

Synthesis of telechelic monodispersed diols

2. Telomerization of undecylenol with bis(2-mercapto ethyl) ether and bis(2-mercapto ethyl) sulfide and physical properties

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Summary

The synthesis of telechelic monodispersed diols produced from the radical telomerization of an excess of undecylenol with commercially available α, ω -dithiols $\text{HSC}_2\text{H}_4\text{XC}_2\text{H}_4\text{SH}$ ($X = \text{O}, \text{S}$ or CH_2) initiated by peroxides is presented. In each case, the diols were obtained selectively and quantitatively and they were characterized by both ^1H and ^{13}C NMR. Their physical characteristics (T_g , T_m and decomposition temperatures) were determined. Such compounds are thermally more stable than polydispersed telechelic commercially available diols.

Introduction

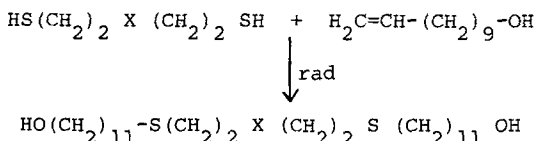
In previous articles (1-3) we detailed the bibliography about the synthesis of monodispersed telechelic diols performed by several international teams (4-7) or in our group (1-3,8) by alkaly catalyzed addition of epoxy (7) or by telomerization of undecylenic monomers with α, ω -dithiols (3,9,10). We showed that the radicalar initiation of such telomerization led to the expected diols selectively and quantitatively.

It was noticed that polymethylenedithiols (3) and bis(2-mercapto-ethyl) ether (9,10) were mainly employed but only one article (7) mentions the use of dithiols which exhibit a thioether group. Furthermore, almost no data about the physical properties of these oligomers have been reported in the litterature.

The goal of this paper concerns the synthesis of novel monodispersed telechelic diols prepared from the bismonoaddition of undecylenol onto $\text{HS}(\text{CH}_2)_2 \text{X}(\text{CH}_2)_2 \text{SH}$ telogens where X = oxygen, sulfur. Furthermore, the comparison of their physical properties (melting, glass transition and decomposition temperatures) to those of the diol obtained from the 1,5-pentanedithiol (where X designates a methylene group) and to those of a commercially available polydispersed diol is also described.

Results and Discussion

The synthesis of telechelic monodispersed hydroxyl-terminated polythioether, whether exhibiting an ether group or not, has been performed in batch. This deals with the addition of an excess of undecylenol onto bis(2-mercaptoethyl) sulfide, bis(2-mercaptoethyl) ether or 1,5-pentanedithiol, in the presence of initiator, according to the following scheme :



X	diol	FW
S	1	494
O	2	478
CH ₂	3	476

1°) Synthesis of telechelic monodispersed diols

The reaction involving 1,5-pentanedithiol was described in a previous article (3) and we detail below the synthesis of the diols in which the other dithiols were utilized. We used the t-butyl peroxyvalate as initiator because of its efficiency and its low half-life even at 70°C. An initial [dithiol]/[undecylenol] molar ratio of 0.45 was chosen and the reactions were carried out at 70°C in acetonitrile.

After 3 hours of reaction, the diols were precipitated and recrystallized from acetonitrile to eliminate any residual starting materials. The GPC chromatograms of both crystalline products show a unique sharp peak (11). Then, they were characterized by ¹H and ¹³C NMR.

The ¹H-NMR spectra (Figure 1) of both diols show :

- a broad peak in the 1.1 - 1.4 10⁻⁶ range corresponding to the methylenic chain ;
- a triplet centered at about 2.5 10⁻⁶ which is assigned to the methylene group in the position about the sulfur ;
- a signal at about 3.5 10⁻⁶ characteristic of the methylene group adjacent to the hydroxyl end-group.

Furthermore, the absence of the following protons is noted :

- the ethylenic protons of the hydroxylated olefin (no signal appears in the $4.5-6.0 \cdot 10^{-6}$ range),
- the allylic protons $\text{CH}_2-\text{CH}=\text{CH}_2$ which usually are present at $2.0 \cdot 10^{-6}$ on the $^1\text{H-NMR}$ spectrum of undecylenol,
- the proton of the $-\text{SH}$ end-group usually characterized by a triplet at $1.55 \cdot 10^{-6}$. These statements above give evidence of the purity of these diols.

