Articles

"Perfect Comb" ADMET Graft Copolymers

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Received May 23, 2001; Revised Manuscript Received July 13, 2001

ABSTRACT: "Perfect comb" graft copolymers are synthesized via acyclic diene metathesis (ADMET) polymerization using well-defined ruthenium catalyst systems to yield precisely spaced polyethers along an unsaturated polyolefin backbone. The graft is placed in a symmetrical α,ω-diene prior to ADMET polymerization to ensure exact graft placement at each functional site along the polymer backbone—no mistakes are made. The polyether grafts are essentially monodisperse as shown by MALDI analysis, while the polyolefin backbone exhibits a dispersity of 2.0. Such well-defined poly(ethylene-*graft*-ethylene oxide) copolymers will be interesting in several applications.

Introduction

Structure control in polymer synthesis obviously is important to all of us interested in creating new materials. Given the constraints associated with synthesizing polymers possessing entirely new repeat units, chemists today often focus on intriguing polymeric architectures made from common monomers such as those produced from typical chain and step polymerizations.[1,2] This paper presents an innovative graft architecture for the assembly of polyolefin and polyether repeat units; we have been able to prepare "perfect" combs wherein the *teeth* are comprised of essentially monodisperse poly(ethylene oxide) while the *backbone* is an unsaturated polyolefin. Furthermore, and most importantly, the run length between adjacent teeth is exact along this polyolefin backbone.

It is evident that controlling each aspect of a polymerization scheme can alter the resulting polymer's topology, composition, or placement of functional groups at various sites along the polymer.[2] One topology of particular interest to us is the graft copolymer array. Creating this architecture is challenging, since the synthesis of such copolymers with precise placement of the graft has been documented as being a nontrivial target when using typical polymerization methods.[3]

We know that acyclic diene metathesis (ADMET)[4,5] chemistry successfully yields unsaturated, linear, high molecular weight polymers possessing various functional groups, both within and pendant to it (Figure 1).[6−11] If desired, these functional groups can be placed at exact intervals along the backbone, something not previously demonstrated. Consequently, the goal in this research has been to exploit the ADMET polymerization scheme in the preparation of novel graft copolymer structures.

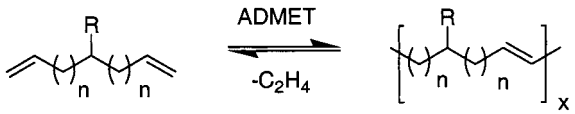

Figure 1. ADMET polymerization of functionalized monomers.

Monomer design is central to this work. Our approach to creating perfect comb polymers involves inserting the graft a priori into a symmetrical α,ω-diene before ADMET polymerization, meaning we invoke the macromonomer approach in step polymerization chemistry. Macromonomers are usually found in chain polymerization, and in fact macromonomers have been used to produce graft copolymers[12] in various chain polymerization schemes. In this case the grafts usually are packed tightly together (in vinyl monomer homopolymerization), or they are randomly distributed in vinyl copolymerization schemes. In this present study, diene macromonomers are converted to polymers via step propagation, condensation-type polymerization (ADMET chemistry) with the distance between graft points precisely being regulated by placing discrete methylene run lengths between them in the monomer.

Our approach produces graft copolymers containing either short or extended polyether grafts, depending upon the graft chemistry employed. Polyether short grafts are produced via S_N2 substitution chemistry, while the long grafts are generated via anionic ring-opening polymerization of ethylene oxide.

Both types of polyether grafts—short and long—are of interest. Extended polyethers such as poly(ethylene glycol) (PEG) are nontoxic, biocompatible, and highly water-soluble. The combination of hydrophilic polyethers grafted to a polyolefin backbone proves to be an interesting application for exploration. These polyethylene-based materials will have an increased solubility

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10.1021/ma0108970 CCC: $20.00
Published on Web 08/31/2001

