Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of Unsaturated Polythioethers

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ABSTRACT: A series of symmetrical α,ω-unsaturated thioethers have been polymerized under standard acyclic diene metathesis (ADMET) conditions. Poly(thio-3-hexene-1,6-diyl) (**7**), poly(thio-4-octene-1,8-diyl) (**8**), and poly(thio-5-decene-1,10-diyl) (**9**) were synthesized in bulk from the corresponding bis(alkenyl) sulfides (**2**, **3**, and **4**, respectively) in the presence of the catalyst $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCMe(CF_3)_2)_2$ (**5**). Poly[(thio-5-decene-1,10-diyl)-*co*-(1-octenylene)] (**10**) was prepared from the copolymerization of bis(5-hexenyl) sulfide (**4**) and 1,9-decadiene. The polymerizability of the α,ω-dienes appears to be a function of the number of methylene spacers between the sulfur moiety and the terminal olefin. In the case of the monomer diallyl sulfide (**1**), where one methylene spacer is present, no polymerization was observed in the bulk, but rapid cyclization to 2,5-dihydrothiophene (**6**) was observed in solution. All polymers were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopies as well as elemental analysis, GPC, TGA, and DSC. These results suggest that sulfur-containing polymers are now accessible via ADMET polymerization.

Introduction

The viability of acyclic diene metathesis (ADMET) polymerization in the synthesis of unsaturated polymers is now well established.[1–6] Acyclic diene metathesis polymerization is an equilibrium, step-propagation condensation reaction where the production and removal of a small alkene, typically ethylene, drive the reaction forward (Figure 1).[1] In this manner, unsaturated hydrocarbon polymers[1,2] as well as polymers and oligomers containing ether,[3] carbonyl,[4] silyl,[5] and ferrocenyl[6] moieties have been prepared.

The catalysts employed for ADMET polymerization are the Lewis acid-free Schrock's catalysts of the type $M(CHR')(NAr)(OR)_2$ where M = W[7] or Mo,[8] Ar = 2,6-$(i\text{-}Pr)_2C_6H_3$, R′ = CMe_2Ph, and R = $CMe(CF_3)_2$. These classes of alkylidene complexes are perhaps better known for their applications in ring-opening metathesis polymerization (ROMP) where they act as initiators in the metathesis of cyclic olefins.[9] ROMP is a chemically different process from ADMET polymerization in that the thermodynamic driving force for ROMP is derived from the release of ring strain in the monomer unit and the polymer forms via a chain growth process.[10]

Common to both processes is the ability of the molybdenum complexes to initiate polymerizations with monomers possessing a range of functional groups. For the ADMET studies mentioned above, a general rule of monomer structure has evolved where, if a functional group is separated from the terminal alkene by three or more methylene spacers, the reaction will proceed cleanly to generate linear, high molecular weight polymers.[3–5] In some cases, two or fewer methylene spacers will also provide polymer or oligomer, but the result varies depending upon the functionality involved. A well-defined mechanistic interpretation of these observations is not presently available, but it has been denoted in our laboratories as the "negative neighboring group effect."

In an attempt to further explore the negative neighboring group effect and extend the range of functional groups which may be incorporated into polymers made via ADMET, a series of symmetrical α,ω-unsaturated thioethers have been polymerized under bulk ADMET conditions. The present studies demonstrate that ADMET is equally productive, as compared to previous ADMET systems,[3–5] when sulfur is located directly in the main chain.

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

To our knowledge, these polymers are the first linear, unsaturated polythioethers made in this way,[11] and this novel reaction suggests that the catalytic molybdenum complexes involved in the ADMET polymerization mechanism are more stable to Lewis bases than was previously thought. Furthermore, new classes of sulfur containing polymers now appear to be accessible under ADMET polymerization conditions.