However we observe the difference of chemical shifts for the methylene group in the position about X which is low fields shifted when X is the oxygen atom (Table 1).

The $^{13}\text{C-NMR}$ spectra (Figure 2) exhibit the expected peaks (Table 2) but the main difference lies also on the chemical shifts of the methylene group in the position about X.

Similarly we note the absence of the signals at about 24, 120 and $140 \cdot 10^{-6}$ characteristic of the carbon atoms of the methylene in the position of the mercapto end-group, and of the ethylenic carbon atoms of the undecylenol.

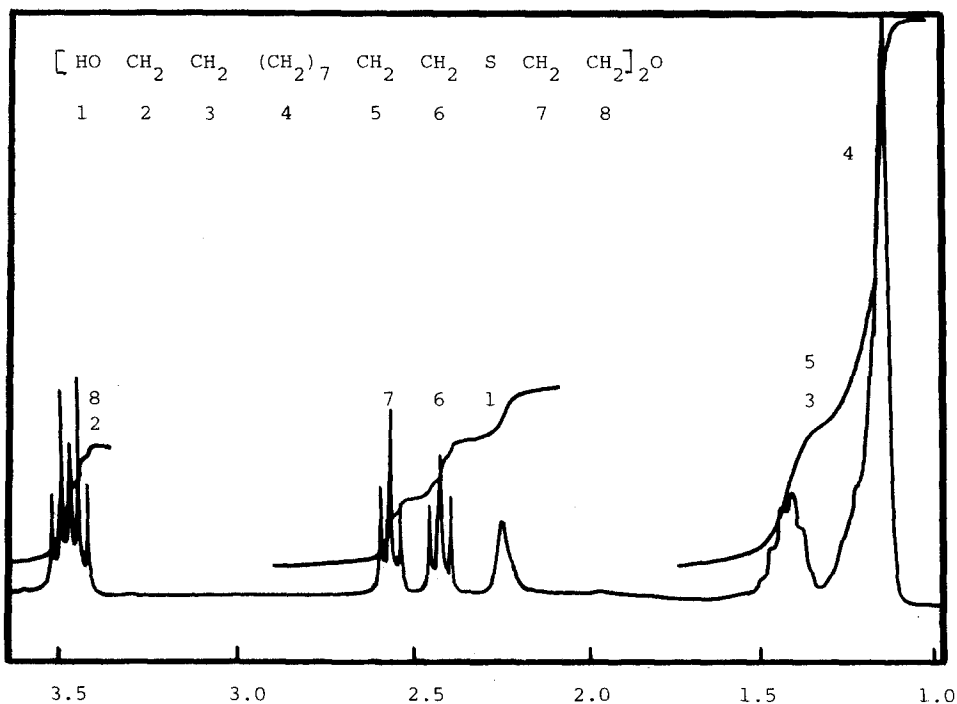


Figure 1 : $^1\text{H-NMR}$ spectrum of $\text{HO}(\text{CH}_2)_{11}-\text{SC}_2\text{H}_4\text{OC}_2\text{H}_4\text{S}(\text{CH}_2)_{11}\text{OH}$

2°) Physical properties of the diols

The thermostability and the melting and glass transition temperatures of the synthesized diols are detailed below.

Diol	X	HO	CH ₂	CH ₂	(CH ₂) ₇	CH ₂	CH ₂	CH ₂	SCH ₂	CH ₂	X
1	S	1.5 (s)	3.6 (m)	1.5 (m)	1.3 (m)	1.5 (m)	2.6 (t)	2.8 (m)	2.8 (m)	2.8 (m)	-
2	O	2.2 (s)	3.6 (m)	1.4 (m)	1.2 (m)	1.4 (m)	2.4 (t)	2.6 (t)	2.6 (t)	3.5 (t)	-
3	CH ₂	1.6 (s)	3.6 (t)	1.5 (m)	1.3 (m)	1.5 (m)	2.5 (t)	2.5 (m)	2.5 (m)	1.6 (m)	1.3 (m)
1	S	-	63.0	32.4	25.7-29.7	29.2	32.4	32.8	32.8	32.8	-
2	O	-	62.4	31.3	25.5-29.5	28.9	32.4	33.1	33.1	70.4	-
3	CH ₂	-	62.9	32.0	25.7-29.7	29.2	32.2	32.7	32.7	29.3	28.1

Table 1 : ¹H-NMR (upper part) and ¹³C-NMR (lower part) characteristics of the diols 1, 2 and 3 (in parantheses are the shapes of the signals : s for singlet, t for triplet and m for multiplet).

