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On the Polymerization Behavior of Telomers: Metathesis versus Thiol−Ene Chemistry

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ABSTRACT: The potential of butadiene ditelomers for the synthesis of polymers has been investigated for the first time following two different approaches: acyclic diene metathesis (ADMET) polymerization and thiol−ene polyaddition. The feasibility of both step-growth polymerization methods has been investigated by focusing on the particular polymerization behavior of these unusual monomers. It has been shown that ring-closing metathesis of the studied ditelomers predominates in the first steps of ADMET, followed by oligomerization and double bond isomerization. On the other hand, during thiol−ene polyaddition, additional isomerization reactions, converting allyl ether moieties to vinyl ether moieties, were observed. Generally, the thiol−ene polymerization approach led to higher molecular weight polymers with better characteristics and interesting material properties.
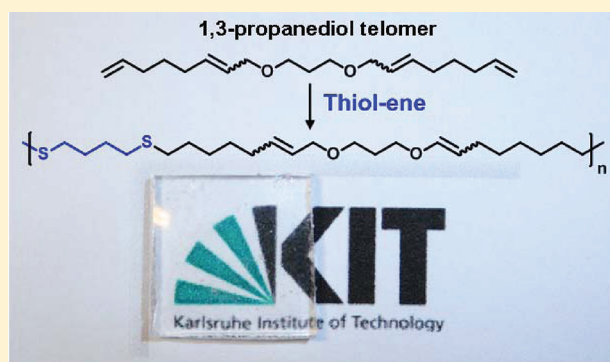
INTRODUCTION

Along with the idea of substituting petroleum-based feedstocks with renewable ones, the development of more sustainable and environmentally benign technologies for the production of versatile building blocks and polymers has become one of the most important items on the agenda of industry as well as academia.[1] In light of this general desire for more efficient and at the same time environmentally friendlier processes, the addition of nucleophiles to olefins and alkynes, typical examples of 100% atom-efficient reactions, can be considered as particularly attractive green processes. Among these reactions, the telomerization reaction,[2] a synthetic methodology originally discovered by Smutny in 1967,[3] is reported to provide linear dimerization products of 1,3-dienes (such as 1,3-butadiene and isoprene) via 1,6- or 3,6-addition of an appropriate nucleophile (e.g., alcohols,[4] water,[5] amines and ammonia,[6] sugar[7] and polyols,[8] starch,[9] and carbon dioxide[10]) in good yields for countless applications. This valuable process enables, for instance, the synthesis of intermediates for natural products or fine chemicals synthesis[11] and the preparation of amphiphilic compounds that find use as surfactants or emulsifiers if the proper diene/nucleophile combination is selected.[12] In addition, if the applicability of telomers, in particular α,ω-diene ones, could be extended to polymerization reactions, this would open up new opportunities for building high molecular weight and value-added materials. Notably, our literature survey has shown only a limited number of studies reporting the use of telomers as monomers for polymer synthesis. One example is the copolymerization of ethylene with 2,7-octadienyl methyl ether, a monotelomer available from the telomerization of 1,3-butadiene with methanol and palladium catalysts.[13] However, ditelomers have not yet been investigated for step-growth polymerizations. Since telomers contain double bonds, it should be possible to polymerize them using acyclic diene metathesis (ADMET) polymerization. This polymerization technique is advantageous since the catalysts employed are tolerant toward many functional groups, the reaction conditions are mild, and a wide range of molecular architectures are accessible.[14] Another well-established concept, the radical-initiated thiol−ene reaction,[15] has also been widely applied in the field of polymer science.[16] The so-called thiol−ene click reaction, discovered in 1905 by Posner,[17] is a well-known example of this type of reaction. Extensive investigations in the context of the reaction mechanism, polymerization kinetics, and monomer reactivity[18] have revealed that, in addition to being highly efficient under benign reaction conditions (compatible with water and oxygen), the thiol−ene coupling reaction is regioselective, metal-free, orthogonal to many functional groups, and provides quantitative or near-quantitative yields with simple or no chromatographic separation required.[14,19] Furthermore, some studies have already focused on the direct synthesis of linear oligomers and polymers through step-growth and addition/chain polymerizations of diolefins with dithiols.[20]

Thus, in order to broaden the application possibilities of butadiene telomers, we report here a comparative study on the polymerization of α,ω-diene telomers using two straightforward and simple chemical pathways: the acyclic diene metathesis and thiol–ene polymerizations as versatile tools to convert such valuable monomers into potentially useful macromolecular materials.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. Thin layer chromatography (TLC) was performed on silica gel TLC cards (layer thickness 0.20 mm, Fluka). Permanganate reagent was used as developing solution.

All ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired in CDCl$_3$ (99.8 atom % D, Armar Chemicals) as solvent using Bruker AVANCE DPX spectrometers operating at 300 and 400 MHz for ^{1}H NMR and 75.5 and 100 MHz for ^{13}C NMR. Chemical shifts (δ) are given in ppm relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm) for ^{1}H NMR. The ^{1}H NMR spectra were referenced to the residual proton impurities in the CDCl$_3$ at δH 7.26 ppm. The ^{13}C NMR spectra were referenced to ^{13}CDCl$_3$ at δC 77.00 ppm. For the analysis of the polymers the relaxation time was set to 5 s.

Molecular weight and PDI (M_w/M_n) values of the polymers were obtained by SEC (GPC) using a LC-20A system from Shimadzu equipped with an SIL-20A autosampler and an RID-10A refractive index detector in THF (flow rate 1 mL min^{-1}) at 50 °C. The analysis was performed on three different column systems; (A): PLgel 5 μm MIXED-D column (Varian, 300 mm × 7.5 mm, 10000 Å) with SDV gel 5 μm precolumn (PSS, 50 mm × 8.0 mm), (B): two PSS SDV column system (5 μm 300 mm × 7.5 mm, 1000 Å, 10000 Å) and (C): three PSS SDV column system (5 μm 300 mm × 7.5 mm, 100 Å, 1000 Å, 10000 Å). All determinations of molar mass were performed relative to linear poly(methyl methacrylate) standards (Polymer Standard Service, M_P 1100–981000 Da).

Differential scanning calorimetry (DSC) experiments were carried out under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} with a DSC821e (Mettler Toledo) calorimeter up to a temperature of 250 °C using a sample mass in the range of 8–15 mg. Data from second heating scans are reported unless special heating treatments were applied. The glass transition temperature, T_g, is reported as the midpoint of the heat capacity change.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851e instrument (Mettler Toledo) at a heating rate of 10 °C × min^{-1} under nitrogen. The weights of the samples were of about 8 mg.

All chemicals were used as received: Pd(dba)$_2$ (dba, bis(dibenzylideneacetone) (Aldrich), TOMPP (tris(o-methoxyphenyl)phosphine), 1,3-propanediol (>99%, Fluka), 1,3-butadiene (Linde Gas), 1,4-benzoquinone (**BQ**, >99%, Aldrich), 1-octanethiol (>98.5%, Aldrich), 1,4-butanedithiol (**DT1**, >97%, Aldrich), 2-mercaptoethyl ether (**DT2**, >95%, Aldrich), 3,6-dioxa-1,8-octanedithiol (**DT3**, >95%, Aldrich), benzylidenebis(tricyclohexylphosphine) dichlororuthenium (**C1**, Grubbs catalyst first generation, Aldrich), benzylidene [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene] dichloro(tricyclohexylphosphine) ruthenium (**C2**, Grubbs catalyst second generation, Aldrich), (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(o-isopropoxyphenylmethylene) ruthenium (**C3**, Hoveyda−Grubbs catalyst second generation, Aldrich), [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro [2-(1-methylacetoxy)-phenyl]methylene ruthenium(II) (**C4**, Umicore MS$_1$), ethyl vinyl ether (99%, Aldrich), 2,2′-azobis(2-methylpropionitrile) (**AIBN**, 98%, Aldrich) was used after recrystallization from methanol. All solvents (technical grade) were used without purification.

General Procedure for Ditelomers (1, 2, and 3) Synthesis. A standard telomerization procedure[4a] was adapted in order to maximize ditelomer formation for 1,3-propanediol. The reactions were performed inside a 100 mL stainless steel Parr autoclave. In a typical run, the autoclave was first loaded with the alcohol (0.12 mol), Pd(dba)$_2$ (4.85 × 10^{-5} mol) and the ligand TOMPP (tris(o-methoxyphenyl)-phosphine) (3.8 × 10^{-4} mol) at room temperature after which the autoclave was cooled to −40 °C. 1,3-Butadiene was directly condensed

in the reactor and the autoclave was heated to the reaction temperature of 80 °C and kept at that temperature until the pressure had dropped to less than 3 bar after around 12 h (indicating that the reaction was finished). An excess of butadiene (1,3-butadiene:alcohol molar ratio of 6:1) was employed in all experiments in order to ensure complete telomerization of the alcohol. Three different phosphine to metal ratios were used in the telomerization of 1,3-butadiene with 1,3-propanediol: 4:1 (telomer **1**), 8:1 (telomer **2**), and 16:1 (telomer **3**). After purification of the products, the amount of the ditelomer of 1,3-propanediol was calculated to be more than 91%. The telomer products were isolated by column chromatography, for which a silica gel column (internal diameter: 50 mm, height: 250 mm, dead volume: 70 mL) was loaded with the telomer products. Two column volumes of hexane were eluted and discarded, after which the telomers were separated using a hexane:diethyl ether (9:1 v/v) mixture as the eluent. Pooled fractions were dried in vacuum and purity checked by ^{1}H NMR. The linear-to-branched (l/b) ratio was determined from the GC and NMR analysis of the isolated products.

