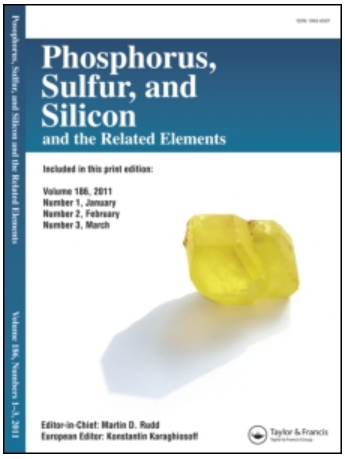

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF TELECHELIC MONODISPERSED DIOLS. PART 3. TELOMERIZATION OF NONCONJUGATED DIENES WITH COMMERCIALLY AVAILABLE OR SYNTHESIZED MERCAPTO-ALCOHOLS

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To cite this Article Améduri, Bruno , Berrada, Khalid , Boutevin, Bernard and Bowden, Roy D.(1993) 'SYNTHESIS OF TELECHELIC MONODISPERSED DIOLS. PART 3. TELOMERIZATION OF NONCONJUGATED DIENES WITH COMMERCIALLY AVAILABLE OR SYNTHESIZED MERCAPTO-ALCOHOLS', Phosphorus, Sulfur, and Silicon and the Related Elements, 83: 1, 39 — 47
To link to this Article: DOI: 10.1080/10426509308034345
URL: http://dx.doi.org/10.1080/10426509308034345

Phosphorus, Sulfur, and Silicon, 1993, Vol. 83, pp. 39–47
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SYNTHESIS OF TELECHELIC MONODISPERSED DIOLS. PART 3. TELOMERIZATION OF NONCONJUGATED DIENES WITH COMMERCIALLY AVAILABLE OR SYNTHESIZED MERCAPTO-ALCOHOLS†

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(Received July 6, 1993; in final form August 10, 1993)

The synthesis of telechelic monodispersed diols produced from the radical telomerization of commercially available nonconjugated dienes (1,5-hexadiene and 1,9-decadiene) with an excess of commercial (2-mercapto ethanol) or synthesized thio-alcohol, initiated by peroxydes is presented. In each case, the diols were obtained selectively and in excellent yields and were characterized by both ^{1}H and ^{13}C-NMR. The thermostability of these latter diols is much better than that of polydispersed commercially available diols such as polyethylene glycol or poly(THF).

Key words: Telechelic diol; monodispersity; radical telomerization; mercapto-alcohol; thermostability.

INTRODUCTION

Several ways of obtaining monodispersed telechelic oligomers have been previously reviewed[1–7] or performed from redox[8–15] or radical telomerization.[1,15–18] In this last case, the monoaddition of hydroxylated olefines with functional thiols[16] or dithiols[1,17,18] in the presence of classical initiators led to the expected α,ω-diols in excellent yields, thanks to the efficient reactivity of the mercapto group onto the double[19–21] or triple[22–24] bonds.

However, the bismonoaddition of functional telogens which exhibit a trichloromethyl end-group onto nonconjugated dienes, catalyzed by metal salts[9,10,12] or ruthenium complex[11] or initiated by peroxydes[25–27] produced interesting telechelic compounds, but their yields remained poor to medium.

Thus, it has been planed to perform such a reaction in radical telomerization from other telogens—essentially α,ω-mercapto-alcohols. Furthermore, the liter-

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ature shows that almost no work has been investigated, except the radical addition of undecenic derivatives with mercapto-alcohols,[16] and the base catalyzed reaction between a thio-alcohol and an epoxy.[28]

In this paper, the synthesis and the physical properties of new telechelic monodispersed diols from the radical bismonoaddition of commercial or synthesized[29] telechelic mercapto-alcohol onto commercially available nonconjugated dienes is presented.

RESULTS AND DISCUSSION

Synthesis of Diols

The telomerization of 1,5-hexadiene or 1,9-decadiene with an α,ω-mercapto-alcohol was investigated according to the following reaction (Table I):

$$H_2C{=}CH{-}(CH_2)_x{-}CH{=}CH_2 + HS{-}Q{-}OH \xrightarrow{\text{rad.}} HO{-}Q{-}S(CH_2)_{x+4}S{-}Q{-}OH$$

As in previous work[1,18] the tertiobutyl peroxypivalate was used because of its efficency for initiating such reactions.