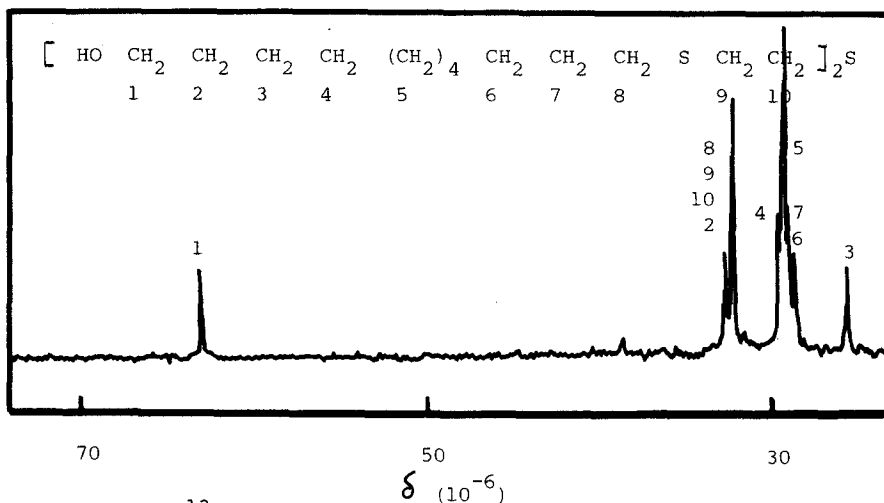


Figure 2 : ^{13}C -NMR spectrum of $\text{HO}(\text{CH}_2)_{11}\text{-SC}_2\text{H}_4\text{SC}_2\text{H}_4\text{S}(\text{CH}_2)_{11}\text{-OH}$

a) Thermostability

The thermogravimetric curves of the diols 1, 2 and 3 performed under a nitrogen atmosphere are presented in the Figure 3. The presence of the central oxygen atom lowers the decomposition temperature. The diol 2 starts to decompose from 260°C whereas the compounds 1 and 3 are still stable up to 305°C . However, it was noted that both the temperatures for which there is 50% weight-loss and that at the end of the decomposition - i.e. that from which the residual weight is constant- are higher for diol 2.

Furthermore, it can be observed that the thermostability of these monodispersed diols is higher than that of a polydispersed commercially available one, (e.g. poly (THF) which is regarded as one of the most stable polyethers). The softness of the poly (THF) may direct a certain orientation from which successive eliminations of THF molecules occur like a depolymerization.

Thus the thioether link is not weak in such diols as might have been expected. However the telechelic 1 is the least thermostable of these three diols.

Diol	X	T_m ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
1	S	98	24.6
2	O	78	9.4
3	CH_2	95	12.0

Table 2 : Melting temperatures and glass transition temperatures of diols 1, 2 and 3