Thiol−Ene Model Reaction. The thiol−ene model reactions were performed in a carousel reaction station RR98072 (Radleys Discovery Technologies, U.K.). Into a reaction tube, 0.5 g (1.71 mmol) of the ditelomer and 1.0 g of 1-octanethiol (6.84 mmol) were introduced and degassed via 3 times 200 mbar vacuum and subsequent Ar purge. The reaction were conducted either radically (model reaction A) or thermally induced (model reaction B) under solvent-free conditions at the desired reaction temperature (75 and 70 °C for the respective model reactions A and B). In the case of radical-initiated reactions, 2.5 mol % (0.04 mmol) of **AIBN** was added to the reaction mixture. The reactions were followed with TLC with hexane−ethyl acetate (15:1, v:v) as eluent. Moreover, the monomer conversion was calculated from integration of corresponding ^{1}H NMR signals. A relaxation time (d_1) of 5 s was used in the ^{1}H NMR analyses in order to obtain reliable integral values. The reaction products were purified by column chromatography with hexane−ethyl acetate (15:1, v:v) as eluent.

Model Reaction Products. ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 6.20 (d, −CH=CH−O−CH$_2$−, J = 12.6 Hz, 1H$_{trans}$), 5.91 (dd, −CH=CH−O−CH$_2$−, J = 6.2, 1.3 Hz, 1H$_{cis}$), 5.72−5.62 (m, −CH=CH−CH$_2$O−$_{trans\ isomer}$, −CH=CH$_2$ branched telomer), 5.58−5.48 (m, −CH=CH−CH$_2$−O−$_{trans\ isomer}$, −CH=CH−CH$_2$−O−$_{cis\ isomer}$), 5.17−5.11 (m, −CH=CH$_2$ branched telomer), 4.81−4.68 (m, −CH=CH−O−CH$_2$−, 1H$_{trans}$), 4.37−4.25 (m, −CH=CH−O−CH$_2$−, 1H$_{cis}$), 3.99 (d, J = 4.8 Hz, −CH=CH−CH$_2$−O−$_{cis\ isomer}$), 3.89 (d, J = 5.9 Hz, −CH=CH−CH$_2$−O−$_{trans\ isomer}$), 3.79−3.64 (m, −CH=CH−O−CH$_2$−CH$_2$−CH$_2$−O−), 3.48 (t, J = 6.4 Hz, −O−CH$_2$−CH$_2$−CH$_2$−O−), 2.57−2.46 (m, −CH$_2$−S−CH$_2$−), 2.10−1.98 (m, −CH$_2$−CH=CH−), 1.90−1.79 (m, −O−CH$_2$−CH$_2$−CH$_2$−O−, −CH=CH−O−CH$_2$−CH$_2$−CH$_2$−O−), 1.67−1.52 (m, −S−CH$_2$−CH$_2$−CH$_2$−), 1.42−1.31 (m, −CH$_2$−), 0−92−0.84 (t, −CH$_3$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 146.18 (−CH=CH−O−CH$_2$− $_{cis\ isomer}$), 144.99 (−CH=CH−O−CH$_2$−$_{trans\ isomer}$), 134.31 (−CH=CH−CH$_2$−O−$_{trans\ isomer}$), 134.17 (−CH=CH−CH$_2$−O−$_{cis\ isomer}$), 126.95 (−CH=CH−CH$_2$O−$_{cis\ isomer}$), 126.80 (−CH=CH−CH$_2$O−$_{trans\ isomer}$), 106.78 (−CH=CH−O−CH$_2$−$_{cis\ isomer}$), 104.09 (−CH=CH−O−CH$_2$−$_{trans\ isomer}$), 74.88 (−CH=CH−O−CH$_2$−CH$_2$−CH$_2$−O−), 71.80 (−CH=CH−CH$_2$−O−$_{trans\ isomer}$), 67.38 (−O−CH$_2$−CH$_2$−CH$_2$−O−), 66.65 (−CH=CH−CH$_2$−O−$_{cis\ isomer}$), 32.35 (−CH$_2$−S−CH$_2$−), 32.29 (−CH$_2$−S−CH$_2$−), 32.15 (−CH$_2$−CH=CH−O−), 31.93 (−CH$_2$−CH=CH−CH$_2$−O−), 30.37 (−O−CH$_2$−CH$_2$−CH$_2$−O−), 30.13 (−CH=CH−O−CH$_2$−CH$_2$−CH$_2$−O−), 29.79 (−S−CH$_2$−CH$_2$−CH$_2$−CH$_2$−), 29.72 (−S−CH$_2$−CH$_2$−CH$_2$−), 28.90 (−S−CH$_2$−CH$_2$−CH$_2$−), 28.67 (−CH$_2$−CH$_2$−CH$_2$=CH−), 28.4 (−CH$_2$−CH$_2$−CH$_2$−CH$_3$), 22.27 (−CH$_2$−CH$_3$), 14.14 (CH$_3$).

Polymerization Reactions. *General Procedure for ADMET Polymerizations.* The ADMET reactions were performed in a carousel reaction station RR98072 (Radleys Discovery Technologies, UK). Ditelomer **1**, **2**, or **3** (0.5 g, 1.71 mmol) was added into the carousel tube. Different amounts of catalysts (**C1**, **C2**, **C3**, or **C4**; see Figure 1) were added separately. The influence of the reaction conditions on the obtained molecular weight was studied (Tables 1, 2, and 3). Ethylene gas (byproduct) was removed by applying gas or
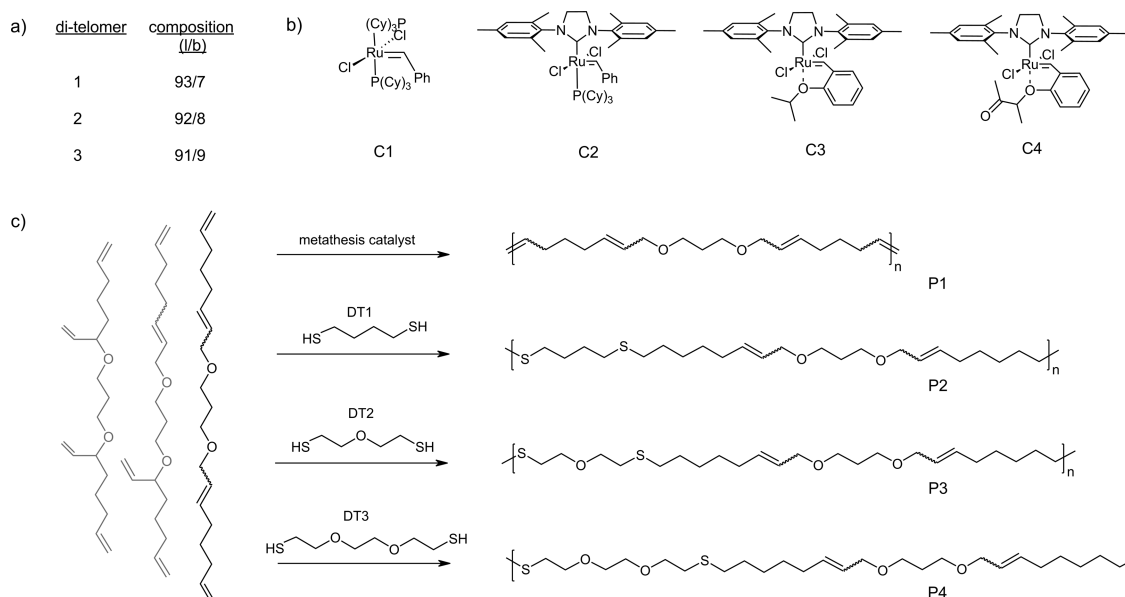
Figure 1. (a) Ditelomer composition as obtained via GC−MS and NMR analysis; (b) metathesis catalysts applied during ADMET studies of the ditelomers; (c) schematic representation of the applied polymerization techniques and idealized products.

Table 1. Selected Results of ADMET Studies of Telomer 1 in the Presence of C1 at Different Reaction Temperatures after 4 h Reaction Time

entry[a]	catal (mol %)	T (°C)	$M_w{}^b$ (Da)	PDI[b] (M_w/M_n)
1	**C1** [0.2]	40	600	1.35
2	**C1** [0.4]	40	650	1.27
3	**C1** [0.8]	40	650	1.32
4	**C1** [1.0]	40	700	1.26
5	**C1** [1.6]	40	750	1.48
6	**C1** [2.0]	40	820	1.50
7	**C1** [0.4]	50	830	1.50
8	**C1** [0.4]	60	750	1.48
9	**C1** [0.4]	70	690	1.42

[a]Additional conditions applied during polymerization: argon was applied for 4 h, unless otherwise specified. [b]GPC was performed on crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight-average molecular weight detected via GPC.