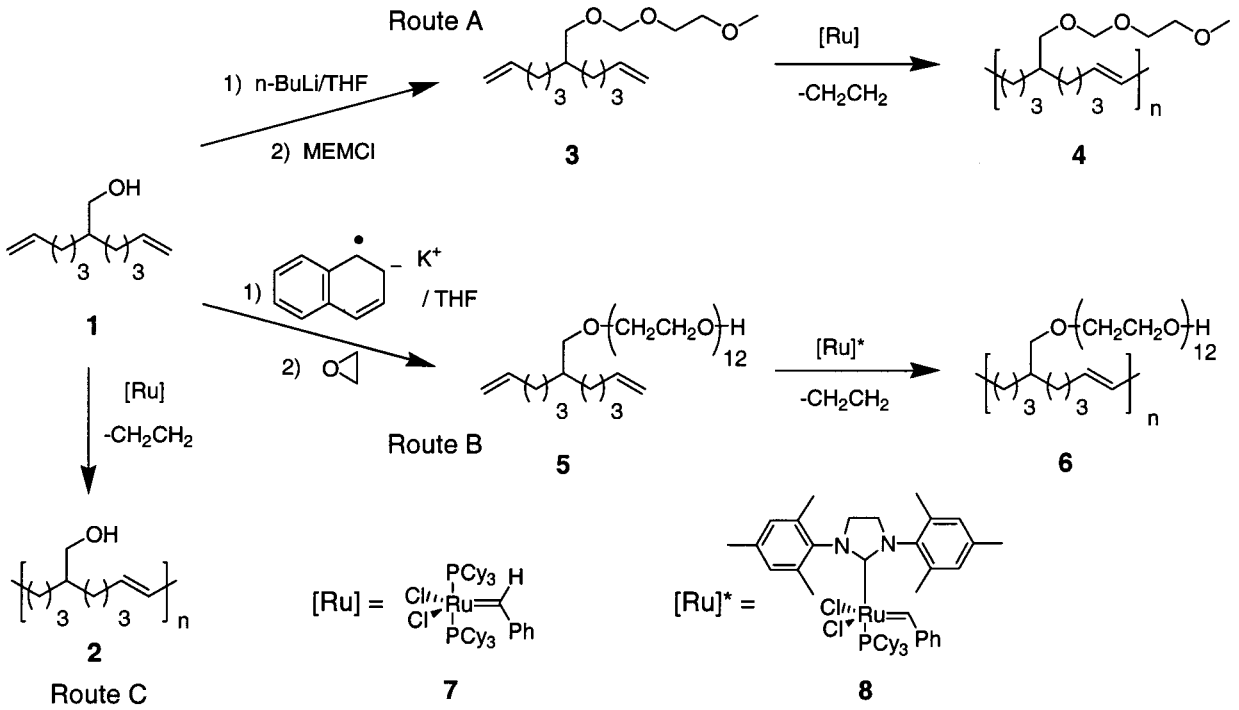

Figure 2. Monomer synthesis and ADMET polymerization schemes.

in polar solvents due to the polyether grafts. Furthermore, grafted PEG materials are known to be valuable in biomedical applications[13] and also are used as compatibilizers in polymer blending.[14] However, no examples have been reported where precise spacing is employed to enhance polymer performance, and it is for these reasons that we have set out to synthesize the first widely spaced, "perfect comb" polyethylene-*g*-polyether copolymers.

Experimental Section

Instrumentation. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained from a Varian Associates Gemini series 300 spectrometer. Chemical shifts were referenced to residual $CDCl_3$ with 0.05% TMS. High-resolution mass spectroscopy data (HRMS) were acquired on a Finnigan MAT95Q hybrid section (Finnigan, San Jose, CA) using electron ionization (EI) mode. Matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained on a Bruker Reflex II (Bruker Daltonics, Billencia, MA). The matrix used was *all-trans*-retinoic acid with $CuCl_2$ used as the cationization reagent. The solvent for both the MALDI matrix and the macromonomers was tetrahydrofuran. Elemental analysis was performed by Atlantic Microlabs Inc., Norcross, GA. Gel permeation chromatography (GPC) was performed with a Waters Associates liquid chromatograph U6K equipped with a tandem ABI Spectroflow 757 UV absorbance detector and a Hewlett-Packard 1047A refractive index detector. Polymer samples were dissolved in THF (approximately 1% w/v) and injected at a flow rate of 1 mL/min into a cross-linked column of polystyrene divinylbenzene from American Polymer Standards. Retention times were calibrated against polystyrene standards from Polymer Labs.