First, the reaction involving commercially available reactants was studied.

1. *Addition of 2-mercapto ethanol onto the dienes.* For both the 1,5-hexadiene and 1,9-decadiene, an initial [2-mercapto ethanol]/[diene] molar ratio of 2.1 was chosen and the reactions were carried out at 70°C in acetonitrile.

These experiments were monitored by size exclusion chromatography (SEC)[30] and the chromatograms show, besides the peaks corresponding to the starting materials that of a product assigned to the telechelic.

Contrary to the α,ω-bis(trichloromethylated) telogens[8-10,14] these reactions led quantitatively and selectively to the 1 and 2 telechelic compounds, as it is required for performing polycondensation.

After 3 hour-reaction, the diols were precipitated and recrystallized from acetonitrile and then, were characterized by ^1H and ^{13}C-NMR.

Table II lists the chemical shifts of the diols 1 and 2. On the ^1H-NMR spectra, it is noted the absence of any triplet at 1.55×10^{-6} assigned to the mercapto end-

TABLE I

Telechelic diols produced from the addition of HO—Q—SH onto $H_2C{=}CH(CH_2)_xCH{=}CH_2$. Molecular weights in parentheses

x	2	6
Q		
C_2H_4	1 (238)	2 (294)
$(CH_2)_{11}SC_2H_4OC_2H_4$	3 (698)	4 (754)

TABLE II

^{1}H and ^{13}C-NMR characteristics of the diols 1 and 2 (the shapes of the signals are in parentheses: s for singlet, t for triplet and m for multiplet)

	diol	HO	CH_2	CH_2	SCH_2	CH_2	CH_2	CH_2	CH_2
^{1}H-NMR	1	2.35 (s)	3.70 (t)	2.70 (t)	2.50 (t)	1.50-1.65 (m)	1.20-1.45 (m)	-	-
	2	2.35 (s)	3.70 (t)	2.70 (t)	2.50 (t)	1.50-1.65 (m)	1.2	——— (m)	1.4
^{13}C-NMR	1	-	60.33	35.40	31.57	29.71	28.47	-	-
	2	-	60.33	35.40	31.77	28.79	———		29.76

group. The central methylene groups between the thioether bridges give both similar shape of the signals and chemical shifts as those of diols obtained in previous work.[1] Furthermore, the methylene group in the β position relative to the hydroxyl function is low fields shifted because of both the electronegative effects of sulfur and oxygen atoms, and such statement appears also from the ^{13}C-NMR characterization. The assignments of other signals have been done by comparison with those of diols synthesized previously[1,18] and are mentioned in Table II.

As these reactions led to the expected monodispersed telechelic diols selectively and in excellent yields, such a pattern was used for the addition of longer chained-mercapto-alcohols, obtained previously.[29]

2. *Telomerization of commercially available dienes with synthesized α,ω-mercapto-alcohols.* The long chained-mercapto alcohol $HSC_2H_4OC_2H_4S(CH_2)_{11}OH$ was produced from the slow dropwise addition of 10-undecenol into a large excess of bis-(2-mercaptoethyl)-ether.[29] The yield was higher than 85%.

In the same way, after 8 hour-reaction, the diols were obtained. The analysis of the infra-red spectra of these resulting products showed the conversion of all the olefinic groups.[30] After precipitation and recrystallization from acetonitrile, the corresponding diols were produced in 70% yields. In both cases, the SEC chromatogram exhibits one sharp peak only.[30]

Then, these diols were characterized by ^{1}H and ^{13}C-NMR. The ^{1}H-NMR spectra (Figure 1) are rather similar to those previously described.[1,18] The same chemical shifts differences of the methylene group adjacent to the sulfur atoms are observed (Table II): those in the β position relative to the oxygen atoms are low field shifted compared to others. Furthermore, the major difference between both spectra of these diols is the integration of the signal centered at about 1.3×10^{-6}, characteristic of the central methylene group and the methylenic chain coming from the 10-undecenol.

The ^{13}C-NMR spectra (Figure 2) are also similar to previous ones.[1,18] They exhibit low field shifted signals, characteristic of the methylene groups adjacent to hydroxyl or ether functions in the $62–71 \times 10^{-6}$ zone and CH_2 group in the α position about sulfur atoms at about 33×10^{-6}. The other chemical shifts are listed in Table III.