Table 2. Selected Results of ADMET Studies of Telomer 1 in the Presence of C2, C3, and C4 at Different Reaction Temperatures after 4 h Reaction Time

entry	catal (mol %)	conditions[a]	T (°C)	$M_w{}^b$ (Da)	PDI[b] (M_w/M_n)
1	**C2** [0.4]	−	40	2200	1.82
2	**C2** [0.4]	**BQ** [0.8]	40	750	1.39
3	**C2** [0.4]	−	60	1500	1.64
4	**C2** [0.4]	−	80	890	1.54
5	**C3** [0.4]	−	40	1100	1.69
6	**C3** [2.0]	−	40	1900	1.74
7	**C3** [2.0]	**BQ** [4.0]	40	4650	1.98
8	**C3** [1.0]	−	80	1900	1.75
9	**C3** [1.0]	**BQ** [2.0]	80	4000	2.01
10	**C3** [1.0]	**BQ** [8.0]	80	4900	2.65
11[c]	**C3** [1.0]	**BQ** [8.0]	80	5600	2.17
12	**C4** [1.0]	−	80	1750	1.78
13	**C4** [1.0]	**BQ** [8.0]	80	1950	1.84
14[c]	**C4** [1.0]	**BQ** [8.0]	80	5450	2.33
15[d]	**C3** [1.0]	**BQ** [8.0]	80	9400 (6350)[e]	5.73 (2.48)[e]
16[d]	**C4** [1.0]	**BQ** [8.0]	80	3800 (2750)[e]	2.71 (2.50)[e]

[a]Additional conditions applied during polymerization: argon was applied for 4 h, unless otherwise specified; BQ: amount of benzoquinone in % with respect to monomer. [b]GPC was performed on crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight-average molecular weight detected via GPC. [c]Vacuum was applied for 4 h instead of gas flow. [d]Reactions were performed for 48 h with continuous argon flow for the first 4 h. [e]GPC data for crude reaction samples after 24 h, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration.

vacuum continuously. The reactions were cooled down to room temperature and quenched in THF by adding ethyl vinyl ether (500-fold excess to the catalyst) with stirring for 30 min at room temperature. Samples were taken periodically to determine the monomer conversion and the molar mass (distribution) of the resulting polymers using ^{1}H, ^{13}C NMR spectroscopy, as well as GPC analysis. The final reaction mixtures were precipitated in ice cold methanol. The yields varied in the range of 50−85%.

General Procedure for Thiol−Ene Polymerizations. The thiol−ene polymerization reactions were performed in a carousel reaction station RR98072 (Radleys Discovery Technologies, U.K.). Into a reaction vessel 0.5 g (1.71 mmol) of the ditelomer (**1**, **2**, or **3**) and the corresponding dithiol compound (see Table 4) were introduced and degassed via 3 times 200 mbar vacuum and subsequent Ar purge. Afterward, the reaction was let to stir magnetically (500 rpm) at the desired reaction temperature (35−70 °C) until the reaction became very viscous and could not be stirred anymore (Table 4). In some cases, desired amounts of **AIBN** (1.0−2.5 mol %) were added to the reaction mixture and reacted at 75 °C (Table 4). The final reaction mixtures were precipitated in ice cold methanol. The yields varied in the range of 70−92%.

Spectroscopic Data of Representative Thiol−Ene Polymers. **P2.** ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 5.85−5.72 (m, −CH=CH$_2$), 5.72−5.62 (m, −CH=CH−CH$_2$−O−$_{trans\ isomer}$, −CH=CH$_2$ $_{branched\ telomer}$), 5.58−5.48 (m, −CH=CH−CH$_2$−O−$_{trans\ isomer}$, −CH=CH−CH$_2$−O−$_{cis\ isomer}$), 5.17−5.11 (m, −CH=CH_2 $_{branched\ telomer}$), 5.01−4.92 (m, −CH=CH_2), 3.99 (d, J = 4.8 Hz, −CH=CH−CH_2−O−$_{cis\ isomer}$), 3.89 (d, J = 5.9 Hz, −CH=CH−

Table 3. ADMET Screening of Monomers 2 and 3 at 80°C with 1.0 mol % C3 (or C4) and 8.0 mol % BQ[b]

entry	monomer	catal (mol %)	T (°C)	$M_w{}^a$ (Da)	PDI^a (M_w/M_n)
1	2	C3 [1.0]	80	5350	4.35
2	2	C4 [1.0]	80	4950	3.85
3	3	C3 [1.0]	80	3500	5.84
4	3	C4 [1.0]	80	4220	3.61

^{a}GPC was performed to crude reaction samples, quenched with ethyl vinyl ether, in THF, containing BHT, with PMMA calibration; M_w is the weight-average molecular weight detected via GPC. ^{b}Additional conditions were applied during polymerization: vacuum was applied for 4 h, unless otherwise specified.

Table 4. Reaction Conditions and Analytical Data of Selected Thiol−Ene Polymerizations[d]

entry	monomer:thiol (ratio)	T (°C)	rxn time (h)	$M_w{}^a$ (Da)	PDI^a (M_w/M_n)
1[b]	1:DT1 = 1:1	35	24 (72)	2180	1.85
2	1:DT1 = 1:1	50	48	19 820	5.60
3[c]	1:DT1 = 1:1	70	24	124 200	27.00
4	1:DT2 = 1:1	35	72	49 900	9.88
5	1:DT2 = 1:1	50	96	48 100	6.40
6	1:DT2 = 1:1	70	56	40 200	9.46
7	1:DT3 = 1:1	50	48	53 800	8.61
8	1:DT1 = 1:0.95	50	72	6380	2.91
9	1:DT1 = 0.95:1	50	56	20 300	5.08
10	1:DT2 = 1:0.95	50	96	20 600	3.61
11	1:DT2 = 0.95:1	50	96	480 000	53.0
12	1:DT1 = 1:1 (2.5 mol % AIBN)	75	1	12 100	3.22
13	1:DT2 = 1:1 (2.5 mol % AIBN)	75	1	13 150	5.01
14	1:DT3 = 1:1 (2.5 mol % AIBN)	75	1	32 600	5.74
15	1:DT3 = 1:1 (1.0 mol % AIBN)	75	4	8350	2.49

^{a}GPC was performed to crude reaction samples in THF, containing BHT, with PMMA calibration; M_w is the weight-average molecular weight detected via GPC. ^{b}Reaction was performed for 72 h, however there was no difference between the GPC data of 24 and 72 h. ^{c}GPC data is for the corresponding soluble part of the crude reaction mixture. ^{d}Additional conditions applied during polymerization: reaction mixtures were degassed via 3 times 200 mbar vacuum and subsequent Ar purge, unless otherwise specified.

$CH_2-O-_{trans\ isomer}$), 3.48 (t, J = 6.4 Hz, $-O-CH_2-CH_2-CH_2-O-$), 2.57−2.46 (m, $-CH_2-S-CH_2-$, $-CH_2-SH_{end\ group}$), 2.10−1.98 (m, 1H, $-CH_2-CH=CH-$), 1.90−1.79 (m, 1H, $-O-CH_2-CH_2-CH_2-O-$, $-CH_2-CH_2-SH_{end\ group}$), 1.74−1.63 (m, $-S-CH_2-CH_2-CH_2-CH_2-S-$), 1.63−1.52 (m, 1H, $-S-CH_2-CH_2-CH_2-$), 1.52−1.42 (m, $-CH_2-CH_2-CH=CH_{2\ end\ group}$), 1.42−1.31 (m, $-CH_2-$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 138.80 ($-CH=CH_2$), 134.31 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 134.17 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 126.95 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 126.80 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 114.73 ($-CH=CH_2$), 71.80 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 67.38 ($-O-CH_2-CH_2-CH_2-O-$), 66.65 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 33.40 ($-CH_2-CH=CH_2$), 33.22 ($-CH_2-CH_2-SH$), 32.35 ($-CH_2-S-CH_2-$), 32.29 ($-CH_2-S-CH_2-$), 31.93 ($-CH_2-CH=CH-$), 30.37 ($-O-CH_2-CH_2-CH_2-O-$), 29.72 ($-S-CH_2-CH_2-CH_2-$), 28.95 ($-S-CH_2-CH_2-CH_2-S-$), 28.90 ($-S-CH_2-CH_2-CH_2-$), 28.67 ($-CH_2-CH_2-CH=CH-$), 28.47 ($-CH_2-CH_2-CH=CH_2$), 24.41 ($HS-CH_2-CH_2-$).

P3. ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 5.85−5.71 (m, $-CH=CH_2$), 5.71−5.61 (m, $-CH=CH-CH_2-O-_{trans\ isomer}$, $-CH=CH_2\ _{branched\ telomer}$), 5.58−5.48 (m, $-CH=CH-CH_2-O-_{trans\ isomer}$, $-CH=CH-CH_2-O-_{cis\ isomer}$), 5.17−5.11 (m, $-CH=$

$CH_2\ _{branched\ telomer}$), 5.01−4.92 (m, $-CH=CH_2$), 3.99 (d, J = 4.9 Hz, $-CH=CH-CH_2-O-_{cis\ isomer}$), 3.89 (d, J = 6.1 Hz, $-CH=CH-CH_2-O-_{trans\ isomer}$), 3.70 (t, J = 6.6 Hz, $-O-CH_2-CH_2-SH_{end\ group}$), 3.60 (t, J = 6.6 Hz, $-S-CH_2-CH_2-O-CH_2-$), 3.47 (t, J = 6.4 Hz, $-O-CH_2-CH_2-CH_2-O-$), 2.87 (t, J = 6.6 Hz, $-O-CH_2-CH_2-SH_{end\ group}$) 2.68 (t, J = 6.9 Hz, $-S-CH_2-CH_2-O-$), 2.53 (t, J = 7.4 Hz, $-S-CH_2-CH_2-CH_2-$), 2.10−1.98 (m, 1H, $-CH_2-CH=CH-$), 1.88−1.79 (m, 1H, $-O-CH_2-CH_2-CH_2-O-$), 1.64−1.52 (m, 1H, $-S-CH_2-CH_2-CH_2-$), 1.52−1.42 (m, $-CH_2-CH_2-CH=CH_2\ _{end\ group}$), 1.42−1.33 (m, $-CH_2-$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 138.81 ($-CH=CH_2$), 134.30 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 134.21 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 126.91 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 126.78 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 114.74 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 70.87 ($-S-CH_2-CH_2-O-CH_2-CH_2-S-$), 69.40 ($-O-CH_2-CH_2-SH$), 67.37 ($-O-CH_2-CH_2-CH_2-O-$), 67.30 ($-O-CH_2-CH_2-CH_2-O-$), 66.63 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 33.40 ($-CH_2-CH=CH_2$), 32.74 ($-S-CH_2-CH_2-O-CH_2-CH_2-S-$), 32.33 ($-CH_2-S-CH_2-$), 31.70 ($-CH_2-CH=CH-$), 30.35 ($-O-CH_2-CH_2-CH_2-O-$), 29.79 ($-S-CH_2-CH_2-CH_2-$), 28.87 ($-S-CH_2-CH_2-CH_2-$), 28.59 ($-CH_2-CH_2-CH=CH-$), 28.53 ($-O-CH_2-CH_2-SH$), 28.44 ($-CH_2-CH_2-CH=CH_2$).

