Macromolecules **2005,** *38,* 2550−2551

Circumventing the Reactivity Ratio Dilemma: Synthesis of Ethylene-*co*-Methyl Vinyl Ether Copolymer

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Received February 7, 2005

Revised Manuscript Received February 14, 2005

Linear copolymers of ethylene and vinyl ethers have never been made. Synthesis of many vinyl copolymers has never been achieved due to large reactivity ratios, a consequence of the inherent reactivity difference of monomers involved in chain polymerization. This type of monomer mismatch, as with ethylene and vinyl ether, has hindered the creation of numerous vinyl copolymers due to the inability to control monomer incorporation.[1] The reactivity ratios for ethylene and methyl vinyl ether are reported to be 0 and 2.7, respectively, in the lone reactivity study on this monomer pair.[2a,b] Further, only five patents exist describing ill-defined materials composed of these two monomers.[3−7]

To force these monomers together, pressures up to 80 000 psi and temperatures up to 400 °C were needed yielding highly branched, low molecular weight materials.[6] The infinitely large reactivity ratio inhibits ethylene incorporation at typical high-pressure conditions (∼10 000 psi), although minimal incorporation can be achieved at elevated temperatures and pressures above 20 000 psi. Regardless of chain polymerization conditions employed, structure control is nonexistent. Consequently, reliable material properties data do not exist for such copolymers, information that would be useful in determining fundamental structure−property relationships.

We report a synthetic route to strictly linear ethylene-*co*-methyl vinyl ether copolymers by choosing step polymerization chemistry to circumvent the reactivity ratio dilemma. The elements of the copolymer's repeat units are installed in a single monomer a priori, an approach that also imposes exact monomer sequencing. This methodology is founded on research to study polymer crystal structure and thermal behavior of conventional ethylene/1-alkene copolymers.[8−11]

The facile synthesis of the metathesis monomer, 12-methoxytricosa-1,22-diene (**3**), is depicted in Scheme 1; ADMET polymerization using Schrock's molybdenum catalyst[12] yields **4**, a high molecular weight, unsaturated ethylene/methyl vinyl ether copolymer. This mild polymerization chemistry, operating at 40 °C, is known to yield well-defined copolymers devoid of branching due to lack of side reactions.[13,14] Exhaustive hydrogenation produces a linear ethylene/vinyl ether copolymer, in this case, polymer **5**, which possesses methoxy pendant groups on every 21st carbon along the polymer backbone. This macromolecule can be thought of as a sequenced ethylene-*co*-methyl vinyl ether copolymer with 9.5 ethylene units for every vinyl ether.

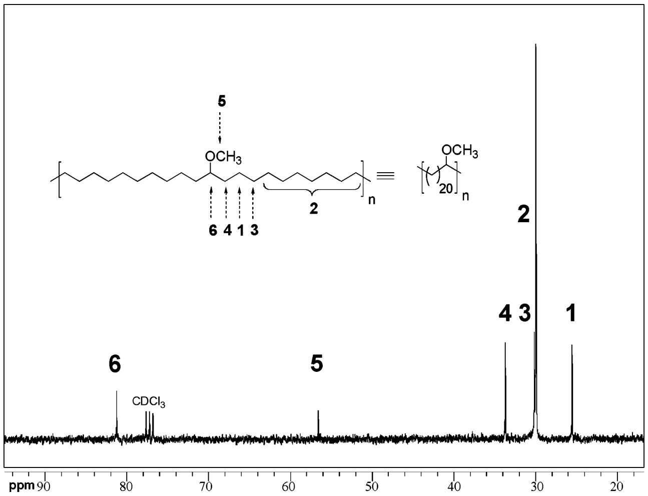
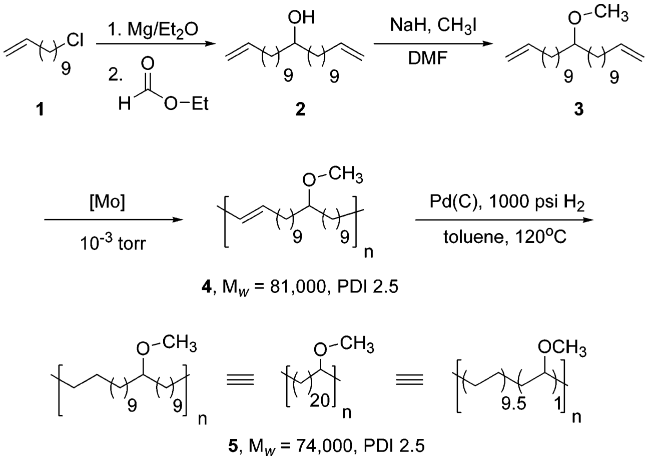


Figure 1. ^{13}C NMR spectrum of ethylene-*co*-methyl vinyl ether copolymer **5** in $CDCl_3$.

