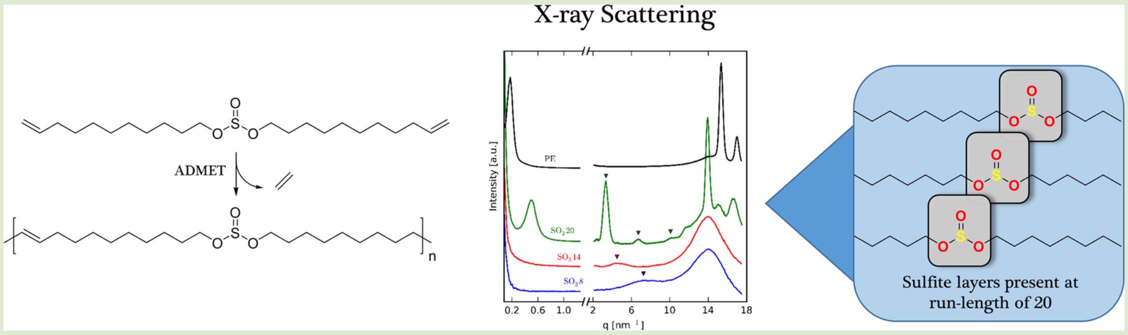
ACS Macro Letters
Letter
pubs.acs.org/macroletters

Precise Sulfite Functionalization of Polyolefins via ADMET Polymerization

Taylor W. Gaines,[†] Tatsuya Nakano,[†,‡] Yoshiki Chujo,[‡] Edward B. Trigg,[§] Karen I. Winey,[§] and Kenneth B. Wagener*,[†]

[†]Butler Polymer Research Laboratory, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States
[‡]Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[§]Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

S *Supporting Information*



ABSTRACT: Copolymers containing sulfite functionalities precisely placed between run lengths of 8, 14, and 20 methylene units were synthesized via ADMET with weight-average molecular weights up to 40 500 g/mol (PDI = 1.89). No such polymer structures have been observed previously. The primary polymer structures and precise nature were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Thermal degradation temperatures up to 310 °C were observed through TGA, and melting points typical of similar unsaturated ADMET polymers were determined by DSC. X-ray scattering was used to compare the polymers to ADMET polyethylene (PE), and when the polymers have 20 carbons between sulfites, the functional groups self-assemble into layers. Higher carbon content incorporation leads to an increase in crystallinity and thermal stability for these polysulfites.

Functionalization of polyolefins with polar moieties is becoming a common theme in ADMET polymerization. The development of highly active and condition-tolerant olefin metathesis catalysts allows for the polymerization of dienes with polar groups, including alcohols,[1,2] urethanes,[3] sugar derivatives,[4] and amino acids[5] to name a few. Such diverse functionalization is a testament to the versatility of ADMET. Precise regioregular structures are afforded free of side reactions associated with conventional polymerization methods (e.g., backbiting in high pressure radical polymerization).[6,7] Elimination of such side reactions allows the investigation of how a precisely located branch or internal functionality affects the polymer's crystalline morphology, which ultimately controls material properties.[8] An early cornerstone of ADMET was the intentional installation of functional defects and branches at known frequencies. With the branch as the only structural defect, its effect is isolated and conclusions could be drawn by comparison to defect-free and commercial samples.[9]

Recently, our group has turned to precision placement of more polar functionalities including carboxylic acids,[10] phosphonic acids,[11] sulfonates,[12] and others.[13] Incorporation of polar functionalities into and on polyethylene backbones at precisely known spacings allows for sophisticated structures, new morphologies, and potential applications (e.g, ion transport). In the present work, our attention has shifted to sulfite ester incorporation. Organic sulfites (sulfite esters) are polar oxidized sulfur groups, similar to sulfurous acid, and have been used as synthetic intermediates, insecticides, plasticizers,[14,15] oxidative inhibitor additives,[16] and even for lithium ion battery applications.[17] This paper reports the synthesis and characterization of unsaturated polymers containing precisely placed sulfite groups within a polyethylene-like backbone. Polymers containing a sulfite every 8th, 14th, and 20th carbon are displayed in Figure 1.

