	7.4	6.6	0.89	7.9	4.03	163.6
	10.0	8.7	0.87	9.9	4.22	163.5
	15.0	12.8	0.85	15.1	3.85	159.1
	20.0	17.2	0.86	20.4	2.44	152.4
	25.0	17.6	0.70	21.2	1.31	149.6
1-hexene oxide	3.0	4.7	1.56	6.9	4.50	169.8
	7.4	6.7	0.90	7.4	4.46	166.9
	10.0	9.5	0.95	12.1	3.81	162.2
	15.0	12.3	0.82	13.1	3.65	161.3
	20.0	14.9	0.74	19.4	2.25	157.6
1-octene oxide	3.0	4.6	1.54	7.1	3.38	166.7
	7.4	6.9	0.94	9.0	4.19	164.1
	10.0	8.2	0.82	10.4	4.04	162.3
	15.0	13.5	0.90	18.5	2.80	159.0
	20.0	9.7	0.48	11.5	1.62	160.3
4-ethyl dioxolane	3.0	4.4	1.47	5.3	3.57	167.9
	7.4	5.0	0.68	7.0	3.54	164.3
	10.0	7.1	0.71	9.1	3.69	162.9
	15.0	7.4	0.49	9.1	4.03	160.8
	20.0	8.4	0.42	11.8	5.29	160.7
	25.0	10.3	0.41	12.2	4.59	160.2
	30.0	11.2	0.37	12.3	3.58	158.1
4-butyl dioxolane	3.0	2.6	0.88	3.5	5.52	169.2
	7.4	4.2	0.57	6.6	3.72	167.7
	10.0	5.3	0.53	8.1	3.61	166.0
	15.0	6.9	0.46	8.7	5.12	163.1
	20.0	8.1	0.41	9.5	3.25	162.3
	25.0	9.1	0.36	12.0	1.75	160.1
	30.0	9.9	0.33	11.5	1.67	159.5
4-hexyl dioxolane	3.0	4.4	1.46	5.9	3.80	167.9
	7.4	4.9	0.66	8.9	5.78	164.6
	10.0	5.6	0.56	6.4	3.53	165.3
	15.0	7.9	0.53	9.6	4.68	163.2
	20.0	7.2	0.36	10.0	2.32	161.0
	25.0	7.8	0.31	9.2	4.48	162.6
	30.0	9.5	0.32	12.3	0.64	160.7

[a] Trioxane (5.00 g, 55.5 mmol) and comonomer in 5.0 mL of 1,2-dichloroethane at 42 °C; initiator added as $BF_3{\cdot}OEt_2$ (0.073 g; 0.514 mmol) in 2.5 mL of cyclohexane; quenched with 5% aqueous Na_2CO_3; reaction times vary from 0.5 to 72 h. [b] Before cure by NMR analysis. [c] Relative rate of comonomer incorporation = mol % incorporation/mol % feed. [d] After curing by NMR/DSC/TGA analysis.

Our initial approach for incorporating well-defined branches into otherwise linear polyoxymethylene exploited the cationic ring-opening copolymerization of trioxane and either 1-alkene oxides or 4-alkyldioxolanes (Figure 2). Accordingly, the two series of copolymers cataloged in Table 1 were synthesized.

Somewhat surprisingly, investigations of branched polyoxymethylene are rare and have been conducted only to address the thermal depolymerization tendencies of POM, not for the purpose of tuning the melting temperature and other nondestruc-

---

* To whom correspondence should be addressed. E-mail: miller@chem.ufl.edu.

† Current address: Department of Chemistry, University of Florida, Gainesville, FL 32611-7200.