Experimental Section

General. ^1H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Varian XL-Series NMR superconducting spectrometer system. All NMR spectra were recorded in $CDCl_3$ with 1% v/v TMS as an internal reference unless otherwise mentioned. Resonances are reported in δ units downfield from TMS at 0.00 ppm. IR spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. HRMS data were recorded on a Finnigan 4500 gas chromatography/mass spectrometer under CI or EI conditions. Gel permeation chromatography (GPC) data were recorded using a Waters Associates liquid chromatograph equipped with an RI detector and are relative to polybutadiene standards. Samples were prepared in THF as eluent and passed successively through 5×10^3 and 5×10^4 Å Phonegel columns at a flow rate of 1 mL/min. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data were recorded on a DuPont 2000 thermal analysis system interfaced to a HIRES TGA 2950 thermogravimetric analyzer and DSC 2910 differential scanning calorimeter, respectively. All thermal analysis was performed in a flowing nitrogen atmosphere.

Monomer Preparation. Diallyl sulfide (**1**) and 1,9-decadiene were purchased from Aldrich Chemical Co. Monomers **2**–**4** were synthesized in the manner reported by Butler and Price,[12] and full spectroscopic characterizations are provided below.

Bis(3-butenyl) Sulfide (2). ^1H NMR: 5.79 (m, 1H), 5.05 (m, 2H), 2.54 (t, J = 7.1 Hz, 2H), 2.29 (m, 2H). ^{13}C NMR: 136.6, 115.6, 33.9, 31.4. IR (NaCl, thin film): 2917, 1640, 1439, 991, 910 cm^{-1}. HRMS: 142.0810, calcd for $C_8H_{15}S$ 142.0994.

Bis(4-pentenyl) Sulfide (3). ^1H NMR: 5.78 (m, 1H), 4.99 (m, 2H), 2.49 (t, J = 7.1 Hz, 2H), 2.15 (m, 2H), 1.66 (m, 2H). ^{13}C NMR: 137.6, 114.8, 32.6, 31.2, 28.6. IR (NaCl, thin film): 2928, 1640, 1439, 991, 910 cm^{-1}. HRMS: 170.1053, calcd for $C_{10}H_{19}S$ 170.1208.

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Bis(5-hexenyl) Sulfide (4). ^{1}H NMR: 5.79 (m, 1H), 4.97 (m, 2H), 2.50 (t, J = 7.1 Hz, 2H), 2.05 (m, 2H), 1.7–1.4 (m, 4H). ^{13}C NMR: 138.3, 114.4, 33.2, 31.8, 28.9, 27.9. IR (NaCl, thin film): 2927, 1640, 1439, 991, 910 cm^{-1}. HRMS: (M + H) 199.1525, calcd for $C_{12}H_{23}S$ 199.1436.

Polymerizations. All glassware was scrupulously cleaned and then oven dried for 24 h before use. Monomers were purified prior to polymerization reactions by stirring over calcium hydride under high (<10^{-5} Torr) vacuum for 5 days (**3**, **4**) or successive high-vacuum transfers onto potassium-mirrored flasks until no reaction was observed (**1**, **2**, 1,9-decadiene). The molybdenum-based Schrock's catalyst **5** was synthesized as reported in the literature.[8]

Polymerizations were initiated in an argon atmosphere under glovebox conditions. A round-bottomed flask (50 or 100 mL) equipped with a high vacuum Teflon valve and magnetic stirring bar was charged with neat monomer (1.0–1.5 g) followed by addition of pure catalyst **5**. Ethylene began to evolve from the mixture almost immediately after the catalyst came in contact with the monomer, and the reaction was continued until a viscosity increase was qualitatively observed. The flask contents were then sealed and the flask placed on a high vacuum line where the polymerization was continued at temperatures from 25 to 50 °C under dynamic high vacuum. Pure ethylene was collected from the polymer reaction as distillate. No other compounds were observed in the distillate as determined by ^{1}H NMR except for residual monomer (<1%) in the case of **2**. Monomer to catalyst ratios as well as reaction times and temperatures are listed below.