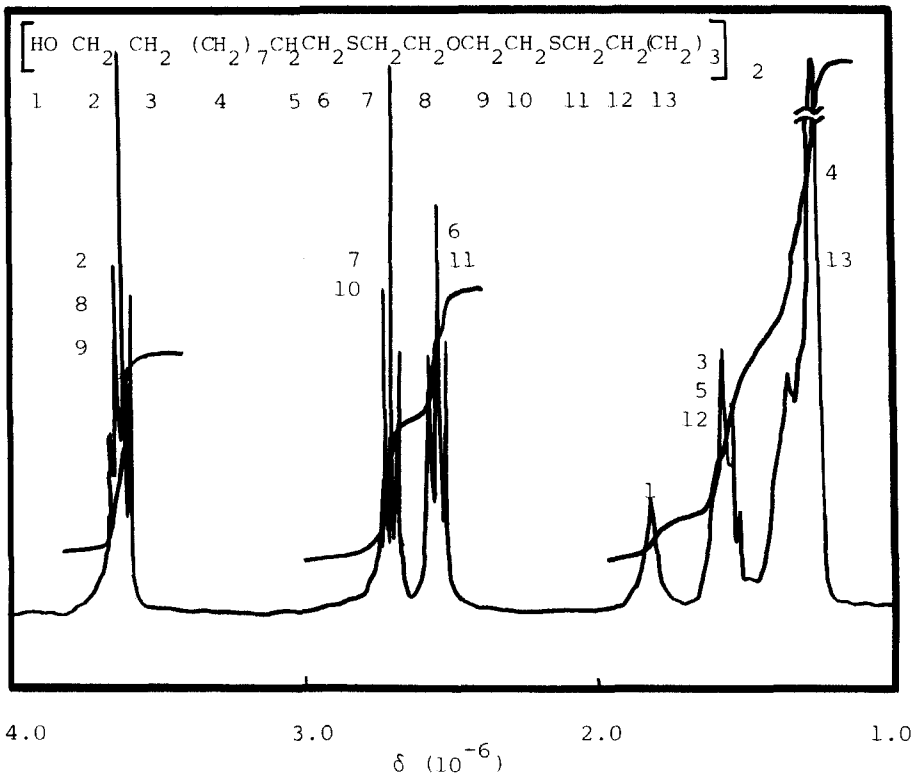

FIGURE 1 ^{1}H-NMR spectrum of diol 4.

Thermostability of Diols

The thermal behavior of diol 4 was investigated by thermogravimetric analysis (TGA). Figure 3 exhibits the TGA curves performed under a nitrogen atmosphere of diol 4 and of polydispersed commercially available commonly used diols: polyethylene glycols 1,000 and 10,000, and Terathane 650. These results show a clear superiority of our diols as shown by the high temperature shift of the TGA curve of about 60°C (when compared with Terathane 650) and of about 100°C (by comparison with polyethylene glycols 1,000 and 10,000). However, the thioether groups are usually less thermostable than their oxygenated homologues and this is clear when their bond-energies are taken into account: 65 and 85 kcal/mol at 25°C for the thioether and ether groups, respectively.

This is very interesting for our products but it seems difficult to explain. Nevertheless, it is well known that polysulfides are very stable and are used in sealants for their thermal resistance and their hydrophobic properties. However, our diols are crystalline[30] and the sulfide radicals susceptible to be formed can easily recombine. Both phenomena can be responsible for the improved high temperature behavior.