P4. ^{1}H NMR (300 MHz, CDCl$_3$, δ in ppm): 5.87−5.72 (m, $-CH=CH_2$), 5.72−5.63 (m, $-CH=CH-CH_2-O-_{trans\ isomer}$, $-CH=CH_2\ _{branched\ telomer}$), 5.59−5.50 (m, $-CH=CH-CH_2-O-_{trans\ isomer}$, $-CH=CH-CH_2-O-_{cis\ isomer}$), 5.18−5.12 (m, $-CH=CH_2\ _{branched\ telomer}$), 5.03−4.93 (m, $-CH=CH_2$), 4.00 (d, J = 4.8 Hz, $-CH=CH-CH_2-O-_{cis\ isomer}$), 3.90 (d, J = 5.9 Hz, $-CH=CH-CH_2-O-_{trans\ isomer}$), 3.74 (t, J = 6.7 Hz, $-O-CH_2-CH_2-SH_{end\ group}$), 3.66−3.60 (m, $-CH_2-O-CH_2-CH_2-O-CH_2-$), 3.49 (t, J = 6.4 Hz, $-O-CH_2-CH_2-CH_2-O-$), 2.89 (t, J = 6.7 Hz, $-O-CH_2-CH_2-SH_{end\ group}$) 2.70 (t, J = 7.0 Hz, $-S-CH_2-CH_2-O-$), 2.53 (t, J = 7.3 Hz, $-S-CH_2-CH_2-CH_2-$), 2.09−1.99 (m, $-CH_2-CH=CH-$), 1.90−1.80 (m, $-O-CH_2-CH_2-CH_2-O-$), 1.64−1.53 (m, $-S-CH_2-CH_2-$), 1.53−1.43 (m, $-CH_2-CH_2-CH=CH_2\ _{end\ group}$), 1.43−1.33 (m, $-CH_2-$).

^{13}C NMR (75 MHz, CDCl$_3$, δ in ppm): 134.45 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 134.24 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 126.77 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 126.44 ($-CH=CH-CH_2-O-_{cis\ isomer}$), 71.76 ($-CH=CH-CH_2-O-_{trans\ isomer}$), 71.19 ($-S-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-S-$), 70.43 ($-S-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-S-$), 67.34 ($-O-CH_2-CH_2-CH_2-O-$), 32.68 ($-S-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-S-$), 32.28($-S-CH_2-CH_2-CH_2-$), 31.28 ($-CH_2-CH=CH-$), 30.32 ($-O-CH_2-CH_2-CH_2-O-$), 29.79 ($-S-CH_2-CH_2-CH_2-$), 28.84 ($-S-CH_2-CH_2-CH_2-$), 28.56 ($-CH_2-CH_2-CH=CH-$).

■ RESULTS AND DISCUSSION

Recently, research in industry and academia is particularly focused on applying benign reaction conditions and using precursors based on renewable feedstocks. In this sense, the 100% atom-efficient Pd-catalyzed telomerization of readily available and cheap 1,3-butadiene with renewable 1,3-propanediol is an elegant way to synthesize the herein studied monomers with minimum environmental impact.[21] It must be pointed out that 1,3-propanediol can be obtained directly either from corn or any plant oil as a renewable raw material,[22] and thus the telomerization process can, in principle, be integrated in a 100% biomass-based synthesis platform as long as butadiene is obtained from renewable sources, for instance from bioethanol.[23] With the application as surfactant precursor in mind, previous studies were aimed at optimizing conditions for formation of the monotelomer of 1,3-propanediol.[20] However, as the ditelomer product was required for our polymerization studies, telomerization conditions were adapted by using a larger excess of butadiene (1,3-butadiene:1,3-propanediol molar ratio of 6:1) and a longer reaction time at 80 °C under solvent-free conditions.

Using the Pd/TOMPP complex as telomerization catalyst, the ditelomers were obtained with full conversion of the diol substrate and a yield of 92%. The structures of the 1,3-propanediol-based ditelomers were confirmed by the means of ^{1}H NMR and ^{13}C NMR with a 95% (*E*)-configuration of the double bond in the hydrophobic chains. Telomerization products are almost inevitably obtained as a mixture of the linear (1-addition product) and branched (3-addition) octadienes. Controlling the linear to branched ratio (l/b; the linear product is often preferred) remains a challenge. It is known that higher phosphine to palladium ratios result in increased stability of the catalyst, but also in lower l/b ratios. As full conversion to the ditelomer, but also a l/b ratio that is as high as possible is required for the present application, a balance needs to be struck in the P/Pd ratio.[2] Thus, in order to achieve a selective synthesis of the linear (versus branched, designated as l/b ratio) ditelomer, the ratio of phosphine to metal was varied from 4:1, 8:1 to 16:1. The final diethers consisted of different linear/branched ratios as shown in Figure 1. As expected, a slight decrease (from 93% to 91%) was observed when the relative amount of phosphine was increased to 16 equiv.

ADMET Polymerizations. The efficacy of the telomers (**1**, **2**, and **3**) as monomers was evaluated using two polymerization methods. The first route focuses on the reactivity of the ditelomers in the presence of metathesis catalysts. As mentioned in the Introduction, it is well-known that, in addition to the construction of many complex and important low molecular weight molecules, the metathesis reaction has enabled the synthesis of diverse polymers.[24] So far, concerning the transformation of the hydrophobic chain of different monotelomers [such as (*E*)-1-phenoxy-2,7-octadiene or the (peracetylated)-octadienyl ether of xylose], the activity of several Ru-based Grubbs first and second generation catalysts, as well as Re- and W-based complexes, has been investigated.[25] In those cases where Ru-based catalysts were used, compounds corresponding to a metathesis involving internal double bonds were observed. However, up to date olefin metathesis has not been applied to ditelomers. As the ditelomers can be considered α,ω-dienes, they would be suitable monomers for acyclic diene metathesis (ADMET) polymerization. Nevertheless, ditelomers also possess internal double bonds and thus cannot be considered traditional α,ω-dienes, but participation of the internal olefins in ADMET would nonetheless still lead to polymer formation. Therefore, the ADMET reactions of monomers **1**, **2**, and **3** were investigated (Figure 1). The readily available Ru-based metathesis catalysts should be more suitable for these ditelomers, given their functional group tolerance.[13] In order to study the scope and limitations of the ADMET polymerization, extensive optimization studies involving changes of catalyst, temperature and substrate (the effect of l/b ratio) were carried out. Since ADMET polymerization is ideally performed in bulk monomer to maximize monomer concentration and favor formation of polymer,[26] the reactions were performed under solvent-free conditions. Moreover, ADMET chemistry relies on ethylene removal, which drives the reaction in this step-growth polymerization.[13] Therefore, unless otherwise specified, a continuous gas flow (argon or nitrogen) was applied throughout the reactions, which were run for 4 h. Furthermore, all results presented stem from at least two individual reactions. Monitoring of these reactions by GPC and NMR provided the necessary insights to fully understand the polymerization behavior of these new monomers. The primary screening of the ADMET reaction of telomers **1**, **2**, and **3** was

focused on the effects of catalyst loading and temperature on the conversion to the desired polymer. The crucial point in this study was to retain the internal double bonds of the monomers unreacted. Ru–benzylidene metathesis catalysts are known to have better activities at mild temperatures.[27] Furthermore, low reaction temperatures reduce the extent of the possible isomerization during ADMET. Thus, the efficiency of some classical metathesis catalysts such as Grubbs first (**C1**) and second (**C2**) generations were initially compared at 40 °C with monomer **1**, which possesses the highest l/b ratio (Table 1 and Table 2). When 0.2 mol % **C1**, one of the most widely studied metathesis catalysts, in relation to the ditelomer was used (Table 1, entry **1**), **1** was recovered along with 30% dimeric product. Since further gradual increasing of the catalyst loading up to 2.0 mol % (entries 2−6) did not significantly change this result, a catalyst loading of 0.4 mol % **C1** was chosen for exploring the effect of the temperature on **C1**. Although it has been reported that **C1** does hardly show any side reactions up to a polymerization temperature of 90 °C,[28] temperatures higher than 70 °C were not applied here, because of catalyst decomposition in the current system.[29] Therefore, in attempts to favor higher conversions, the reaction temperature was varied from 50 until 70 °C. However, the higher reaction temperature was found not to have a considerable effect on the polymerization reaction, as evidenced by GPC (Table 1, compare entries 7−9). Moreover, also longer reaction times did not result in higher molecular weights, leading us to conclude that **C1**, at least under the applied bulk conditions, is unsuitable for the polymerization of these telomers.