It is important to note that the absence of impurities in the monomers are critical to the success of forming high molecular weight polymers. Insufficient drying or even extended exposure (days) of the thioethers to ambient room light in an argon atmosphere sometimes led to marked decreases in metathesis reactivity and polymer weights. Potential thermal and photochemically induced decomposition pathways for the sulfur-containing monomers require complete purification procedures prior to catalyst addition.

To quench the polymerization, the reaction mixture was exposed to air. Polymers were isolated in high yield (>95%), and NMR, IR, and elemental data were collected using the crude polymers prior to purification by precipitation from toluene/methanol. Thermal data were collected after purification. Experimental conditions were not optimized for polymer yields or properties.

Poly(thio-3-hexene-1,6-diyl) (7). Ratio **2**:**5** ≅ 2000:1; rt, 45 min; 45 °C, 5 d. ^{1}H NMR: 5.50, 2.55, 2.29. ^{13}C NMR: 129.6 (trans C=C, 84%), 128.7 (cis C=C, 16%), 32.6 (*trans*-allyl, 84%), 31.8, 27.5 (*cis*-allyl, 16%). IR (NaCl, thin film): 2916, 1441, 971 cm^{-1}. Anal. Calcd: C, 63.36; H, 8.82; S, 27.82. Found: C, 63.13; H, 8.82; S, 27.45.

Poly(thio-4-octene-1,8-diyl) (8). Ratio **3**:**5** ≅ 1000:1; rt, 72 h; 45 °C, 4 d. ^{1}H NMR: 5.41, 2.49, 2.13, 1.63. ^{13}C NMR: 129.8 (trans C=C, 80%), 129.4 (cis C=C, 20%), 31.5, 31.3 (*trans*-allyl, 81%), 29.2, 26.3 (*cis*-allyl, 19%). IR (NaCl, thin film): 2923, 1436, 967 cm^{-1}. Anal. Calcd: C, 67.61; H, 9.86; S, 22.53. Found: C, 67.54; H, 9.86; S, 22.57.

Poly(thio-5-decene-1,10-diyl) (9). Ratio **4**:**5** ≅ 2000:1; rt, 12 h; 45 °C, 4 d. ^{1}H NMR: 5.38, 2.47, 1.97, 1.48. ^{13}C NMR: 130.1 (trans C=C, 81%), 129.6 (cis C=C, 19%), 32.0, 31.9 (*trans*-allyl, 81%), 29.1, 28.7, 26.7 (*cis*-allyl, 19%). IR (NaCl, thin film): 2925, 1437, 967 cm^{-1}. Anal. Calcd: C, 70.59; H, 10.59; S, 18.82. Found: C, 70.51; H, 10.60; S, 18.77.

Poly[(thio-5-decene-1,10-diyl)-*co*-(1-octenylene)] (10). Ratio **4**:1,9-decadiene:**5** ≅ 1000:1000:1; rt, 72 h; 45 °C, 4 d. ^{1}H NMR: 5.35, 2.48, 1.98, 1.52, 1.27. ^{13}C NMR: 130.8, 130.3, 130.2, 129.8, 129.6, 129.2, 32.5, 32.1, 32.0, 29.7, 29.6, 29.5, 29.3, 29.1, 29.0, 28.9, 28.9, 28.8, 28.7, 27.2, 26.8, 26.7. IR (NaCl, thin film): 2925, 1438, 966 cm^{-1}. Anal. Calcd: C, 76.19; H, 11.11; S, 12.70. Found: C, 76.23; H, 11.14; S, 12.61.