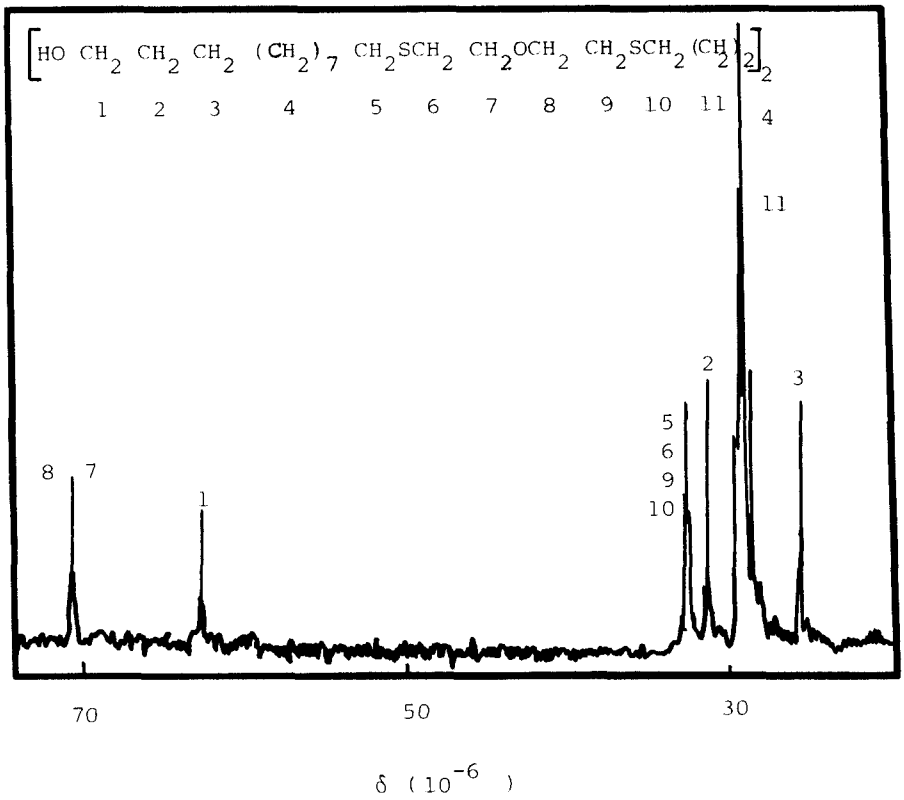

FIGURE 2 ^{13}C-NMR spectrum of diol 3.

TABLE III

^{1}H and ^{13}C-NMR characteristics of diols 3 and 4

	diol	HO	CH_2	CH_2	$(CH_2)_7$	CH_2	CH_2	SCH_2	CH_2	OCH_2	CH_2	SCH_2	CH_2	CH_2	CH_2	CH_2
^{1}H-NMR	3	1.8 (s)	3.6 (m)	1.6 (m)	1.2-1.5 (m)	1.6 (m)	2.6 (t)	2.7 (t)	3.6 (m)	3.7 (m)	2.7 (t)	2.6 (t)	1.6 (m)	1.3 (m)	-	-
	4	1.8 (s)	3.6 (m)	1.6 (m)	1.2-1.5 (m)	1.6 (m)	2.6 (t)	2.7 (t)	3.6 (m)	3.6 (m)	2.7 (t)	2.6 (t)	1.6 (m)	1.2	(m)	1.5
^{13}C-NMR	3	-	62.2	31.5	25.7	29.8	31.5	32.7	70.7	70.7	32.7	31.5	28.8	29.4	-	-
	4	-	62.6	31.3	25.5	29.6	33.0	33.5	70.5	70.5	33.2	32.4	27.3			29.2