Differential scanning calorimetry (DSC) data were obtained with a Perkin-Elmer 7 series thermal analysis system with Pyris software. DSC samples (2−8 mg) were analyzed with liquid nitrogen as the coolant and under a helium as the carrier gas at a flow of 25 mL/min. The instrument was calibrated for peak onset temperature using indium and ultrapure *n*-octane as standards. Samples were scanned at a heating rate of 10 °C/min from −120 to 40 °C with data collected during the second cycle in the appropriate temperature ranges.

Materials. Grubbs' ruthenium benzylidene catalyst $RuCl_2(=CHPh)-(PCy_3)_2$ (**7**) and second generation Grubbs' catalyst $RuCl_2(=CHPh)-(PCy_3)$(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (**8**) were synthesized according to literature techniques.[15,16] A sample of 2-(4-pentenyl)-hept-en-1-ol was synthesized according to earlier literature reports.[8] Tetrahydrofuran (THF) was distilled from a Na/K alloy using benzophenone as the indicator. Naphthalene (Aldrich) was recrystallized in methanol and used to prepare a 0.3 M solution of potassium naphthalenide in THF. Methoxyethoxymethyl chloride (Aldrich) was dried with CaH_2 prior to use. Ethylene oxide (Aldrich) was condensed over CaH_2 at a temperature of −78 °C and stirred for 45 min. *n*-BuLi was then added dropwise and stirred for 1 h. The ethylene oxide was then distilled under vacuum into a clean, dry Schlenk flask.

(Substitution of Methoxyethoxymethyl Chloride) Synthesis and Characterization of 6-[(2-Methoxyethoxy)-methoxy]methylundeca-1,10-diene (3). In a flame-dried, argon-purged 250 mL three-neck flask equipped with a stir bar were combined 2.55 g (14.0 mmol) of **1** (Figure 2) and 125−150 mL of THF. The solution was cooled to 0 °C, and 9.63 mL of 1.6 M *n*-butyllithium (Aldrich) was added via syringe over a 5−10 min period. The solution was stirred for 15 min at 0 °C and then warmed to room temperature. After an additional 30 min of stirring, the solution was recooled to 0 °C, and 1.92 mL (16.8 mmol) of methoxyethoxymethyl chloride (MEMCl) was added via syringe. After addition of MEMCl, the solution was warmed to room temperature and monitored by TLC for 17−19 h. The reaction was quenched with 3 N HCl, washed with DI water, extracted with Et_2O, and dried over $MgSO_4$. The organic layers were filtered and concentrated at a reduced pressure and purified by column chromatography with a mobile phase of 3:1 hexanes:ethyl acetate. Isolated yield of **3**: 35.6%. Spectral properties observed: ^{1}H NMR ($CDCl_3$): δ 1.34 (br m, 9H), 1.99 (q, 4H), 3.36 (s, 3H), 3.40 (d, 2H), 3.54 (t, 2H), 3.65 (t, 2H), 4.67 (s, 2H), 4.93 (br m, 4H), 5.73 (br m, 4H). ^{13}C NMR ($CDCl_3$): δ 26.13, 30.83, 34.09, 38.06, 58.98, 66.65, 70.70, 71.76, 95.62, 114.31, 138.90. EI/HRMS: $[M + 1]^+$ calcd for $C_{16}H_{31}O_3$, 271.22; found, 271.23. Anal. Calcd for $C_{16}H_{31}O_3$: 71.06 C; 11.20 H. Found: 71.45 C, 11.05 H.