The intention of this study is to incorporate the sulfite functionality into the polyolefin backbone, essentially creating a sulfurous acid ester polyolefin, and to investigate the effect of sulfite concentration on properties and morphology. Exploiting the distinctive precise nature of ADMET, the sulfite

Received: April 21, 2015
Accepted: May 11, 2015
Published: May 20, 2015

DOI: 10.1021/acsmacrolett.5b00258

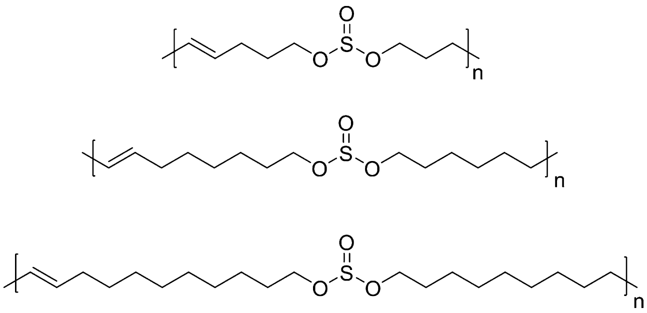
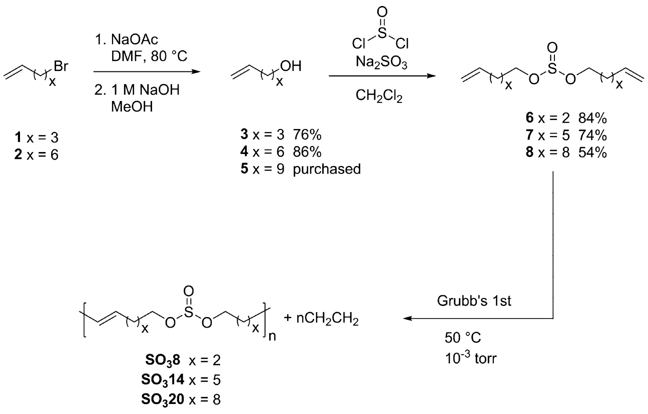


Figure 1. Sulfite-containing polymers synthesized with a sulfite precisely placed every 8th, 14th, and 20th carbon.

concentration effect is an isolated variable from which morphological trends may be elucidated.

The synthesis of precision sulfite monomers is easy, accomplished in two steps. Symmetrical *α*,*ω*-diene sulfite-containing monomers **6**,**7**, and **8** in Scheme 1 of varying lengths were synthesized from an appropriate alkenyl alcohol and thionyl chloride along with sodium sulfite in dichloromethane. Synthesis of the starting alcohols **3**, **4**, and **5** was dictated by the commercial availability of each. Alcohols **3** and **4** were synthesized by acetoxylation of the respective alkenyl bromides **1** and **2**, followed by hydrolysis of the acetate, according to a literature procedure,[18] while **5** was purchased directly. Alcohols were purified via column chromatography before use to ensure that no mono-olefin or mixed-length alkyl species would be present in symmetrical monomers **6**, **7**, and **8**. Monomers were synthesized according to a mild literature procedure by the reaction of alcohols **3**, **4**, and **5** with thionyl chloride and sodium sulfite in dichloromethane at room temperature.[19] The technique varies somewhat from typical procedures that use harsher conditions such as refluxing thionyl chloride. Milder methods prevent alkene side reactions, because such by-products would be carried through to polymerization, ultimately inhibiting polymerization reactions and reducing molecular weights. Monomers were all purified by column chromatography and purity was confirmed by mass spectrometry, elemental analysis, and NMR before proceeding to polymerization. The ^{1}H NMR spectrum of monomer **7** in Figure 2a shows the olefin resonances at around 5.0 ppm (external olefin) and 5.8 ppm (internal olefin). After polymerization using common ADMET conditions (Grubb's first generation catalyst and high vacuum at 50 °C), conversion to polymer **SO$_3$14** is apparent in Figure 2b, which shows only the internal olefins at 5.4 ppm; no end-group olefins are observed. The molecular weight and thermal data for each polymerization are summarized in Table 1.

Scheme 1. Synthesis of Precision Poly(unsaturated sulfites) with Known Spacing Lengths via ADMET[a]



[a]**SO$_3$** denotes the sulfite group and the following number denotes carbon spacing. For example, **SO$_3$8** corresponds to a sulfite precisely located after 8 carbons.