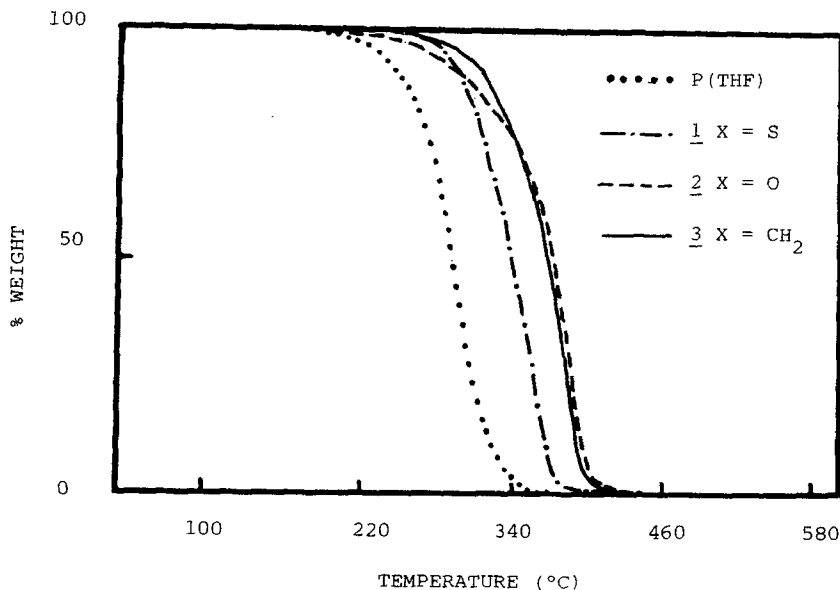


Figure 3 : TGA curves of diols $\text{HO}(\text{CH}_2)_{11}\text{-SC}_2\text{H}_4 \text{ X } \text{C}_2\text{H}_4\text{S}(\text{CH}_2)_{11}\text{-OH}$

b) Transition - temperatures

The melting and glass transition temperatures, determined by differential scanning calorimetry (DSC), are listed in table 2.

The DSC curves (Figure 4) of these diols exhibit unique sharp endothermic peaks which also can be assigned to the purity and the monodispersity of such diols. The heat-capacity jumps which show clear Tg's can also be observed.

The diol 2 has a melting temperature lower than those of the other diols whereas that of the diol 1 is the highest (Table 2).

A similar series is observed for the Tg's. This might be explained by the presence of the central sulfur atom which may stiffen the diol 1, whereas the ether group of the diol 2 and the size of the central aliphatic group of the diol 3 bring softness.

Conclusion

The preparation of telechelic monodispersed diols can be performed by the addition of a two fold excess of undecylenol onto bis(2-mercaptoethyl) ether or bis(2-mercapto ethyl sulfide with a peroxidic initiation. Such syntheses are fast simple and lead to the corresponding diols selectively and in quantitative yields, much better than those obtained in redox telomerization.

Furthermore, it can be noticed that these diols are rather stable since the less thermostable one starts to decompose from 260°C and they are more stable than polydispersed telechelic commercially available ones.

Both the melting and glass transition temperatures of these different diols follow the same decreasing scale :

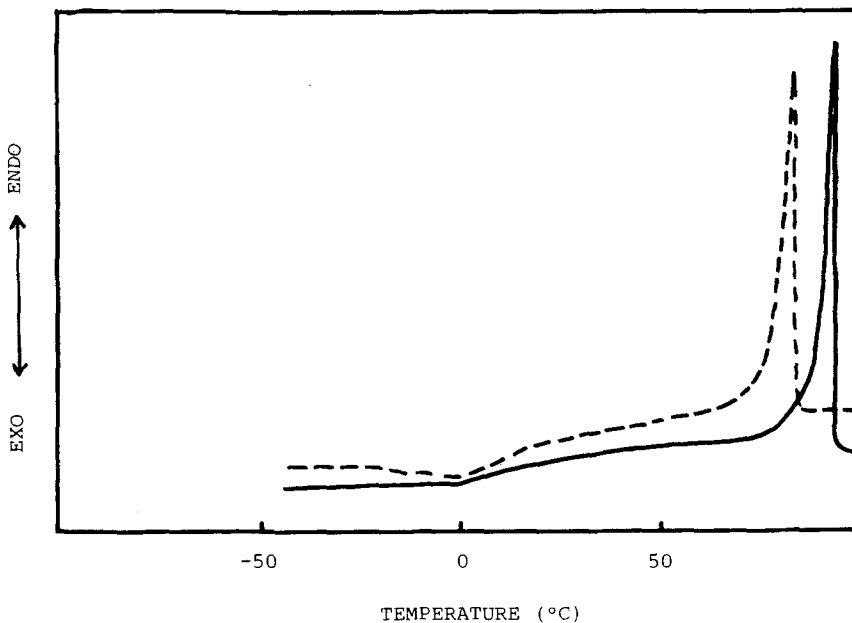
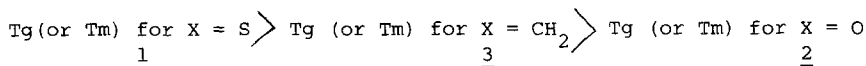


Figure 4 : DSC curves of diol 1 (full line) and diol 2 (dotted line)

Acknowledgments

We are indebted to ICI, Materials (Runcorn, U.K.) for its financial support.

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