Results and Discussion

The broad technical applications of sulfur-containing polymers created a desire to investigate potential approaches via ADMET polymerization in their synthesis.[13] In keeping with previous ADMET studies[3–5] for investigating functional group compatibility with Schrock's metathesis alkylidenes, a series of four α,ω-unsaturated thioethers were chosen as model compounds where the terminal diene unit was sequentially separated from the thio moiety with one to four methylene spacers (compounds **1**–**4**, Figure 2). Dienes **1**–**4** may be purchased (**1**) or synthesized from simple reagents in one step (**2**–**4**)[12] and efficiently purified for ADMET investigations.

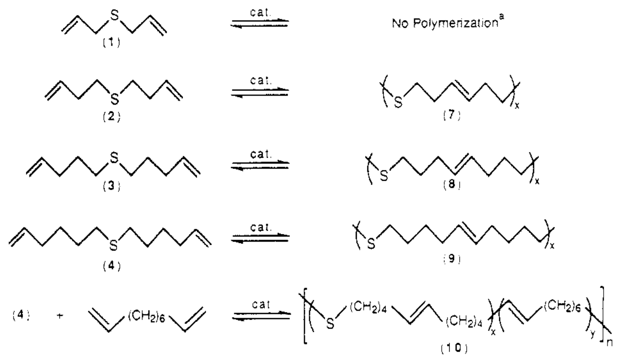


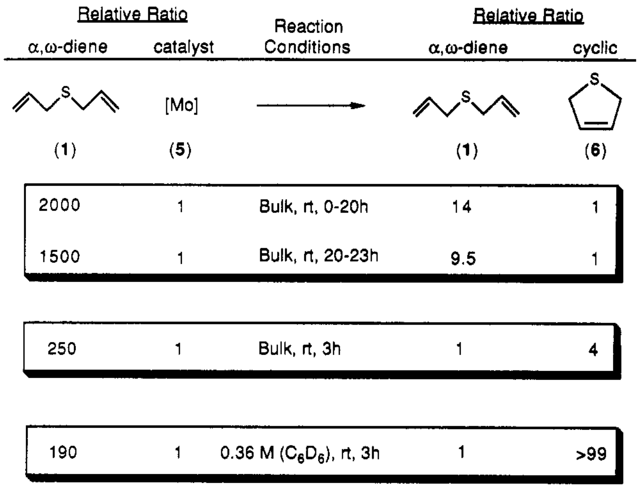
Figure 2. Bulk ADMET polymerization of α,ω-unsaturated thioether monomers to unsaturated polythioethers. Key: (a) see Figure 3 and Discussion.

An initial concern in these investigations was the potential ability of the sulfur group to act as a Lewis base and bind to a molybdenum complex at some stage in the metathesis cycle. In this manner, the catalyst could become poisoned and decompose, or a molybdenum intermediate in the metathesis cycle could become relatively stabilized and slow or stop the propagation rate needed to form high polymers. Lewis base binding effects have been reported previously for similar ROMP systems[14] as have the formation of stable metallacyclobutanes in the metathesis of ester-containing olefins.[15]

Despite these concerns, previous successful ADMET bulk polymerizations of acyclic dienes possessing Lewis basic moieties warranted the investigation of sulfur-containing monomers. More recently, Schrock has reported the successful ROMP preparation of a sulfur-containing polymer from a methyl thioether-substituted norbornene monomer,[16] further suggesting that the sulfur moiety would be tolerated in the ADMET reaction mechanism. In this report, we describe our findings where simple α,ω-unsaturated thioethers were successfully polymerized under standard ADMET conditions. The rules and conditions of reactivity vs monomer structure have been found to match closely with those of the previously reported oxygen ethers with the tungsten analog of the catalyst.[3]