(Ring Opening of Ethylene Oxide) Synthesis and Characterization of 5. In a flame-dried, argon-purged three-neck flask equipped with a condenser and stir bar were

combined 0.3 g (1.65 mmol) of **1** and 100−125 mL of THF. Subsequently, 5.5 mL of 0.3 M potassium naphthalenide solution was added via syringe and stirred for 30 min at room temperature. The slight green color of the solution ensured that a minimal excess of potassium naphthalenide was present. Via a calibrated delivery buret, 2.10 mL (42.1 mmol) of condensed ethylene oxide (EO) was added very slowly over 5 min. The reaction was stirred at room temperature for 30 min and then brought to 45 °C and stirred for 24 h. Finally, the mixture was cooled to room temperature and quenched with acidic MeOH. The organic layer was dissolved in $CHCl_3$, washed with deionized water, and concentrated under reduced pressure. The resulting product was placed under vacuum (10^{-1} mmHg) at 65 °C for 4 days to remove any residual naphthalene present, after which a yellow oil was isolated. Isolated yield of **5**: 35.5%. Spectral properties observed: ^{1}H NMR ($CDCl_3$): δ 1.37 (br m, 9H), 1.58 (br s, 1H), 2.10 (q, 4H), 3.34 (d, 2H), 3.56 (m, 48H), 4.98 (m, 4H), 5.82 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 25.76, 30.50, 33.78, 37.57, 60.96, 70.20, 72.20, 74.19, 113.92, 138.62. Anal. Calcd for $C_{36}H_{70}O_{13}$: 60.84 C; 9.86 H. Found: 60.65 C; 9.86 H.

Synthesis and Characterization of 9. Synthesized as above. Isolated yield of **9**: 50.6%. Spectral properties observed: ^{1}H NMR ($CDCl_3$): δ 1.42 (br m, 9H), 1.62 (br s, 1H), 2.08 (q, 4H), 3.38 (d, 2H), 3.60 (m, 80H), 4.94 (m, 4H), 5.79 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 25.99, 30.71, 34.00, 37.78, 61.78, 70.41, 72.53, 74.43, 114.16, 138.86. Anal. Calcd for $C_{52}H_{101}O_{21}$: 58.81 C; 9.51 H. Found: 55.48 C; 9.57 H.

Synthesis of ADMET Graft Copolymers. General Procedure for Bulk Polymerization. The α,ω-diene monomers were dried and degassed prior to polymerization by performing freeze/pump/thaw cycles. Inside an argon-purged drybox, monomer and catalyst (100:1; monomer:catalyst ratio) were combined in a Schlenk tube containing a magnetic stir bar. The tube was removed from the drybox and immediately connected to the vacuum line. The pressure was reduced in intervals, eventually reaching a full vacuum of 10^{-2} mmHg. After full vacuum was attained, the temperature was increased to 50−60 °C. These polymerization conditions were typically conducted from 72 to 90 h.

General Procedure for Solution Polymerization. The α,ω-diene monomers were taken inside an argon-purged drybox and combined with the catalyst (100:1; monomer: catalyst ratio) in a Schlenk tube equipped with a magnetic stir bar. The tube was removed from the drybox and immediately connected to a Schlenk line. Dry solvent was then added by syringe; the reaction was then subjected to a steady flow of argon to drive the ethylene from the mixture. The solution was then heated to 50 °C and stirred vigorously for 72 h. Solvent was evaporated upon completion of the reaction.

Results and Discussion

Monomer Synthesis. The synthesis of graft copolymers possessing a controlled graft length and an exact run length along the polymer backbone is achieved by first symmetrically positioning the graft within the diene monomer itself. These diene monomers then are converted into true graft copolymers via ADMET polycondensation chemistry. Short chain polyether grafts are placed along the α,ω-diene via substitution chemistry using methoxyethoxymethyl chloride (MEMCl) (Figure 2, route A) leading to monomer **3**, while the long chain polyether graft is introduced into the monomer by initiation of ethylene oxide polymerization with a primary alcohol functional group **1**[8] (Figure 2, route B) leading to macromonomer **5**.