The catalyst screening showed that **C2** (0.4 mol %) was more effective at low temperature, with better consumption of **1** (entries 1, 3 and 4, Table 2). However, also this catalyst did not afford high molecular weight polymers. Efforts to increase the molecular weight by increasing the catalyst amount from 0.4 to 2.0 mol % at 40 °C showed similar trends as in the case of **C1**.

Hoveyda–Grubbs second generation catalyst (**C3**) possesses metathesis efficiency similar to Grubbs second generation catalyst (**C2**), but with different substrate specificity. It was already reported that **C3** was employed successfully in many ADMET reactions.[13] Under the initial conditions (i.e., at 40 °C and 0.4 mol % of catalyst) only 50% of oligomer formation with 35% monomer recovery was observed together with 15% undefined low molecular weight product formation (GPC data). Thus, high catalyst loadings were used to improve the yield of high molecular weight products. Reactions of **1** with loadings of 0.4, 0.8, 1.0, and 2.0 mol % of **C3** gave low-molecular-weight oligomers with conversions increasing with the catalyst loading (up to 80% at 2.0 mol % of **C3**). Encouraged by this result, the ADMET reaction of **1** in the presence of 1.0 mol % of **C3** was performed at 80 °C, a typical polymerization temperature for ADMET reactions. The results of this experiment indicated high activity of **C3** after 4 h at 80 °C. However, even at 90% conversion, appreciably high molecular weights were not achieved. On the other hand, unidentified low molecular weight products were observed at higher retention times by GPC. The use of 2.0 mol % **C3** resulted in lower conversion of **1** with high amount of undefined small product formation (detected by GPC). A switch to another metathesis catalyst with chelating alkylidene ligand, **C4** (Figure 1b), gave similar results at 80 °C with loadings of 1.0 mol % as with **C3** (cf. entries 8 and 12 in Table 2).

After these studies, it became apparent that the reason for the inability to achieve a higher degree of polymerization could be the *in situ* isomerization of the double bonds during metathesis.[30] Previous studies showed that, depending on the nature of the reacting olefinic partners, the reaction conditions, as well as the nature of the catalyst, double bond isomerization reactions may occur.[31] Double bond isomerization occurs as result of ruthenium hydride formation, which can be suppressed by the addition of hydride scavengers, e.g., 1,4-benzoquinone (**BQ**).[30] Thus, catalysts **C2**, **C3**, and **C4** were examined with the same set of experiments in the presence of **BQ**. Rather unexpectedly, the inclusion of **BQ** did not show efficient isomerization inhibition at 40 °C for **C2**; in contrast, a drop of the molecular weight was detected, as observed by GPC (Table 2, entries 1 and 2). On the other hand, at 80 °C with a loading of 1.0 mol % **C3** and 8.0 mol % **BQ**, an increase of the molecular weight up to 4900 Da was observed (entry 10, Table 2). To investigate whether the **BQ** addition would favor an increase in molecular weight through longer reaction times, reactions 10 and 13 in Table 2 were reproduced and run for 48 h with initial argon flow for 4 h (entries 15 and 16, respectively). The GPC data of the reactions showed the catalysts to be still active even after 24 h in the presence of **BQ** with the molecular weight values clearly increasing.

Since the kinetics during ADMET are dictated by the removal of ethylene, a possible reason why ADMET mainly produced low molecular weight polymers, even in the presence of the isomerization inhibitor, could be inefficient ethylene removal. Therefore, an efficient ethylene removal by applying vacuum, instead of inert gas flow, was investigated. Indeed, when ADMET was performed under vacuum for 4 h in case for **C3** (entry 11, Table 2), the efficiency was substantially improved. For catalyst **C4**, the effect of applied vacuum was more pronounced (compare entries 13 and 14, Table 2), showing higher monomer conversions (monitored via NMR and GPC). Moreover, running the reactions detailed in entries 11 and 13 of Table 2 overnight (after applying vacuum for 4 h) resulted in highly viscous, sticky materials that were soluble in chloroform.

Monomer **1** is a mixture of linear and branched telomers with an l/b ratio of 93/7. Since the branched monomers possess 3 or 4 terminal double bonds, they act as branching points leading to the formation of hyperbranched structures. In order to get a more accurate picture of both the mechanism and the scope and limits of the reaction, the other two monomers **2** and **3**, which possess lower l/b ratios, were reacted under the optimized conditions: 1.0 mol % **C3** (or **C4**) at 80 °C under vacuum for 4 h. The results presented in Table 3 show a clear tendency for both catalysts (**C3** and **C4**): the molecular weights increase with the branching ratio of the monomers, which supports the polymerizations to highly branched systems and is due to the presence of a higher amount of more reactive terminal double bonds. Furthermore, the same set of experiments was performed for 24 h, with continuous vacuum for the first 4 h. The results of this set are also in line with the formation of hyperbranched structures. Furthermore, in the case of monomers **2** and **3**, the higher content of branched telomers led to gelation caused by cross-linking. Once cross-linked, the characterization of these materials (entries 3 and 4 in Table 3) was troublesome as they were no longer soluble in any common solvents such as THF, CHCl$_3$, DMSO, and DMF.

Presumably, in the reactions performed with constant flow of argon, the failure in directing the reaction of monomer **1** toward high molecular weight was due to other interfering intra- and intermolecular metathesis reactions. The intramolecular metathesis of a α,ω-diene could yield ethylene and an unsaturated carbocycle (or heterocycle) via ring-closing metathesis (RCM), whereas the intermolecular reaction would result in the release of ethylene with oligomer or polymer formation via ADMET. The GPC traces for almost all products in Table 1 and Table 2 were multimodal, with several distinct peaks in the low molecular weight range, suggesting that low molecular weight cyclic products were formed along with linear chains. Thus, to gain more evidence whether the RCM was occurring, control experiments under dilute solvent conditions (dichloromethane as solvent) with two different catalyst amounts (0.4 and 5.0 mol % **C2** or **C3** per **1**) were performed. Surprisingly, even under the dilute solvent conditions, oligomer formation as well as RCM took place in the first 30 min of the reactions (under continuous gas flow). To better understand the polymerization mechanism of monomer **1** ^{1}H NMR analysis was performed at different reaction times with additional 2D-NMR, ^{1}H,^{1}H–COSY, and heteronuclear multiple-quantum correlation (HMQC) experiments to confirm the structures drawn in Figure 2. The NMR analysis of both control experiments and ADMET polymerizations at different reaction times clearly showed that RCM of the terminal and internal double bonds did take place (with release of cyclopentene, see Figure 2), yielding a mixture of products (RCM products and new monomer structure suitable for further ADMET). Cyclopentene and 1,6-heptadiene were collected from the ADMET reaction as distillate. Along with these compounds, a ring-opening metathesis compound (dimer) was observed in the distillate as determined by ^{1}H NMR and GC–MS. The isolated mixture of cyclopentene and 1,6-heptadiene amounted to 1/5th of the total reaction mixture. The rate and the yield of RCM reaction depended on the reaction conditions, e.g., whether argon flow or vacuum was applied; under vacuum, the RCM was observed only in the first 5 min of the reaction. However, with a continuous gas flow, the RCM occurred for approximately 45 min. The formation of the ring-closing product between the terminal and internal double bond was evidenced by ^{1}H NMR, which showed a decrease of the terminal double bond proton resonances at 5.81 (5, in Figure 2a) and 4.97 ppm (4) and the appearance of new terminal double bond protons at 5.91 (1) and 5.20 ppm (2) belonging to the allylic ether. Furthermore, it was observed that the products from step a in Figure 2 subsequently reacted via ADMET, either with themselves or with unreacted monomers, thus giving a mixture of products as shown in Figure 2b. These metathesis reactions led to polymer formation (as observed by GPC); however, ^{1}H NMR analysis of the products also revealed that further double bond isomerization took place (Figure 3). The vinyl ether signals observed (hydrogens 1, 2, 3, and 4 in Figure 3), which have similar intensities as the signals belonging to the internal olefins formed by direct ADMET, illustrate this. The isomerization of the allylic (ether) double bonds to the vinyl position gave a 1:1 mixture of *trans* (1 and 2 in Figure 3) and *cis* (3 and 4) isomers. While this can be considered a nondisturbing side reaction in most polymerizations, the isomerization of allyl ethers to vinyl ethers has to be considered as it can lead to slow catalyst deactivation (ethyl vinyl ether[32] is the typical reagent used to quench metathesis reactions catalyzed with ruthenium alkylidenes). Moreover, a small amount of terminal double bond isomerization was also observed (Figure 3). Along with the aforementioned points, in ADMET polymerization the
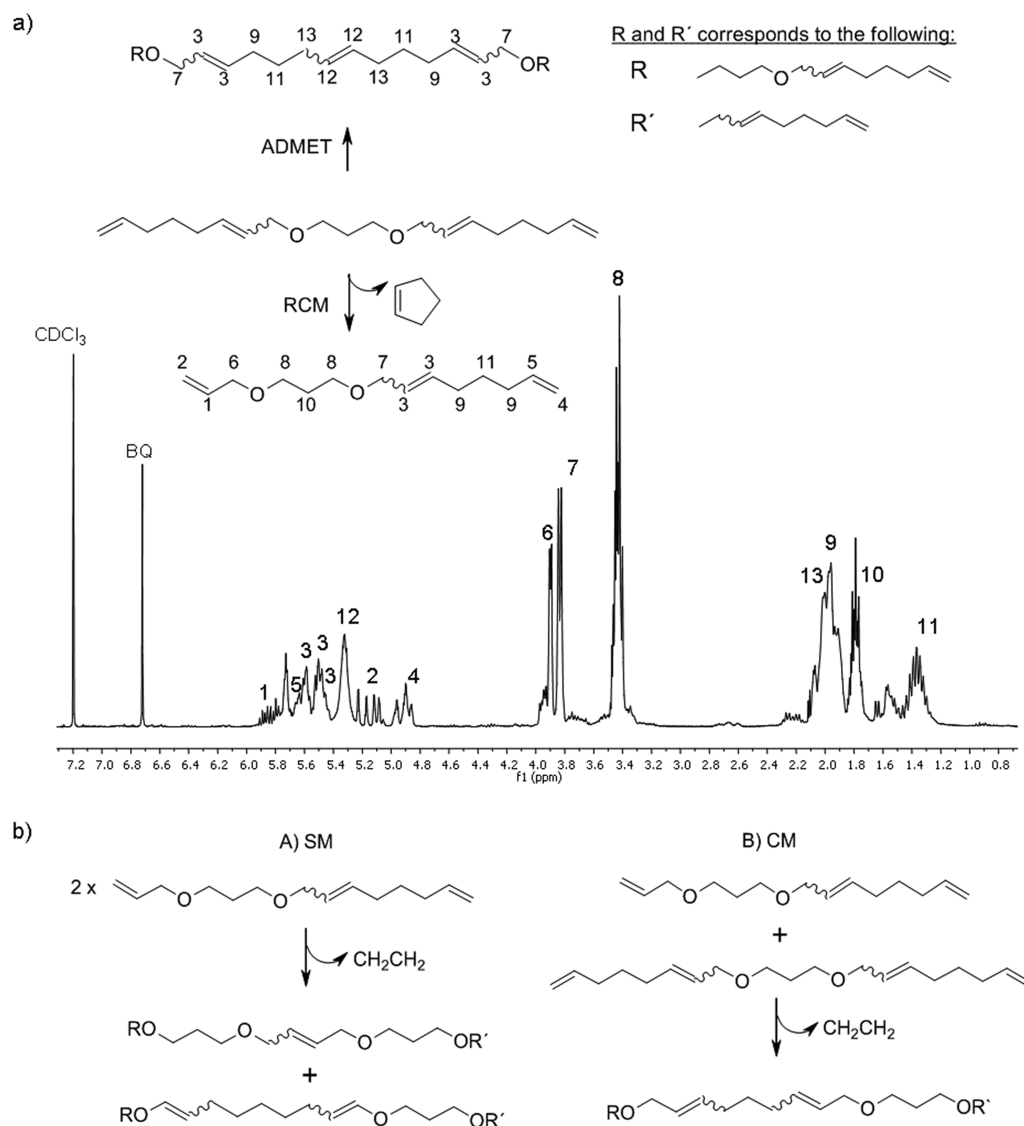
Figure 2. Study of the polymerization mechanism by means of NMR analysis: (a) initial reactions observed (first 30 min of ADMET reaction) (entry 11, Table 1); (b) subsequent reactions of RCM product.