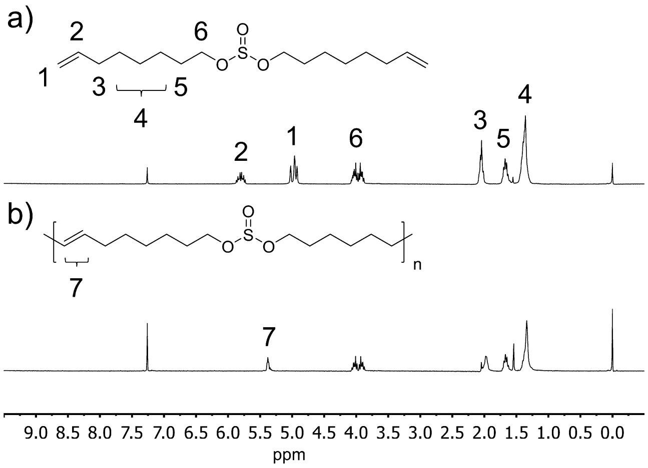


Figure 2. (a) Sulfite monomer **7** ^{1}H NMR with labeled peaks. b) Polysulfite **SO$_3$14** ^{1}H NMR after polymerization displaying no detectable end-groups from sulfite monomer **7**.

Table 1. Molecular Weight and Thermal Data for Poly(unsaturated sulfites) via ADMET

sulfite polymer	$\overline{M}_n \times 10^3$ (g/mol)[a] (PDI)[b]	sulfite per 500 carbons	T_m (°C)	ΔH_m (J/g)
SO$_3$8	7.3 (1.75)	63	amorphous	
SO$_3$14	7.6 (2.51)	36	7	49
SO$_3$20	21.4 (1.89)	25	37	63

[a]Molecular weights obtained by GPC using THF at 40 °C compared to polystyrene standards (g/mol). [b]Polydispersity index ($\overline{M}_w/\overline{M}_n$).

Number-average molecular weights ranged from 7300 to 21400 g/mol for the poly(unsaturated sulfites), with the lower-concentration sulfite **SO$_3$20** possessing the highest molecular weight. We suspect that proximity of the sulfite functionality to the catalysis site may be affecting the mechanism and somewhat inhibiting ADMET reactions for monomers with short methylene spacer lengths. Considering the thermal data for the same polymers (Table 1), a decrease in sulfite concentration leads to a noticeable increase in crystallinity. As sulfite content is decreased from 63 per 500 carbons (**SO$_3$8**) to 36 per 500 carbons (**SO$_3$14**) polymers are no longer amorphous, but are low melting semicrystalline substances. However, increasing the melting temperature above room temperature requires a smaller sulfite to carbon ratio (**SO$_3$20**, 25 sulfites per 500 carbons). Nevertheless, the melting temperatures and heats of fusion are slightly lower than those of a 100% alkene-containing carbon backbone, presumably due to the rotational flexibility accompanying sulfite incorporation. All three sulfite polymers display thermal degradation temperatures between 225 and 310 °C at 5% decomposition (Figure 3). Increasing the carbon content not only increases the degree of crystallinity, but also improves the thermal stability of the

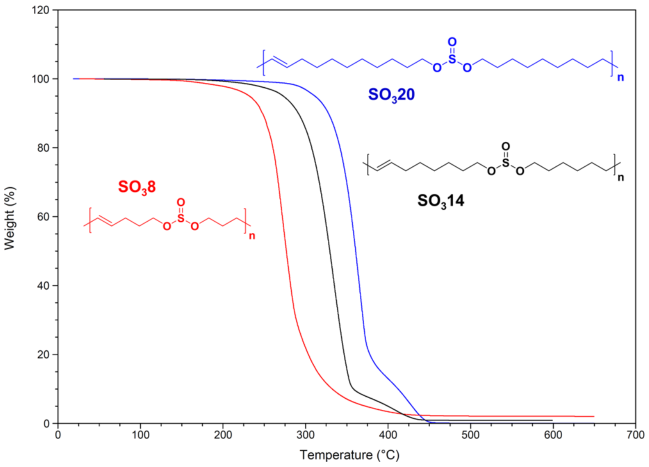


Figure 3. TGA thermograms of each poly(unsaturated sulfite) acquired at 10 °C per minute under N_2 gas purge.

sulfite-containing polymers. More characterization data, including ^{1}H and ^{13}C NMR, IR, and thermal data, are available in the Supporting Information.