10.1021/ma702066y CCC: $37.00

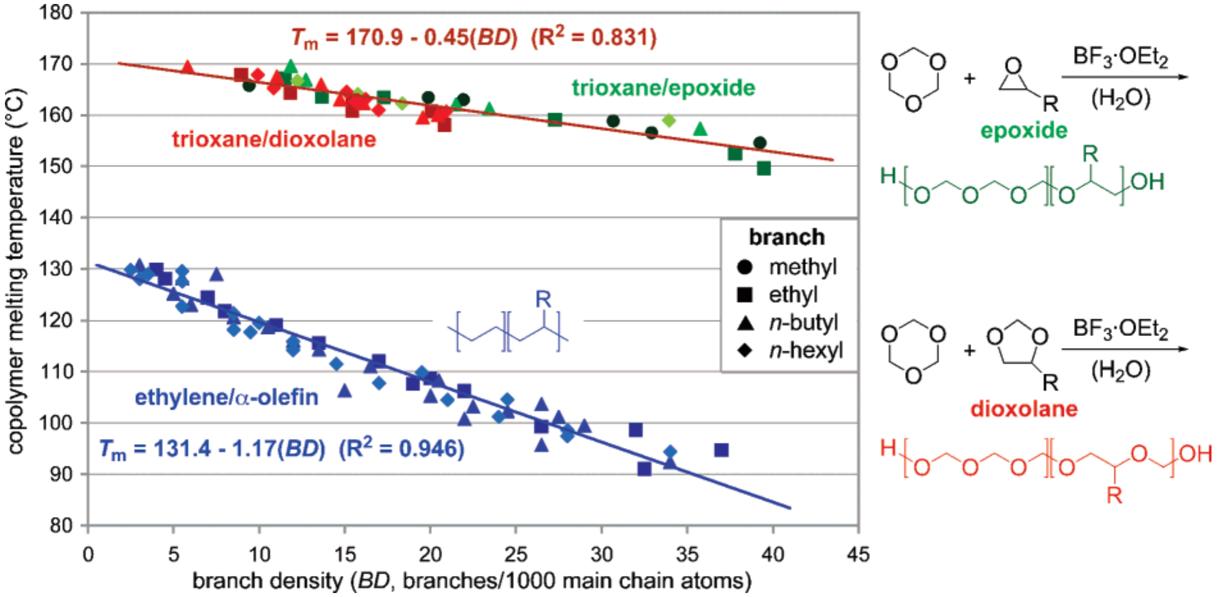


Figure 2. Comparative melting point trends for polyoxymethylene copolymers (red, green) and polyethylene copolymers[11] (blue).

tive thermomechanical properties. One butylene oxide copolymer[6] and a few propylene oxide copolymers have been reported in the patent literature[7]—but no copolymers with higher alkene oxides have been reported. Copolymers with long chain 4-alkyldioxolanes are found in a single report (initiator = CF_3SO_3H), but the comonomer incorporation rates average only 33%, comonomer incorporation is uniformly low (0.3−1.6 mol %), and copolymer melting temperatures are not reported.[8] Thus, a useful comparison to commercial LLDPE resins, having 1−25 mol % comonomer incorporation,[1] cannot be made with the available data.

We have addressed these shortcomings by identifying $BF_3{\cdot}OEt_2$ as a superior cationic initiator for the copolymerization of trioxane with 1-alkene oxides or with 4-alkyldioxolanes. As shown in Table 1, the former system allows for high relative comonomer incorporation rates, averaging 0.97 and ranging from 0.48 to 1.56, indicating several instances where the epoxide is more reactive than trioxane. Additionally, a wide range of comonomer incorporations is accessible—from 4 to 18 mol %. Note that epoxide relative incorporation rates (average of 0.97) are generally higher than those for dioxolane (average of 0.59).

As predicted, the melting temperatures of the copolymers are depressed compared to that of POM homopolymer, which has a T_m of 181 °C.[9] Figure 2 illustrates the dependence of copolymer melting temperature on branch density (*BD*)—here quantified as the number of branches per 1000 main chain atoms.[10] Note that the melting temperature is linearly correlated to the branch density but is ostensibly independent of the comonomer's identity (epoxide or dioxolane; R = methyl, ethyl, *n*-butyl, or *n*-hexyl).

Regression analysis for all 43 copolymers in Table 1 yields the linear relationship $T_m = 170.9 - 0.45(BD)$ (Figure 2). The related analysis by Mirabella and Crist[11] for a series of LLDPE copolymers yields $T_m = 131.4 - 1.17(BD)$. The obtained slopes are a direct measure of a branch's ability to disrupt crystallinity.[12] Evidently, a given branch is less effective at disrupting the crystallinity of the oxygenated polymer (slope = −0.45) because its numerous local dipoles result in stronger chain−chain interactions than those found in the pure hydrocarbon polymer (slope = −1.17). While 8.5 branches per 1000 main chain atoms are sufficient to effect a 10 °C melting point depression in LLDPE, 22 such branches are required to effect the same melting point depression in LLDPOM. The quotient of the slopes provides the first quantitative "branch effect" comparison between these two copolymer classes and indicates that considerably more branches (−1.17/−0.45 = 2.6 times) are required to plasticize polyoxymethylene than polyethylene. Nonetheless, the coherent melting temperature dependence suggests that the properties of polyoxymethylene can be finely tuned via copolymerization strategies akin to those proven exceedingly useful for commercial LLDPE.