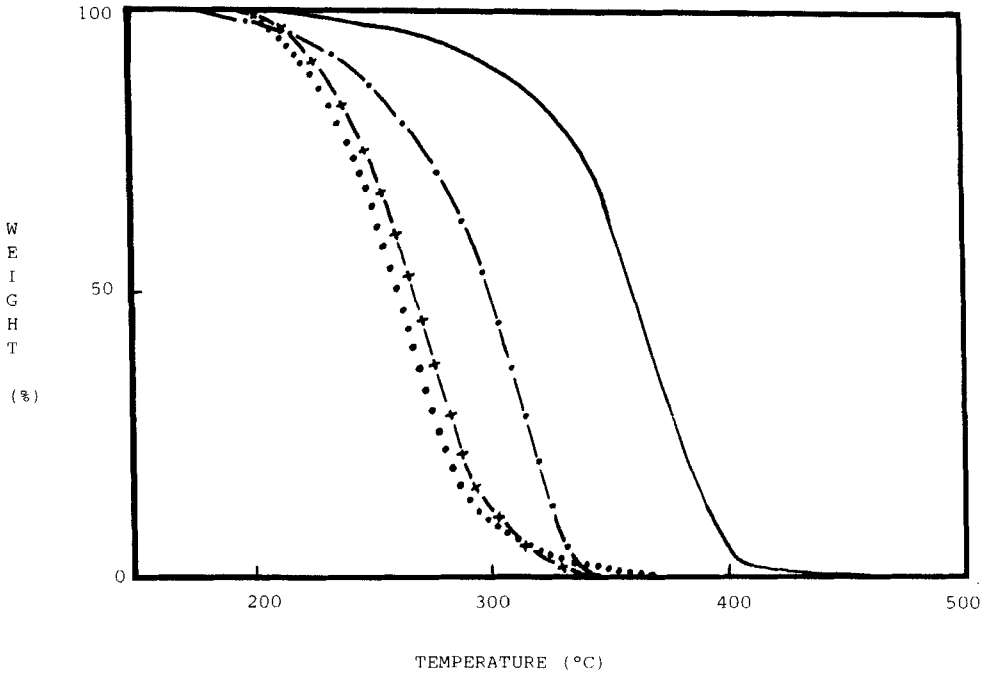

FIGURE 3 Thermogravimetric curves of PEG 10,000 (•••••••), PEG 1,000 (-×-×-), tetrathane 650 (-·-·-) and diol 4 (————).

EXPERIMENTAL

Apparatus

Because of low boiling point of 1,5-hexadiene (Eb_{760} = 58–59°C) the telomerizations of such a monomer were carried out in Carius tubes. However, the different reactions using 1,9-decadiene were performed either in Carius tubes (CT) or at atmospheric pressure (Eb_{760} = 169°C) in a two-necked round-bottom flash equipped with a condenser and a device for the introduction of nitrogen.

The Carius tubes had the following characteristics:

Type of CT	Small	Medium
Thickness, mm	2	3
Outside diameter, mm	23	40
Length, mm	260	310

These tubes were first saturated with nitrogen and then filled with the reactives, under nitrogen, cooled in a liquid nitrogen/acetone mixture ($T \sim -80$°C), sealed, and placed into the cavity of a block made of aluminum, put in a shaken autoclave equipped with a thermoregulator. At the end of the reaction the tube was left at room temperature and then cooled with liquid nitrogen and opened.

These reactions were monitored by SEC using a Trivector Trilab apparatus equipped with a Knauer HPLC (Model 64) pump. THF was used as the eluent (flow 1.5 mL/min at T = 30°C). The separation was carried out with a set of three Polymer Lab columns. The diameters of the pores were 1000, 500, and 50 Å. The detection has been performed by a Knauer differential refractometer.

The different pure telomers were characterized by ^{1}H and ^{13}C NMR at room temperature. ^{1}H NMR spectra were recorded on a Bruker CW 60 apparatus or for a higher resolution on a Bruker WM 360 or Bruker AC 250, by using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. The letters s, d, t, q, and m designate singlet, doublet, triplet, quartet, and multiplet, respectively.

The ^{13}C NMR spectra were performed on a Bruker WP 80 apparatus and the telomers were generally diluted in $CDCl_3$ (reference).

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC-4 apparatus equipped with a TADS microcomputer; the apparatus was calibrated with indium which has a melting temperature of 156.6°C and an enthalpy of fusion of $28.5 J \cdot g^{-1}$. After its insertion in the DSC apparatus, the sample was first cooled to −70°C for 10 min. A first scan was made at a heating rate of $40°C \cdot min^{-1}$, up to 100°C, where is stayed for 1 min. Then, it was quenched to −70°C at a cooling rate of $320°C \cdot min^{-1}$, and was left for 5 min at that temperature before a second scan at a heating rate of $10°C \cdot min^{-1}$. The values of the glass transition temperature (T_g) reported in this paper were taken at the half-height of the heat capacity jump of the glass transition, and those of the melting temperature (T_m) correspond to the value of the maximum of the endotherm peak.

The thermogravimetric analyses were conducted with a TG2 Perkin-Elmer 1 under nitrogen at a heating rate of 10°C, min^{-1}.

Synthesis of Telechelic Monodispersed Diols

From commercially available mercapto-alcohol

Telomerization of 1,5-hexadiene with 2-mercaptoethanol

The Carius tube was filled with a mixture composed of 0.09 g (0.0005 mol) of *t*-butyl peroxypivalate, 10.0 g (0.128 mol) of 2-mercaptoethanol in 20 g of acetonitrile and 4.8 g (0.058 mol) of 1,5-hexadiene. This solution was heated up to 75°C for two hours. After cooling down to room temperature the tube was frozen in liquid nitrogen and then opened. The diol was precipitated and then recrystallized from acetonitrile. 13.0 g of white crystals were obtained (yield = 94%). T_m = 95°C.