In addition to thermal analysis, X-ray scattering provided insight on sulfite−sulfite interactions and how crystallinity is affected by sulfite functionalization. X-ray scattering data for **SO$_3$20**, **SO$_3$14**, and **SO$_3$8** are presented in Figure 4, along with ADMET PE for comparison. The X-ray scattering confirms that **SO$_3$20** is semicrystalline at room temperature, while **SO$_3$14** and **SO$_3$8** are amorphous (Note that scattering experiments were performed at room temperature, above the T_m of **SO$_3$14**). Clearly, increased sulfite incorporation disrupts chain order and crystallization while longer methylene spacings are necessary for semicrystallinity. In **SO$_3$20**, the peak at q = 0.5 nm^{-1}(L ~ 13 nm) indicates the presence of crystallites that are smaller than those in ADMET PE, whose intercrystallite peak occurs at 0.17 nm^{-1}(L ~ 37 nm). The sharp, well-defined peak at q = 13.9 nm^{-1}, further indicates a well-ordered crystalline structure in **SO$_3$20**. As evidenced by the positions of peaks at q > 13 nm^{-1}, the crystal structure of **SO$_3$20** is different from the typical orthorhombic structure of ADMET PE. The peak at 13.9 nm^{-1} is consistent with a monoclinic PE-like crystal structure, as is the peak at 16.6 nm^{-1}.[20] The weak feature at ~15 nm^{-1} may indicate the coexistence of an orthorhombic crystal structure. Polymers **SO$_3$8** and **SO$_3$14** show no peaks at low q and a broad peak at 14 nm^{-1}, indicating amorphous structures.

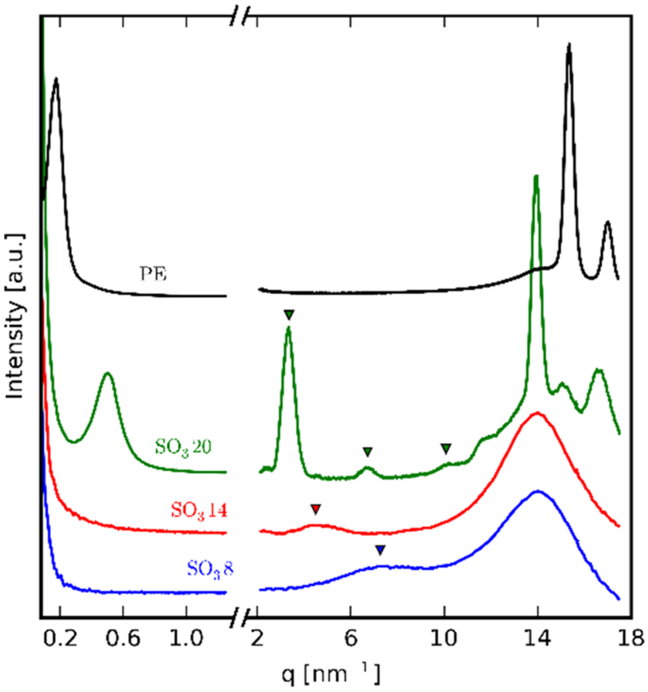


Figure 4. X-ray scattering of **SO$_3$8**, **SO$_3$14**, **SO$_3$20**, and ADMET PE collected at room temperature. Intercrystallite correlation peaks are present at low q for PE and **SO$_3$20** only. Sulfite correlation peaks are indicated with inverted triangles. Crystal diffraction peaks are present at high q for PE and **SO$_3$20** only. Data are rescaled and shifted vertically for clarity.

The sulfite correlation peaks are indicated with inverted triangles in Figure 4. Polymer **SO$_3$20** has three peaks at relative positions q^*:$2q^*$:$3q^*$, indicating 1-dimensional periodicity. This suggests that the sulfite groups form layers within the crystal structure, driven by favorable polar interactions between sulfites. The periodicity of this layered structure is 1.9 nm, while the calculated all-trans length of the polymer repeat unit is 2.8 nm. This difference suggests that the layers of sulfite groups are tilted relative to the chain axis, in contrast to precise poly(ethylene-*co*-phosphonic acid),[21] wherein the acid layers are perpendicular to the alkyl spacers. Both **SO$_3$8** and **SO$_3$14** show single broad peaks indicating disordered or liquid-like arrangements of sulfite groups, either isolated or as small aggregates of the functional groups. The morphological trends of these polymers are similar to those observed in precise poly(ethylene-*co*-1-methylimidazolium bromide),[13] precise poly(ethylene-*co*-acrylic acid), and precise poly(ethylene-*co*-phosphonic acid):[21] polymers with shorter hydrocarbon segments are amorphous, because the high density of functional groups disrupts the polyethlyene crystal structure. Similarly, the layered morphologies have previously been observed in semicrystalline precise copolymers when the alkyl spacer is longer.