This chemistry is clean and leads to a single graft site symmetrically placed within each monomer unit. Thus, polymerization of the monomer will lead to a graft in each repeat unit of the polymer formed via step macromonomer polymerization. To aid in the structural characterization of these rather large monomers, we have employed MALDI-TOF to gather precise molecular weight data. MALDI-TOF provides absolute molecular mass information, which is difficult to measure by commonly employed analytical methods such as NMR and GPC. Figure 3a displays these data for macromonomer **9**, data which have led to further clarification of the polymerization mechanism. The number of ethylene oxide repeat units was determined to be 25, a value in agreement with that obtained from ^{1}H NMR. In addition, the polydispersity of the ethylene oxide graft was calculated to be 1.06 from this spectrum.

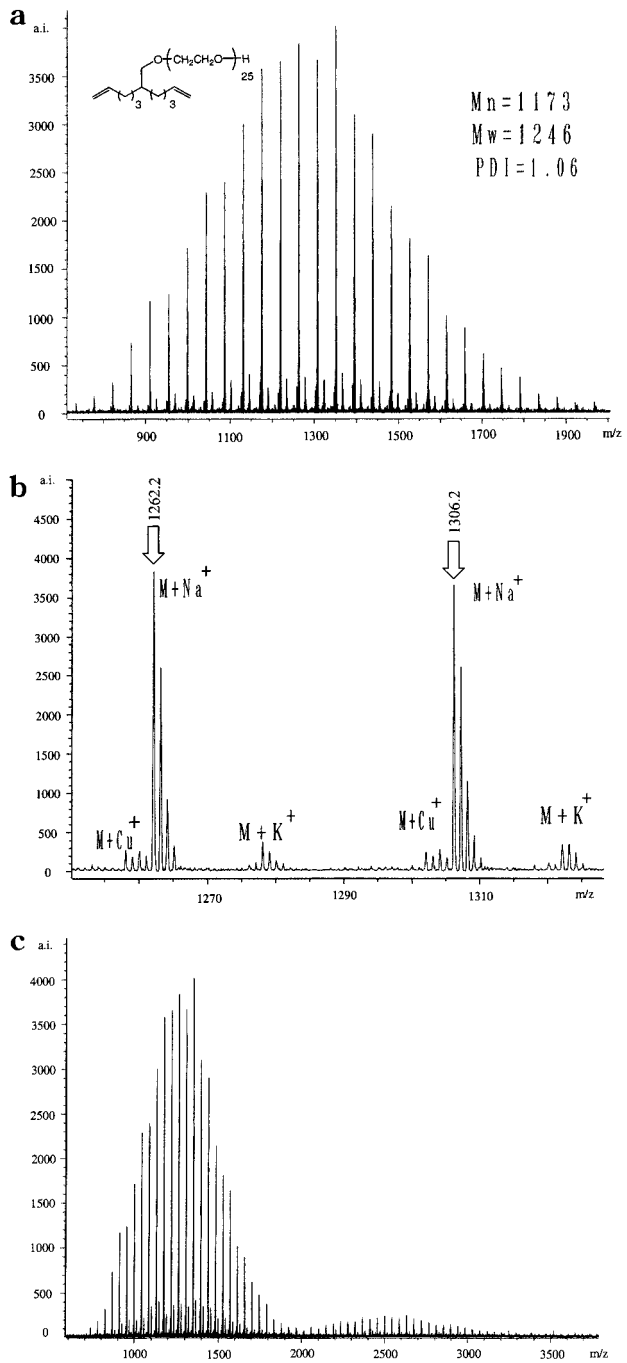

Figure 3. (a) MALDI-TOF of ethylene oxide macromonomer (**9**). (b) Expanded view of MALDI spectrum. (c) MALDI-TOF of dimerization process.

Figure 3b shows an expanded view of the MALDI spectrum of the monomer and illustrates cationization by Cu^+, Na^+, and K^+. The Na^+ and K^+ were adventitious ions arising from the solvent, an important point to note.