polymerizability of a monomer can be limited by the number of methylene spacers between the olefin and the ether oxygen.[33] Thus, it could be that, to some extent, also the so-called "negative neighbouring group effect" is a reason for the somewhat poor polymerization results. Moreover, in some cases, self- and cross-metathesis reactivity was observed for monomers with only one methylene spacer present.[34] Finally, oligomerization of diallylic ethers has been reported before.[35] All this contributes to the observed rather poor polymerizability of the ditelomers via ADMET.

In summary, although it is possible to react the monomers with low catalyst loadings and relatively low temperatures via metathesis, the presence of branched telomers in the monomer mixture caused cross-linking at high monomer conversions. Moreover, ADMET was not sufficiently regioselective, allowing RCM events to take place. In addition, olefin isomerization events led to vinyl ether moieties within the polymer backbones.

Thiol−Ene Polymerizations. Thiols have a strong tendency to react with terminal double bonds in radical-initiated reactions. Therefore, in order to establish an alternative polymerization pathway for monomers **1**, **2** and **3**, the transfor-

mation of the ditelomers was also investigated in the presence of thiols as comonomers.

Initially, the model compound 1-octanethiol was reacted with telomer **1** under radical-initiated (model reaction A) or thermally induced (model reaction B) conditions using a molar ratio of 4:1 (thiol:**1**). Although low temperatures are generally favorable for thiol−ene additions, elevated reaction temperatures are required to avoid high viscosity or crystallization during polymerization. Furthermore, it was shown that in dithiol/diene mixtures, which are free of oxygen, radicals can also form spontaneously under initiator-free conditions.[19] Therefore, the model reaction was carried out at 70 °C without initiator. Although Hawker and colleagues showed that thiol−ene coupling reactions do not strictly require deoxygenation[36] when performed under solvent-free conditions, both model reactions were nonetheless kept under vacuum (200 mbar) for 5 min prior to exposing to heat and/or addition of initiator in order to remove oxygen, which is an efficient radical scavenger in these types of reactions.[35] The dithioether generated from the reaction performed in the presence of the radical initiator (**AIBN**) was the expected anti-Markovnikov diaddition product
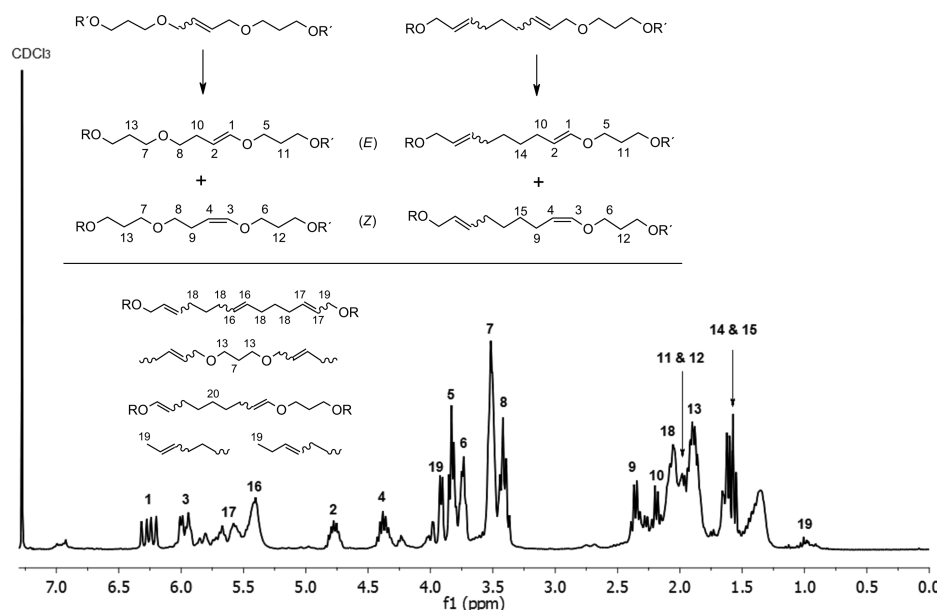
Figure 3. NMR spectra of a sample of the crude reaction mixture of entry 11, Table 1, taken after 2 h, showing the isomerization occurring during the ADMET reaction.

(Figure 4). As illustrated by the disappearance of the protons associated with the terminal double bonds (5.78 and 4.96 ppm) and homoallylic (1.46 ppm) signals, and the appearance of proton signals corresponding to the thioether product (methylenes in α- (2.52 ppm) and β-position (1.60 ppm) to the sulfur atom, the conversion was found to be essentially quantitative after 1 h at 75 °C (for complete description of the NMR data see the Experimental Section). Interestingly, the ^{1}H NMR spectra displayed also new significant signals at $\delta_{\rm H}$ 6.20 (d, J = 12.6 Hz, 1H$_{trans}$), 5.91 (dd, J = 6.2, 1.3 Hz, 1H$_{cis}$), 4.81–4.68 (m, 1H$_{trans}$) and 4.37–4.25 (m, 1H$_{cis}$) due to a migration of the internal allyl ether double bonds to the vinylic position (cis and trans isomers were observed), along with a corresponding decrease of the integral value of the internal double bond signal (Figure 4). The thermally induced reaction without added initiator, on the other hand, resulted in a lower yield (90%) (model reaction B) after a significantly longer reaction time (20 h) at 70 °C. However, in this case, the aforementioned internal double bond migration occurred to a much lesser extent; just 3% internal allyl ether double bond migration was detected in contrast to 27% migration in case of model reaction A (compare results in Figure 4). While the extent of olefin migration may not be substantial under standard thiol−ene addition conditions, its occurrence is of considerable fundamental importance, since it involves hydrogen atom transfer between thiyl and allylic species.[37]

Thiols are efficient hydrogen donors, and since C−H bonds are stronger than S−H bonds [bond dissociation energy (BDE) = 91 kcal/mol],[38] thiyl radicals are usually regarded as unreactive with respect to hydrogen abstraction. Hydrogen atom transfer reactions are usually very sensitive to enthalpic polar effects, however. It was indeed reported that thiyl radicals can abstract hydrogen atoms from thermodynamically favorable allylic systems[36] in water/alcohol mixtures as well as from other C−H activated compounds.[39] Since an allylic C−H bond is unusually weak (BDE = 82 kcal/mol),[37] the free radical abstraction of such hydrogens is easier than for nonallylic hydrogens. The migration of the double bond could thus be explained by the mechanism proposed in Figure 5. This involves a favorable allylic hydrogen abstraction, followed by trapping of either the intermediate allylic radical or the more stable additional resonance form (step b in Figure 5) by a thiol to regenerate the initial structure or to form the internal vinyl ether (in the latter case). It should be noted that the hydrogen atom transfer between the electron-rich C−H bond in the ditelomer and the electrophilic thiyl radical is favored, if there is an appropriate polarity match between radical and the alkene (step a in Figure 5).[40] The same assumption could be applied for step c (Figure 5), where the hydrogen atom is transferred from the electrophilic thiol, acting here as a hydrogen atom donor, to the nucleophilic carbon-centered radical.