Attempted Polymerization of Diallyl Sulfide (1). When 1 equiv of catalyst **5** was added to 2000 molar excess of diallyl sulfide (**1**) in the bulk, the instantaneous evolution of ethylene was observed which subsided shortly thereafter. Analysis of the mixture by ^{1}H NMR showed three new resonances assigned to ethylene (5.28 ppm) and cyclization product 2,5-dihydrothiophene (**6**) (5.43 and 3.49 ppm in C_6D_6). Subsequent analysis by ^{13}C NMR and GC/MS confirmed the assignment of **6**.[17] The ratio of acyclic diene **1** to cyclic **6** was 14:1 as determined by ^{1}H NMR integration. This ratio did not change when the monomer/catalyst mixture was diluted with either dry benzene-d_6 in an inert atmosphere or with wet benzene-d_6 after exposure to air. Furthermore, no change in the ratio of **1** to **6** was observed over the course of 20 h while the neat mixture was stirred in an argon atmosphere.

When additional catalyst was added to the 1 day old mixture (ca. 33% increase in **5**), a second brief evolution



Relative Ratio α,ω-diene (1)	catalyst (5)	Reaction Conditions	Relative Ratio α,ω-diene (1)	cyclic (6)
2000	1	Bulk, rt, 0-20h	14	1
1500	1	Bulk, rt, 20-23h	9.5	1
250	1	Bulk, rt, 3h	1	4
190	1	0.36 M (C_6D_6), rt, 3h	1	>99

Figure 3. Cyclization reactivity of diallyl sulfide (1) to form 2,5-dihydrothiophene (6).

of ethylene was observed, and the ratio of 1 to 6 was lowered to 9.5:1 with no further change after several hours of stirring. Subsequent removal of volatile products by high vacuum ($<10^{-5}$ Torr) distillation at room temperature left reacted catalyst 5 in the vacuum flask. Addition of 1,9-decadiene to the catalyst afforded no reaction, indicative of catalyst decomposition or deactivation.

When a new 250:1 ratio mixture of monomer to catalyst was prepared, the same reaction was observed. In this instance, however, cyclization product 6 was the major component of the mixture in a 4:1 ratio to diallyl sulfide. When a similar monomer/catalyst reaction was prepared and diluted with dry benzene-d_6 immediately after catalyst addition, 2,5-dihydrothiophene (6) was formed in a 99% NMR yield with no diallyl sulfide resonances observed in the respective NMR spectra.

These observations are similar to the reactivity of diallyl ether and 5, where in the bulk an equilibrium mixture of oligomer and 2,5-dihydrofuran was formed.[18] Why in the present case oligomers do not form under bulk conditions remains open to question at this time. The unsaturated five-membered ring product 6 is apparently thermodynamically favored due to its comparatively low ring strain. In solution, where cyclization would be kinetically favored, the catalyst appears to remain sufficiently reactive in the presence of 1 to complete one intramolecular metathesis cycle and form 6. This cyclization result is consistent with Fu and Grubbs' ring-closing of α,ω-unsaturated ethers, amines, and amides with catalyst 5.[19] It is interesting to speculate that in the bulk, the Lewis basic dihydrothiophene 6 is reacting to poison the catalyst after its formation. This hypothesis would explain the increased conversion of diallyl sulfide (1) to 2,5-dihydrothiophene (6) as a function of increased catalyst addition.

Synthesis of Unsaturated Polythioethers 7–9. When a catalytic amount (≤0.1%) of 5 was added to acyclic dienes 2, 3, or 4, where the number of methylene spacers between the terminal double bond and sulfur atom are two, three, and four, respectively, the evolution of ethylene ensued. Upon an increase in viscosity of the polymeric oils, high vacuum was applied to the mixtures to remove ethylene and drive the equilibrium. The polymers 7, 8, or 9 were stirred at room temperature until the viscosity disallowed magnetic agitation, at which point the products were heated to 50 °C where stirring was continued. When ethylene evolution was visually observed to have stopped or when the polymers again became too viscous to stir, the reactions were quenched.