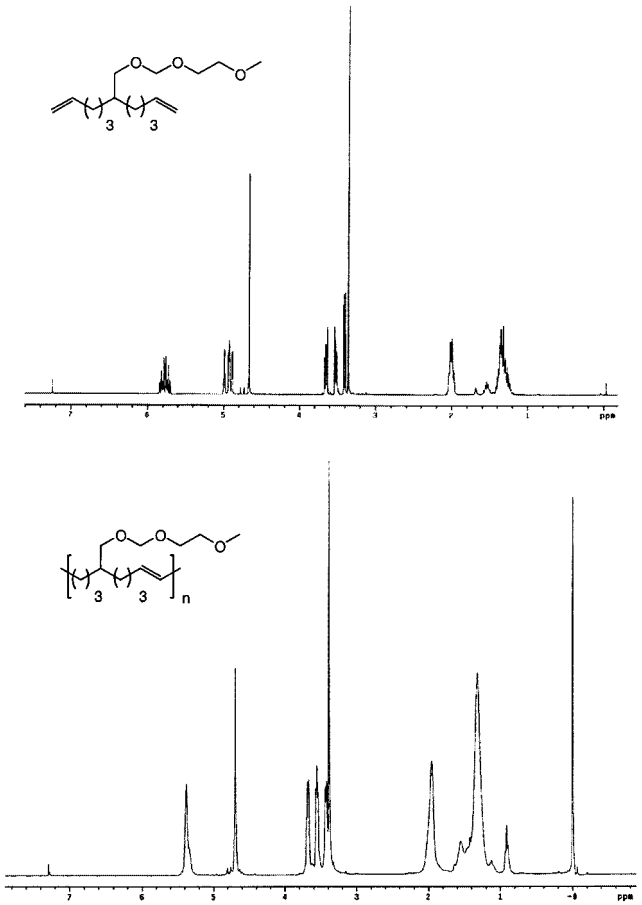

Figure 4. 300 MHz ^{1}H NMR spectra: (top) MEM graft monomer **3**; (bottom) MEM graft polymer **4**.

Consequently, the number- and weight-average molecular weights are corrected for the shift due to these cations. MALDI-TOF analysis demonstrates the precision by which these macromonomers are prepared. Very narrow polydispersities are evident; further, it is obvious that graft lengths can be chosen at will.

The precise nature of graft placement in this chemistry suggests the possibility of producing "perfect" polyether comb polymers that could mimic the behavior of crown ethers. Figure 3c suggests this possibility, for the spectrum clearly shows that the cationization agent, copper(II) iodide, interacts in a specific manner with the macromonomer **9**. Inspection of the spectrum reveals a second set of peaks at approximately 2500 *m*/*z*, unevi-quocally showing the coordination of polyether grafts to the copper ion, even in the macromonomer. Each polyether-based graft will operate independently of one another in the copolymer as long as there is sufficient spacing between graft sites; thus, the potential for specific ion bonding exists. Since each grafted polyether chain exhibits lower entropy than its analogous free chain, complexation in the crown sense is enhanced. Consequently, these graft copolymers could prove useful in specific metal complexation without exhibiting the toxic effects known for true crown ether structures.

Polymer Synthesis and Characterization. Polymerization of the macromonomers **3** and **5** was performed using standard ADMET techniques. Because of ruthenium benzylidene metathesis catalysts being highly tolerant to the presence of functionalities, oxygen, and small amounts of moisture,[15] so these catalysts were chosen to polymerize of the highly functional water-containing macromonomers. Conversion of these macromonomers to the unsaturated polymers (Figure 2, copolymers **4** and **6**) is trivial and can be observed by ^{1}H NMR. As the polymerization proceeds, the α,ω-diene terminal olefin peaks at 4.93 and 5.73 ppm decrease in intensity while the internal olefin peak of the unsaturated polyolefin at 5.38 ppm becomes more pronounced. This ADMET chemistry is so successful for the short graft monomers that the end group vinyl resonance signals are no longer observable; i.e., high molecular weight graft copolymers are formed (Figure 4). While short chain polyether graft macromonomers polymerize with ease, long chain graft comonomers prove to be more difficult; ^{1}H NMR spectra show that the degree of polymerization is lower for longer grafts **6a** than for shorter grafts **4** (Table 1). Apparently, the long chain PEG units self-organize to complex the catalyst, thereby decreasing the rate of polycondensation. A higher molecular weight copolymer **6b** can be achieved using the second-generation benzylidene, which has been found to be more active. The discrepancy between ^{1}H NMR and GPC results is caused by the fact that GPC is not an absolute method, but rather based upon relative polystyrene standards which do not behave in the same manner as the graft copolymers in solution.