Scheme 1. Synthesis of Ethylene-*co*-Methyl Vinyl Ether Copolymer 5



Microstructure control with this degree of precision is unattainable by chain copolymerization; structural elucidation with ^{13}C NMR illustrates the point well (Figure 1). Symmetry found in the repeat unit results in 12 magnetically different carbon nuclei. Six of these resonances are observed on a macromolecule of M_w 74 000 g/mol: four methylene carbons in the backbone and two carbons bonded to oxygen (resonance 2 in the spectrum comprises seven unresolved carbons). There is no question regarding the linearity of the copolymer or the exact sequence of ethylene and vinyl ether repeat units therein.

Fourier transform infrared (FT-IR) spectroscopy confirms complete hydrogenation of copolymer **4** by monitoring the out-of-plane C−H wag of the olefin appearing at 967 cm^{-1}; no residual olefin remains (Figure 2). The asymmetric C−O−C stretch reflective of the ether pendant group is observed at 1097 cm^{-1}, while the remaining absorbance bands in the FT-IR spectrum suggest disordered crystalline polyethylene segments. In particular, the strong bands at 719, 804, and 1469 cm^{-1} indicate a somewhat unorganized crystal packing structure,[15] possibly due to inclusion of the methoxy group into the polymer crystal as a defect. The band at 1367 cm^{-1} is associated with a kink disorder in the

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10.1021/ma0502755 CCC: $30.25 © 2005 American Chemical Society
Published on Web 03/05/2005

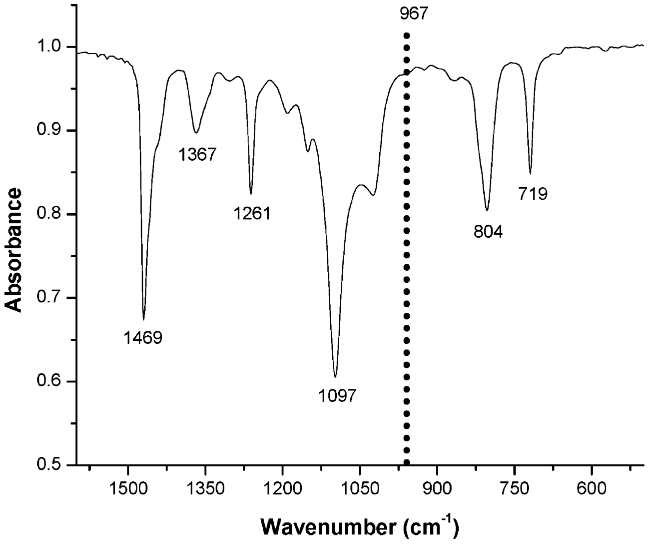

Figure 2. Partial FT-IR spectrum of ethylene-*co*-methyl vinyl ether (**5**) film.

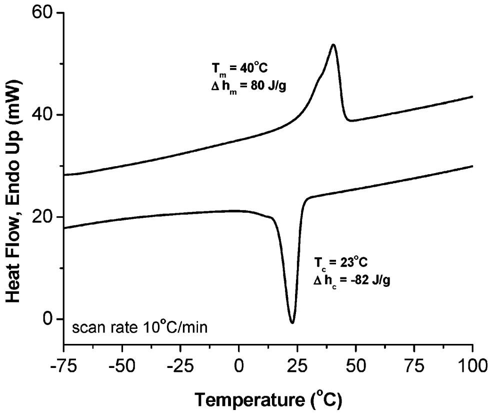

Figure 3. DSC of ethylene-*co*-methyl vinyl ether copolymer **5**.

crystallite[16] and has been observed in high molecular weight polyethylene. These results suggest polyethylene-like crystalline regions with partial inclusion of the methoxy pendant group within the crystalline lattice.

The crystallization behavior revealed in differential scanning calorimetry further confirms the effect of precise structure control (Figure 3). Copolymer **5** exhibits a recoverable endothermic transition at 40 °C (Δh_m = 80 J/g) upon heating and a corresponding exotherm at 23 °C ($\Delta h_c = -82$ J/g) upon cooling. Such thermal transitions can be attributed to the melt and recrystallization of the polyethylene-like crystallites suggested by FT-IR measurements. These thermal data correspond well with our data for similar ethyl branched copolymers of the same ethylene run length.[8] Further studies will compare the distinguishing effects of precisely placed ethyl groups vs methoxy groups, in addition to varying the identity and incorporation level of the vinyl ether comonomer.

The opportunity to examine the behavior of a wide variety of vinyl copolymers unattainable through chain copolymerization is available using this step-growth metathesis methodology. Copolymers of ethylene and any vinyl monomer can now be synthesized containing exact primary structure and predetermined comonomer incorporation levels. Especially attractive are copolymers of other vinyl monomers known not to copolymerize with ethylene due to large reactivity ratio differences like acrylonitrile or isobutylene.

Acknowledgment. The authors of this communication thank the Florida Space Grant Consortium (NASA-FSGC), National Science Foundation (NSF), and the Army Research Office (ARO) for financial support.

Supporting Information Available: Detailed synthetic procedures for all reported molecules and characterization data for polymers including GPC, ^{1}H NMR, ^{13}C NMR, and IR. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0502755