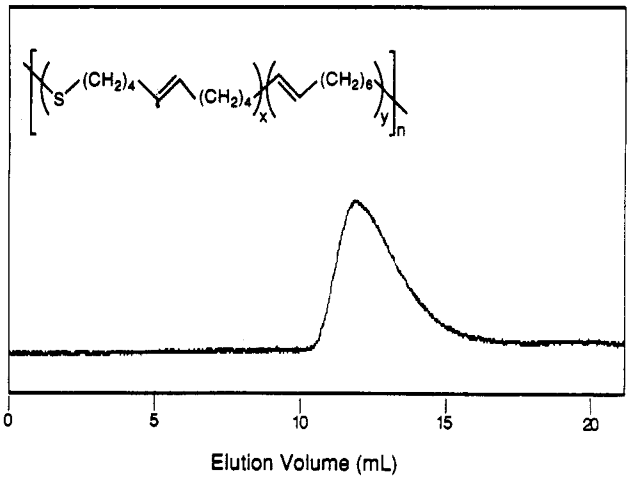


Figure 4. GPC curve of copolymer 10.

Characterization using NMR, IR, GPC, and elemental analysis found products 7–9 to be consistent with the assigned structures and typical of ADMET polymers. ^1H and ^{13}C NMR spectroscopy showed the polymers to be perfectly linear unsaturated thioethers with a trans/cis internal double bond ratio of generally 4:1. Molecular weight values determined by GPC were consistent with those determined by quantitative endgroup NMR integration, and polydispersities approached values of 1.5–2.0, consistent with the ADMET step condensation mechanism. Combustion analysis of the polymers, using NMR-determined molecular weights, clearly showed the expected sulfur content for the assigned polymer structures.

Comparison of number average molecular weights for polythioethers 7 vs 8 and 9 indicate a significant weight increase once three or four methylene spacers separate the terminal diene from the sulfur atom. The transition in reactivity is in accord with other functionalized ADMET polymers where the "negative neighboring group effect" is not observed when three or more methylene spacers are present. An explanation for the somewhat higher molecular weight of polymer 8 as compared to polymer 9 is not known at this time; however, the presence of impurities resultant from the more difficult distillation procedure of high boiling monomer 4 may be responsible. An alternative explanation prescribes the higher weight of polymer 8 to its physical properties. Polymer 8 remains in a "fluid-like" state throughout the course of its formation which allow its reactive ends the mobility necessary to make connections leading to higher weights. In the case of 9, however, the polymer has a higher degree of crystallinity which restricts terminal olefin condensation in the bulk (see Thermal Properties below).

Copolymerization of Unsaturated Thioether 4 and 1,9-Decadiene. When a catalytic amount of 5 (<0.12%) was added to a 1:1 mole mixture of α,ω-unsaturated thioether 4 and 1,9-decadiene, ethylene evolution ensued, leading ultimately to copolymer 10. Full characterization in the manner outlined above once again found the polymer to display properties consistent with the assigned structure. NMR spectroscopy showed the polymer to be perfectly linear with a ratio of ether and octenamer repeat units approximating 1:1. In the ^{13}C NMR spectrum, six unsaturated carbon–carbon double bond resonances were observed as expected for the trans and cis connections of thioether–thioether, octenamer–octenamer, and thioether–octenamer repeat unit combinations.[3] Gel permeation chromatography confirms the synthesis of one copolymer as opposed to a blend of compounds (Figure 4).

Table I. Molecular Weight and Thermal Data for Unsaturated Polythioethers 7–10

polymer	M_n (GPC)[a]	M_w/M_n[a]	M_n (^{13}C NMR)[b]	DSC[c]	TGA[d]
7	3100	1.47	3100	46	295
8	16 330	1.62	17 410	1	370
9	9410	1.86	10 200	23	355
10	34 940	1.31		13	381

[a] Determined relative to polybutadiene standards. [b] Determined by quantitative endgroup integration (internal vs terminal olefinic carbons). [c] Rate: 10 °C/min under N_2, T_m (°C). See also discussion. [d] Rate: 20 °C/min under N_2, temperature (°C) at 10% weight loss.