^1H NMR ($CDCl_3$): δ = 1.35 (m, 4H, $SC_2H_4(\underline{CH_2})_2$); 1.55 (m, 4H, $SCH_2\underline{CH_2}(CH_2)_2\ \underline{CH_2}CH_2S$) 2.25 (broad, shifted with dilution, s, 2H, OH), 2.50 (t, J = 7.0 Hz, 4H; $HOCH_2CH_2S\underline{CH_2}$); 2.70 (t, J = 7.0 Hz; 4H; $HOCH_2\underline{CH_2}S$); 3.70 (t, J = 7.0 Hz; 4H, $HO\underline{CH_2}$).

^{13}C-NMR ($CDCl_3$): δ = 28.47; 29.71; 31.57; 35.40; 60.33.

1,12-dihydroxy-3,10-dithiadodecane.

$C_{10}H_{22}O_2S_2$ (238.41)	Calc	C 50.38	H 9.30	S 26.90%
	Found	51.16	9.08	27.22%

%OH = 14.95 (Calc. 14.27).

Telomerization of 1,9-decadiene with 2-mercaptoethanol

A similar experiment was performed as the previous one, using 10.0 g (0.130 mol) of 2-mercaptoethanol, 20 g of acetonitrile, 8.0 g (0.057 mol) of 1,9-decadiene and 0.2 g (0.0011 mol) of *t*-butylperoxypivalate. This reaction, performed at atmospheric pressure in three-necked round-bottom flask equipped with a condenser and a device for nitrogen, gave identical results. 16.1 g of white crystals were obtained (yield = 96%) T_m = 73°C.

^1H-NMR ($CDCl_3$): δ = 1.30 (m, 12H, $SC_2H_4(C\underline{H_2})_6$; 1.55 (m; 4H; $SCH_2C\underline{H_2}(CH_2)_6C\underline{H_2}CH_2S$); 2.35 broad, s, 2H, OH; 2.50 (t, 4H; J = 7.0 Hz; $SC\underline{H_2}(CH_2)_8CH_2S$); 2.70 (t, 4H, J = 7.0 Hz, $HOCH_2C\underline{H_2}S$); 3.70 (t, 4H, J = 7.0 Hz, $HOC\underline{H_2}$)

^{13}C-NMR ($CDCl_3$): δ = 28.79–29.76; 31.77; 35.40; 60.33.

1,16-dihydroxy-3,14-dithia hexadecane.

$C_{14}H_{30}O_2S_2$ (294.52)	Calc.	C 57.09	H 10.27	S 21.77%
	Found	58.90	9.88	21.16%

%OH = 11.81 (Calc. 11.55).

From synthesized mercapto-alcohol

Monoaddition of 2-mercaptoethyl ether onto 10-undecenol

This reaction occurred in the three necked round bottom flask equipped with a condenser, a device for a nitrogen flow and a dropping funnel containing 12.0 g (0.07 mol) of 10-undecenol dissolved in 30 g of acetonitrile. Such a solution was slowly dropwise added into a stirred mixture composed of 38.9 g (0.28 mol) of 2-mercaptoethyl ether and 0.18 g (0.001 mol) of *t*-butyl peroxypivalate in 50 g of acetonitrile, at 75°C. The reaction was stopped one hour after the complete addition of the 10-undecenol solution. The SEC chromatogram shows the presence of a peak having a retention time lower than that of the dithiol. After distillation of the excess of 2-mercapto ethyl ether, the orange liquid residue (19.7 g) had the following characteristics.

^1H NMR ($CDCl_3$): δ = 1.25 (m, 14H, $(C\underline{H_2})_7CH_2CH_2S$); 1.50 (m, 4H, $C\underline{H_2}(CH_2)_7C\underline{H_2}CH_2S$); 1.60 (t, J = 7.2 Hz, 1H, SH); 1.9 broad, shifted with dilution (s, 1H, OH); 2.50 (t, J = 6.9 Hz, 2H, $(CH_2)_9C\underline{H_2}S$);

2.65 (t, J = 6.9 Hz, 4H, $SC\underline{H}_2CH_2OCH_2C\underline{H}_2SH$); 3.55 (m, 6H, CH_2O).
^{13}C-NMR ($CDCl_3$): δ = 24.5; 26.2; 28.1; 30.0; 32.2; 32.6; 33.1; 62.5; 70.5; 72.2.
17-hydroxy-1-mercapto-3-oxa-6-thiaheptadecane.