Through copolymerization approaches, we have created the first well-defined family of POM copolymers having a wide range of branch content and prescribed branch length. The uniform branch identity has allowed the first direct comparisons between branched polyethylene (LLDPE) and branched polyoxymethylene (LLDPOM)—differentiating the inherent ability of a branch to disrupt crystallinity in these two copolymer classes. This disruptive effect is quantified herein by copolymer melting temperature and will have an important bearing on future attempts to prepare LLDPOM with tunable and marketable thermomechanical properties. Future interest in this family of oxygenated copolymers is anticipated because they derive from a biorenewable C1 platform chemical (methanol)[5,13] and because they are suitable for recycling via chemical depolymerization, unlike related polyolefins. Moreover, α-olefin feedstocks for the proposed comonomers can be derived from ethanol and vegetable oil via the ethenolysis of fatty acid esters or triglycerides,[14] further increasing the biorenewable mass fraction of LLDPOM.

Acknowledgment. This research is supported by The Robert A. Welch Foundation (No. A-1537) and the National Science Foundation (NSF-CAREER 0548197).

Supporting Information Available: Full synthetic details and copolymer characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Simpson, D. M.; Vaughan, G. A. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Ed.; John Wiley & Sons: New York, 2003; Vol. 2, pp 441−482.

(2) Chem Systems. *New Industry Outlooks for Polyethylene and Polypropylene.* 2007 Nextant, Inc., April 11, 2007 (www.chemsystems.com/about/cs/news/archive.cfm).

(3) Masamoto, J. *Prog. Polym. Sci.* **1993**, *18*, 1−84.

(4) Densities are diminished by 8−16%; see the Supporting Information.

(5) (a) Olah, G. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 2636−2639. (b) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *Beyond Oil and Gas: The Methanol Economy*; Wiley-VCH: Weinheim, 2006.

(6) Asahi Chemical Industry Co., Ltd., Japan, Japanese Patent 59129247, 1984.

(7) (a) Celanese Corp. of America, Belgian Patent 619654, 1962. (b) Yahiro, S.; Hata, T.; Matsuzaki, K. Japanese Patent 04108819, 1992. (c) Murao, T.; Yamamoto, K.; Reuschel, G.; Fleischer, D. European Patent 568308, 1993.

(8) Braun, D.; Brückner, U.; Eckardt, P.; Hoffmockel, M. *Angew. Makromol. Chem.* **1999**, *265*, 55−61.

(9) Mück, K.-F. Physical Constants of Poly(oxymethylene). In *Polymer Handbook*, 4th ed.; Brandup, J., Immergut, E. H., Grulke, E. A., Eds.; Wiley-Interscience: New York, 1999; Section V, pp 97−112.

(10) The branch density calculation is based on the mol % incorporation of the *cured* copolymer because the melting temperature obtained corresponds to the copolymer which has presumably depolymerized to the first non-acetal positions during DSC/TGA analysis. See the Supporting Information.

(11) Mirabella, F. M.; Crist, B. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 3416−3427.

(12) For LLDPE, molecular weight does not seem to significantly impact the relationship between branching content and polymer melting temperature (as long as a minimum threshold is achieved). Note that molecular weight determinations for the POM copolymers of Table 1 have not yet been performed. Molecular weight determinations for POM via gel permeation chromatography (GPC) are rare because useful solvents—such as hexafluoroisopropanol and hexafluoroacetone—are almost prohibitively expensive.

(13) Kamm, B.; Kamm, M.; Gruber, P. R.; Kromus, S. In *Biorefineries—Industrial Processes and Products. Status Quo and Future Directions*; Kamm, B., Gruber, P. R., Kamm, M., Eds.; Wiley-VCH: Weinheim, 2006; Vol. 1, pp 3−40.

(14) (a) Mol, J. C. *Green Chem.* **2002**, *4*, 5−13. (b) Patel, J.; Elaridi, J.; Jackson, W. R.; Robinson, A. J.; Serelis, A. K.; Such, C. *Chem. Commun.* **2005**, 5546−5547.

MA702066Y