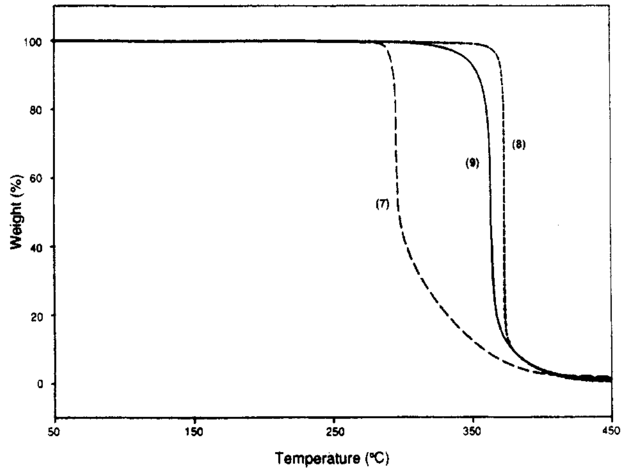


Figure 5. Thermogravimetric analyses of unsaturated polythioethers 7–9.

The above observations suggest that the catalytic molybdenum intermediates involved in polymer formation do not distinguish chemically between the terminal olefins of the thioether and 1,9-decadiene monomers. Finally, copolymer **10** had the highest molecular weight of the series (Table I). Once again, monomer purity may be responsible, but the "fluidlike" state of the copolymer, even at high weights, may facilitate continued productive terminal olefin metathesis.

Thermal Properties of Unsaturated Polythioethers 7–10. Thermogravimetric analysis (TGA) of polymers **7–10** showed all macromolecules to be stable at elevated temperatures (Figure 5 and Table I). In comparison to the oxygen ether analogs,[3] 10% weight loss was found to occur at slightly lower temperatures. This was particularly pleasing in view of the anticipated lower thermal stability due to the relatively weaker carbon–sulfur covalent bond energy.[20] Secondly, stability was found to be directly related to molecular weight, in accord with the oxygen ether system.

In comparison to the saturated analogs of these polymers,[21] the presence of an olefin in the repeat unit apparently leads to no significant change in the polymers' thermal stability. While differences in molecular weight and analysis technique make comparison tenuous, values between the saturated and unsaturated polythioethers fell within 50 °C of each other. Finally, the sharp weight loss of the TGA curves for **7–9** indicated a clean decomposition pathway as expected for these linear polymers.

Differential scanning calorimetry (DSC) showed some startling differences in the melting properties of polymers **7–9** as a function of methylene spacers between the sulfur atom and olefin of the repeat unit (Figure 6 and Table I). Unsaturated polymer **7** showed a three-phase melting transition at 36, 43, and 47 °C. Polymer **8** displayed a two-phase transition at 1 and 7 °C, and polymer **9** displayed only one melting transition at 23 °C. All endotherms remained unchanged after at least three recrystallization/melting cycles. In comparing the melting point vs the number of methylene spacers between the repeat unit sulfur atom and double bond for each polymer, it is observed that the two-methylene spacer polymer **7** had the highest T_m, four-methylene spacer polymer **9** was lower, and finally three-methylene spacer polymer **8** had the lowest T_m of the series.