The model study thus shows that the use of radical initiator shortens the reaction time and results in double bond migration. This migration, leads to a vinyl ether function displaying a different reactivity that might be further exploited in another context.

Encouraged by the successful model study, and in order to demonstrate the feasibility of ditelomers in thiol−ene polymerizations, three different dithiols were investigated: 1,4-butanedithiol (**DT1**), 2-mercaptoethyl ether (**DT2**), and 3,6-dioxa-1,8-octanedithiol (**DT3**), under comparable conditions, in the absence or presence of radical initiator. Compared to the model reactions, the synthesis of polymers could present a number of additional challenges regarding efficiency. Although the internal double bonds of the ditelomers showed quite low reactivity at 70 °C during the model studies, the polymerizations were conducted at three different temperatures in order to obtain more detailed information about the effect of the temperature on the reactivity of the internal double bonds. Monomer **1**, possessing the highest l/b ratio (Figure 1a), was used in the initial optimization studies. The polymerizations were followed by GPC and NMR. The reactions were run until a viscosity increase was qualitatively observed, and then quenched by cooling to room temperature and diluted with an excess of THF to avoid cross-linking. All of the major impurities, including excess reactant and the initiator residue, were easily removed by repeated precipitation, and no chromatography was required.
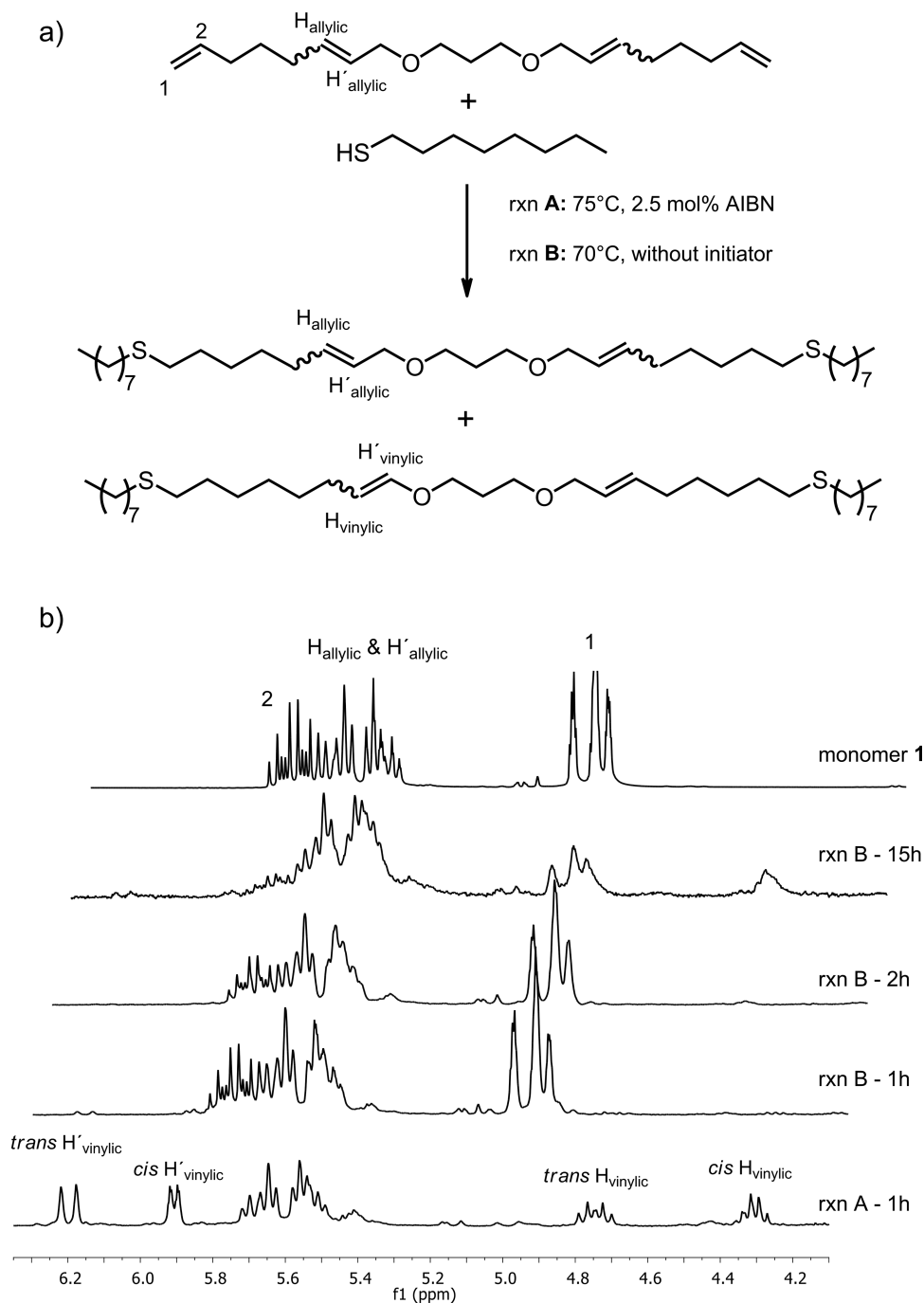

Figure 4. (a) Schematic representation of the model reactions mimicking the products from thiol−ene polymerization. (b) ^{1}H NMR spectra (CDCl$_3$; 300 MHz) comparison of the model thiol−ene reactions A and B with the corresponding monomer: ditelomer **A** (black line, crude reaction mixture of model reaction A, 1 h, with AIBN; blue line, crude reaction mixture of model reaction B, 1 h, without AIBN; light gray line, model reaction B, 2 h; dark gray line, model reaction B, 15 h; red line, monomer: ditelomer **A**).

Monomer **1** was polymerized at 35, 50, and 70 °C with **DT1**, first without the initiator AIBN. The GPC analysis showed that, even after 72 h at 35 °C, the thiol−ene reaction did not occur as efficiently as expected, and only low-molecular-weight oligomers (molecular weight <3000 Da) were formed (Table 4, entry 1). Generally, the results confirmed the internal double bonds to be less reactive than the terminal ones, which is known from literature and is a result of the reversibility of the C−S bond formation.[41] The NMR data of the reaction run at 50 °C (entry 2, Table 4) revealed characteristic peaks attributed to the formation of thioether bonds as well as the repeat units

of thiol monomer and signals from the telomer backbone, which indicated that the reaction occurred. Moreover, the data shows that the internal double bonds remain almost unreacted. When the reaction was performed at 70 °C (Table 4, entry 3), a successful polyaddition was observed; however, prolonging the reaction times (more than 24 h) resulted in gelation. As with the model reactions described above, in the experiments performed at 50 and 70 °C, the internal double bond migration from the allylic to vinylic position was again observed.

To explore the influence of the dithiol structure on the reactivity of **1**, **DT2** was selected as it contains an ether group

and thus resembles more the structure of the 1,3-propanediol ditelomers. The reactions were conducted in analogy to those with **DT1**. Online GPC monitoring of the reactions revealed that the conversion of the ditelomer and of the dithiol were better in comparison to **DT1** (Figure 6a).
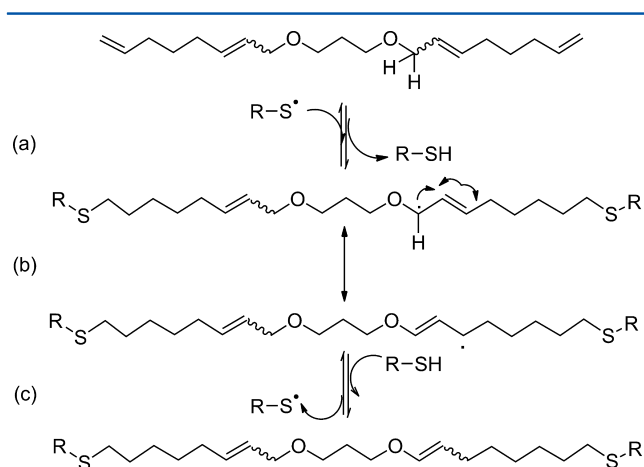

Figure 5. Thiyl radical-mediated olefin migration.