Differential scanning calorimerty (DSC) studies performed on all of the unsaturated graft copolymers are summarized in Table 1. The glass transition tempera-

Table 1. Characterization of ADMET Polyethylene Graft Polyethers

polymer	M_n (NMR)	M_n (GPC)[b]	n	PDI	T_g (°C)
2	NA[a]	24 000	150	1.9	−32
4	NA[a]	15 000	60	2.2	−90
6a	3500	5500	8	1.5	−68
6b	7100	12 000	17	2.1	−68

[a] Terminal olefins were not observable. [b] Molecular weights were measured with respect to polystyrene standards in THF.

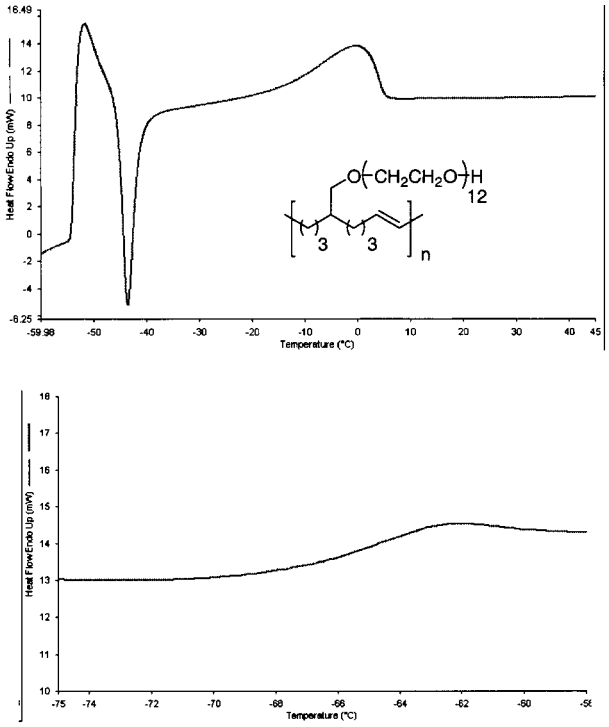

Figure 5. (a, top) DSC thermal behavior of poly(ethylene-*g*-oxyethylene). (b, bottom) Glass transition temperature for the graft copolymer.

ture (T_g) for the primary alcohol polymer (structure **2** in Figure 2) is −32 °C. Interestingly, by merely replacing the alcohol in the graft copolymer with the short MEM branch (structure **4**), the glass transition temperature is dramatically decreased to −90 °C; this result indicates the important influence of the short chain polyether on the macromolecule's overall thermal relaxation behavior.

Unannealed samples of the long chain "perfect comb" copolymer **6b** (Table 1) display particularly interesting thermal behavior, apparently due to its well-ordered structure. The endotherm occurring at −55 °C (Figure 5a) is the result of melting of the well-formed, tethered poly(oxyethylene) grafts. After the melt of the graft occurs, the unsaturated polyolefin backbone crystallizes almost immediately, exhibiting an exotherm at −47 °C, and as heating continues these newly formed polyolefin crystals melt with an onset of −12 °C. A glass transition temperature is also evident at −68 °C (Figure 5b), most likely a reflection of the polyether amorphous phase of the copolymer.

Conclusions

"Perfect comb" graft copolymers are easily accessible using ADMET techniques combined with conventional polymer chemistry. Monomer synthesis is straightforward, and the resulting materials offer promise in a number of applications. These new architectures are being studied in greater detail in order to extend our understanding of structural effects on the physical properties of such systems.

Acknowledgment. We thank the National Science Foundation (Grant DMR9806492) and the Army Research Office for financial support of this work. We also thank Abbott Laboratories for the donation of the Bruker Reflex MALDI-TOF. Special thanks also goes to Dr. Joe Duncan of Mylan Pharmaceuticals for help with the initial DSC experiments and to Mr. Jason Smith for the help in the preparation of this manuscript.

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MA0108970