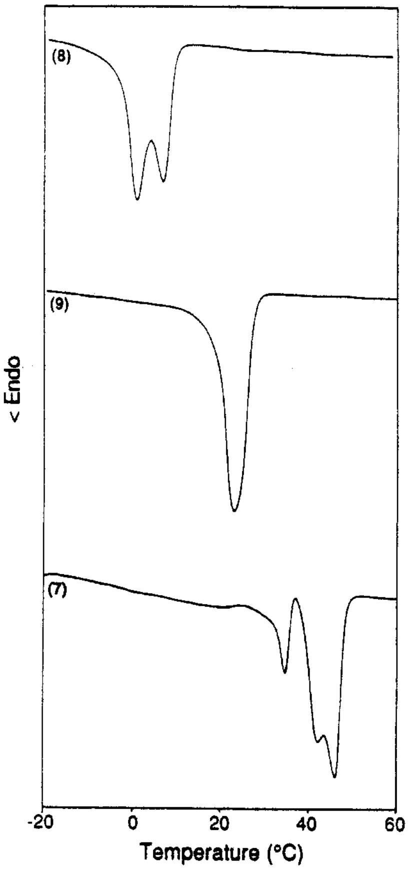


Figure 6. DSC analysis for T_m of unsaturated polythioethers 7–9.

Previous ADMET-synthesized polymers have displayed similar melting point variations as the number of methylene (CH_2) spacers between the functional group and olefin changed from two to three and/or four.[3,4] For example, in the case of unsaturated polyesters,[4a] melting points were observed at 163, 40, and 101 °C for the symmetrical two-, three-, and four-CH_2 spacer polymers, respectively. Symmetrical unsaturated ADMET polyethers and carbonates with three CH_2 spacers were found to have no melting transitions at all.[3,4b] Similar changes in T_m as a function of methylene spacer have been reported for the saturated versions of the sulfur polymers where poly(methylene sulfide) and poly(ethylene sulfide) have high T_m values, the T_m of poly(trimethylene sulfide) is considerably lower, and the T_m for the higher homologues increase again as the number of CH_2 spacers increases.[21,22] In fact, a variety of other polymers possessing a linear chain of methylenes and one functional group per repeat unit also show these trends in melting temperature as the number of CH_2 spacers change.[23]

On the basis of the limited data from ADMET-synthesized polymers, a similar trend in T_m as a function of CH_2 spacers between the functional group and olefin appears to be developing. That is, for the appropriate ADMET polymers made from symmetrical α,ω-unsaturated dienes, the three-CH_2 spacer polymer of the series can be expected to have the lowest T_m. We note, however, that ADMET polymers possess two different groups in the backbone (an olefin and in the present case a sulfur atom), as compared to the monofunctional polymers for which the CH_2 spacer vs T_m relationship was originally observed. Secondly, differences in polymer weights, dispersities, and structures resultant from the synthesis method and degree of polymerization are also expected to affect T_m values. For these reasons, a relationship between the physical properties of ADMET polymers and the number of methylene spacers per functional group and olefin is discussed with prudence.

Finally, DSC analysis of copolymer **10** showed a single endothermic transition at 13 °C which remained unchanged after repeated temperature cycles. As expected, the T_m value was below that of either of the two homopolymers, polymer **9** or 77% trans polyoctenamer (52 °C).[1] This value was also lower than that reported for the oxygen analog of the copolymer which had a T_m of 31 °C for an approximate 2:1 octenamer/ether repeat unit ratio.[3]

Conclusion

A series of unsaturated polythioethers have been synthesized under standard acyclic diene metathesis (ADMET) conditions. Symmetrical α,ω-dienes where the internal sulfur atom is separated from the terminal olefin by two, three, and four methylene spacers all react cleanly to form linear polymers. A relatively lower molecular weight for the two-methylene spacer polymer may suggest that some form of intramolecular deactivation of the catalyst metal center is occurring. When one methylene spacer separates the olefin from the sulfur atom, partial cyclization occurs in the bulk, but quantitative cyclization occurs in solution. All of the polymers synthesized displayed a high degree of thermal stability. Melting transitions were also observed for the polymers which vary with the number of methylene spacers in the polymer repeat unit. A copolymer synthesized using 1,9-decadiene and bis(5-hexenyl) sulfide was also prepared. While the present polymers may be considered too low in molecular weight for practical application, the above results strongly suggest that novel and technologically important polymers containing sulfur in the backbone may now be accessible via ADMET polymerization.

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