The ¹H NMR spectra of entries 4, 5, and 6 (Table 4) showed little variation (Figure 6b). As a common feature, the internal double bonds did not react, as calculated by comparison of the integrals of the characteristic multiplet centered at ~5.53 ppm (¹H of the internal double bond), and the triplet at ~3.50 ppm (4H from the 1,3-propanediol core of monomer **A**, which should not vary throughout the reaction). On the other hand, the integral value of the terminal double bond peak at ~4.95 ppm decreased, confirming the successful thiol−ene coupling. The conversion of the terminal double bonds could be calculated from the characteristic multiplet centered at 4.95 ppm and the triplet at 3.50 ppm. The product obtained at 50 °C showed 75% conversion of terminal double bonds, while the products obtained at 35 and 70 °C showed 84 and 82% conversion, respectively. The polymerization at 35 °C gave the highest conversion of terminal double bonds, but it also resulted in an unsymmetrical molecular weight distribution with high PDI (compare Figure 6). On the other hand, the polymerization at 70 °C gave a higher terminal double bond conversion than at 50 °C, but since the increase both in terminal double bond conversion and in molecular weight (GPC) was small, 50 °C was taken as temperature for further optimization of the reaction conditions. In the initial experiments, the dithiol
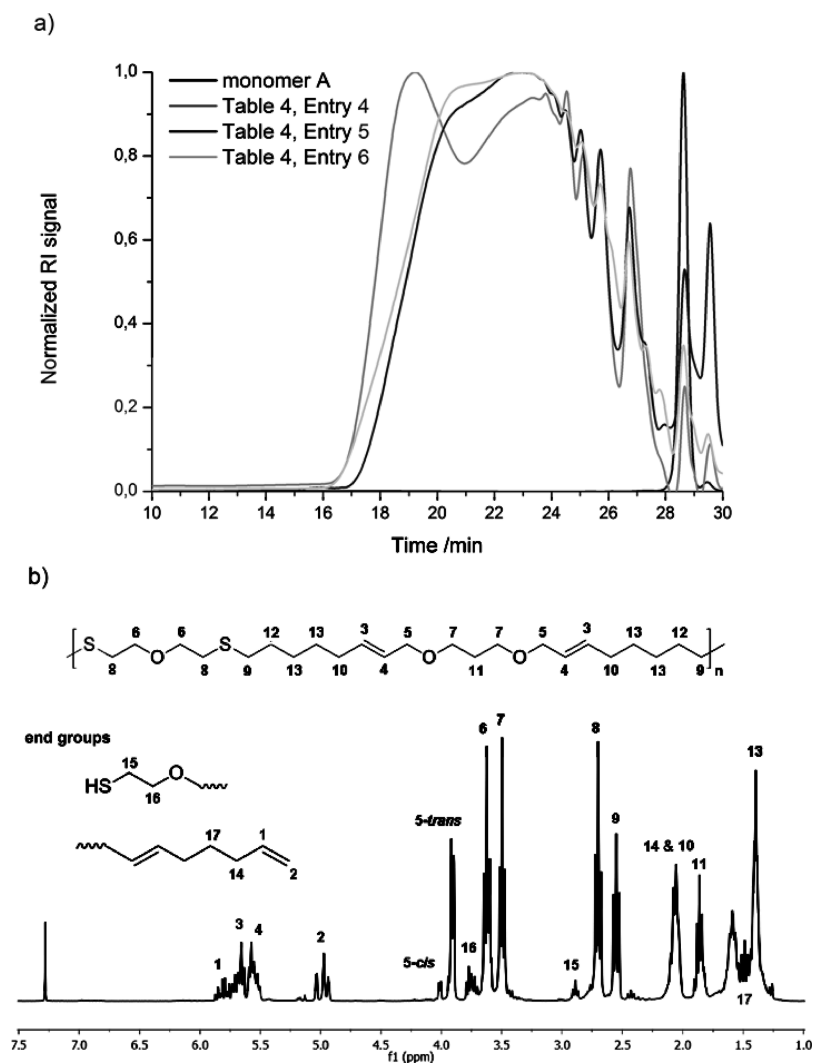

Figure 6. (a) Crude GPC chromatograms and (b) representative NMR data of the thiol−ene reaction product of **DT2** at three different temperatures (35, 50, and 70 °C). (The GPC data was obtained from SEC system with method A.)

amount used was calculated considering the ditelomer samples as pure linear ditelomers. To account for the small percentage of branched ditelomers present (Figure 1a), the effect of varying the ditelomer/dithiol ratio, from 1:1 to 0.95:1 and to 1:0.95, on the polymerizations at 50 °C was studied. Since the branched telomers contain extra terminal double bonds that can more easily react with the dithiols, an increase in the thiol ratio should favor branching reactions and thus should lead to higher molecular weights and higher PDIs (entry 11, Table 4). This was confirmed by the GPC traces of **DT1** (Table 4, entries 2, 8 and 9) and **DT2** (Table 4, entries 5, 10 and 11). The GPC analysis of the samples from the reaction of **1** with slight excess of thiol **DT2** (0.95:1) indeed showed an increase of molecular weight compared to the 1:1 reaction (75% conversion), which was in accordance with the observed 82% conversion of terminal double bonds (determined by ^{1}H NMR); however, ^{1}H NMR analysis also revealed 8% conversion of the internal olefins. Excess of ditelomer (1:0.95) resulted in a drop in conversion of the terminal double bonds to 70%, again in accordance with the lower M_w observed by GPC. These results demonstrate that variation in the temperature did not have a pronounced effect on the reactivity of the internal olefins, but a small excess of dithiol did have a considerable effect on the molecular weights.

Next, **DT3**, was tested in the thiol−ene polymerization of the ditelomers. The third dithiol **DT3** tested, was expected to have a positive effect on the polymerization results in terms of improved compatibility (miscibility) between both monomers (1:1 ratio at 50 °C, Table 4, entry 7). The GPC data of the 24 h crude reaction mixture revealed 92% monomer conversion to the polymer. The higher double bond conversion (80% by ^{1}H NMR) obtained at short reaction time further confirmed the improved polymerization compared to **DT1** and **DT2**.

Since the thermally induced thiol−ene polymerization reactions needed long polymerization times (at least 48 h), AIBN was applied as radical initiator (2.5 mol % to ditelomer molecule) to reduce the reaction time. The AIBN-initiated polymerizations were completed in 1 h (reaction mixture was not stirring anymore) with conversions of 95% for entry 14, Table 4 (by GPC). As with the previously obtained products,

the polymers were completely soluble, although dissolution took time (around 6 h for the polymer with the highest molecular weight). The difference in solubility was attributable to the molecular weight difference. Since the high concentrations of radicals present in the reaction mixture increases the probability of side reactions, also lower AIBN loadings were tested for monomer **1**. From NMR and GPC analysis, it became clear that an initiator loading of 1.0 mol % already results in 95% conversion (by GPC, no carbons corresponding to the end groups detected in ^{13}C NMR). Almost no double bond migration is observed by ^{1}H NMR, thus more well-defined polymers were synthesized (Table 4, entry 15). In the same fashion, additional experiments were performed with monomer **2** and **3** in order to study the effect of the l/b ratio on the polymerizations performed in the presence of AIBN. Indeed, the higher the branching ratio, the higher the molecular weight and also the less well-defined structures with broad PDI values were obtained.

Both the thermally and radical-induced thiol−ene reactions were initially affected by difficulties in reaching the quantitative conversions targeted for polymer synthesis. However, variation of the ditelomer to dithiol ratio and the type of dithiol, led to optimized reaction conditions allowing for the formation of high molecular weight products. Very interestingly, the three dithiols yielded thermoplastic polysulfides of different structures, which could be shaped as transparent and colorless films by casting THF solutions (graphical abstract and Figure 7). To ascertain the thermal properties of the obtained thiol−ene polymers, DSC analysis was performed. The majority of the samples, even when subjected to different heating rates during DSC analysis, did not show any thermal transition in the studied temperature range (from −75 to +250 °C). However, a small T_g at 99 °C (at 20 °C/min) was observed for the polysulfide from entry 2, Table 4, suggesting that the rest of polysulfides possibly have T_gs in the same range, but are not detectable by DSC (Figure 7). It should be noted that the ditelomers monomers have no detectable glass or melting transitions in the studied temperature range and that the investigated polymer (entry 2, Table 4) can be reshaped by redissolution and solvent casting for several times, suggesting that it is not cross-linked. From the TGA analysis performed on the same polymer, it could be seen that the polymers display acceptable thermal stability under nitrogen. Under the given experimental conditions 5% mass loss of the polymer was detected at 306 °C.

■ CONCLUSION

The potential of ditelomers obtained from 1,3-propanediol as monomers for the synthesis of polymers via ADMET and thiol−ene polymerizations has been assessed. Regarding the ADMET pathway, it was shown that the products obtained were different depending on the method used to remove the released ethylene. When a flow of argon was used, mostly ring-closing metathesis products were obtained together with oligomers. On the other hand, when vacuum was applied, low molecular weight polymers were obtained in a ring-closing metathesis−ADMET−olefin isomerization sequence. The thiol−ene polyaddition with different dithiols led to higher molecular weights than the ADMET polymerization. The polymerizations in the presence of a radical initiator (AIBN) were considerably faster than the thermally initiated ones. In both cases, isomerization of the allyl ether to vinyl ether was observed, in a more prominent fashion in the presence of AIBN. The high molecular weight polymers obtained via the thiol−ene route behaved as shapeable and completely transparent thermoplastics.
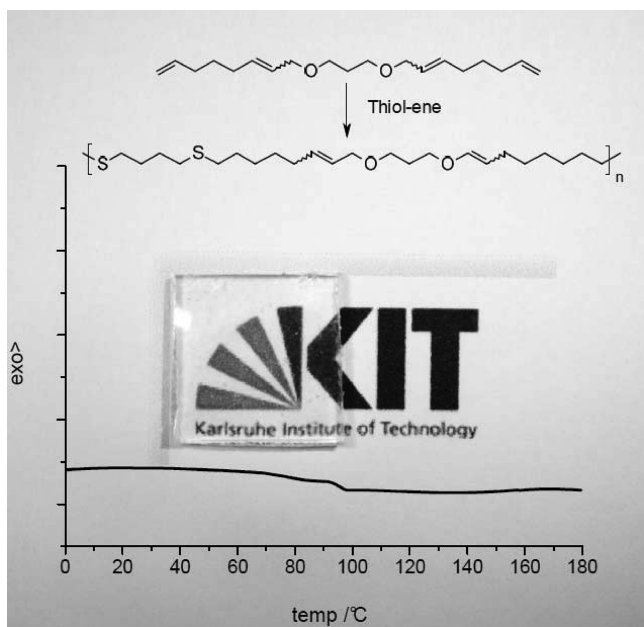

Figure 7. DSC chromatogram for the polysulfide of entry 2 from Table 4.

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Notes
The authors declare no competing financial interest.

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