In summary, we have demonstrated the ability of ADMET to provide unique functionalized polyolefins containing sulfite functionalities at precisely spaced intervals. By systematically and precisely altering the run-length between sulfite groups, the sulfite effect was isolated from conventional polymerization defects, allowing for further investigation. Higher carbon content poly(unsaturated sulfites) possess greater thermal stability and are semicrystalline, whereas increasing the concentration of sulfite moieties results in an amorphous polymer. X-ray scattering data for the semicrystalline polymer support the existence of sulfite layers and interactions similar to those of other precision materials synthesized via ADMET. This study demonstrates and reiterates ADMET's practicality in producing diverse structures with morphological trends not observed using other polymerization techniques.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials, instrument parameters, synthetic procedures, and characterization data (including spectra and thermograms). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00258.

AUTHOR INFORMATION

Corresponding Author

*E-mail: wagener@chem.ufl.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the U.S. Army Research Laboratory and the U.S. Army Research Office under Grant #W911NF-13-1-0362 for their continued financial support, as well as Materia, Inc. for their generous donation of catalysts. E.B.T. and K.I.W. gratefully acknowledge funding from the Army Research Office through W911NF-13-1-0363. Additional financial support for facilities at the University of Pennsylvania was provided by the MRSEC program of the National Science Foundation (DMR 11-20901).

REFERENCES

(1) Thompson Donovan, L.; Wagener Kenneth, B.; Schulze, U.; Voit, B.; Jehnichen, D.; Malanin, M. *Macromol. Rapid Commun.* **2015**, *36* (1), 60−4.

(2) Tuba, R.; Al-Hashimi, M.; Bazzi, H. S.; Grubbs, R. H. *Macromolecules* **2014**, *47* (23), 8190−8195.

(3) Lebarbe, T.; More, A. S.; Sane, P. S.; Grau, E.; Alfos, C.; Cramail, H. *Macromol. Rapid Commun.* **2014**, *35* (4), 479−483.

(4) Shearouse, W. C.; Lillie, L. M.; Reineke, T. M.; Tolman, W. B. *ACS Macro Lett.* **2015**, *4*, 284−288.

(5) Leonard, J. K.; Hopkins, T. E.; Chaffin, K.; Wagener, K. B. *Macromol. Chem. Phys.* **2008**, *209* (14), 1485−1494.

(6) Opper, K. L.; Wagener, K. B. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49* (4), 821−831.

(7) Schulz, M. D.; Wagener, K. B. *Macromol. Chem. Phys.* **2014**, *215* (20), 1936−1945.

(8) Few Chip, S.; Wagener Kenneth, B.; Thompson Donovan, L. *Macromol. Rapid Commun.* **2014**, *35* (2), 123−32.

(9) Rojas, G.; Inci, B.; Wei, Y.; Wagener, K. B. *J. Am. Chem. Soc.* **2009**, *131* (47), 17376−17386.

(10) Baughman, T. W.; Chan, C. D.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2007**, *40* (18), 6564−6571.

(11) Opper, K. L.; Markova, D.; Klapper, M.; Mullen, K.; Wagener, K. B. *Macromolecules* **2010**, *43* (8), 3690−3698.

(12) Opper, K. L.; Wagener, K. B. *Macromol. Rapid Commun.* **2009**, *30* (11), 915−919.

(13) Aitken, B. S.; Buitrago, C. F.; Heffley, J. D.; Lee, M.; Gibson, H. W.; Winey, K. I.; Wagener, K. B. *Macromolecules* **2012**, *45* (2), 681−687.

(14) van Woerden, H. F. *Chem. Rev.* **1960**, *63* (6), 557−71.

(15) McCormack, W. B.; Lawes, B. C. *Kirk-Othmer Encycl. Chem. Technol.*, 3rd ed.; Wiley: New York, 1983; Vol. *22*, pp 233−54.

(16) Guenther, A.; Koenig, T.; Habicher, W. D.; Schwetlick, K. *Polym. Degrad. Stab.* **1997**, *55* (2), 209−216.

(17) Mao, L.; Li, B.; Cui, X.; Zhao, Y.; Xu, X.; Shi, X.; Li, S.; Li, F. *Electrochim. Acta* **2012**, *79*, 197−201.

(18) Weixler, R.; Hehn, J. P.; Bach, T. *J. Org. Chem.* **2011**, *76* (15), 5924−5935.

(19) Kiasat, A. R.; Kazemi, F.; Khosravian, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179* (2), 427−431.

(20) Seto, T.; Hara, T.; Tanaka, K. *Jpn. J. Appl. Phys.* **1968**, *7* (1), 31−42.

(21) Buitrago, C. F.; Alam, T. M.; Opper, K. L.; Aitken, B. S.; Wagener, K. B.; Winey, K. I. *Macromolecules* **2013**, *46* (22), 8995−9002.