$C_{15}H_{32}O_2S_2$ (308.55)	Calc.	C 58.39	H 10.45	S 20.78%
	Found	60.12	10.03	19.94%

Telomerization of 1,5-hexadiene with 17-hydroxy-1-mercapto-3-oxa-6-thiaheptadecane

In a Carius tube was poured a mixture composed of 1.0 g (0.012 mol) of 1,5-hexadiene, 0.19 g (0.0012 mol) of *t*-butyl peroxypivalate, 8.0 g (0.026 mol) of 17-hydroxy-1-mercapto-3-oxa-6-thiaheptadecane and 20 g of acetonitrile. The reaction was performed at 75°C for 5 hours. The diol was precipitated and then recrystallized from acetonitrile. 6.2 g of white crystals were recovered. The yield was 74%, T_m = 69°C, T_g = 12°C.
^{1}H NMR ($CDCl_3$) δ = 1.2–1.4 (m, 32H; $(C\underline{H}_2)_7C_2H_4S$, $SC_2H_4(C\underline{H}_2)_2C_2H_4S$); 1.55 (m, 12H, $HOCH_2C\underline{H}_2$; $C\underline{H}_2CH_2S$); 1.70 singlet, shifted with dilution, 2H, OH; 2.55 (t, 8H; J = 7 Hz, $OCH_2CH_2SC\underline{H}_2$); 2.75 (t, 8H; J = 7 Hz, $OCH_2C\underline{H}_2S$); 3.65 (m, 12H; OCH_2).
^{13}C-NMR ($CDCl_3$): δ = 25.71; 28.81; 29.43; 29.75; 31.51; 32.70; 62.23; 70.71.
1,42-dihydroxy-12,18,25,31-tetrathia-15,28-dioxa ditetracontane.

$C_{36}H_{74}O_4S_4$ (699.25)	Calc.	C 61.84	H 10.67	S 18.34%
	Found	62.10	10.89	18.07%

%OH = 5.19 (Calc. 4.86).

Telomerization of 1,9-decadiene with 17-hydroxy-1-mercapto-3-oxa-6-thiaheptadecane

A similar reaction was performed as previously and required 10 g (0.032 mol) of long mercaptoalcohol, 2.08 g (0.015 mol) of 1,9-decadiene, 0.05 g (0.0003 mol) of *t*-butyl peroxypivalate. 8.5 g of diol were obtained as white crystals (yield = 75%). T_m = 34°C, T_g = 10°C.
^{1}H NMR ($CDCl_3$): δ = 1.2–1.45 (m, 40H, $SCH_2CH_2(\underline{C}H_2)_7$ and $SC_2H_4(C\underline{H}_2)_6C_2H_4S$); 1.55 (m, 12H, $HOCH_2C\underline{H}_2$ and $SCH_2C\underline{H}_2$); 1,8 broad shifted by dilution (s, 2H, OH); 2.55 (t, J = 7.0 Hz, 8H, $OCH_2CH_2SC\underline{H}_2$); 2.72 (t, J = 7.0 Hz, 8H, $OCH_2C\underline{H}_2S$); 3,6 (m, 12H, OCH_2).
^{13}C-NMR ($CDCl_3$): δ = 25.53; 27.33–29.22; 29.58; 31.34; 32.43; 32.98; 33.25; 62.61; 70.51.
1,46-dihydroxy-12,18,29,35-tetrathia-15,32-dioxa hexatetracontane.

$C_{40}H_{82}O_4S_4$ (755.36)	Calc.	C 63.60	H 10.94	S 16.98%
	Found	63.92	10.81	16.82%

%OH = 4.82 (Calc. 4.50).

CONCLUSIONS

The synthesis of telechelic monodispersed diols can be achieved by radical telomerization of nonconjugated dienes with an excess of commercially available or synthesized mercapto-alochols, initiated by peroxydes. Such syntheses are very simple, quick and produce the expected diols selectively and in very satisfactory yields. Furthermore, the longest diol exhibits an interesting thermostability, much higher than those of polydispersed commercially available polyether diols—especially the polytetrahydrofurane regarded as the most stable polyalkylene glycol. Thus, such telechelic monodispersed diols are valuable intermediates for the production of well-defined structured polymers.

ACKNOWLEDGEMENT

The financial help from ICI Materials was greatly appreciated.

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