

Synthesis of telechelic monodispersed diols

1. Telomerization of undecylenol with poly(methylene)dithiols

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Summary

The synthesis of telechelic monodispersed diols produced from the radical telomerization of an excess of undecylenol with commercial α, ω poly(methylene)dithiols, $\text{HS}(\text{CH}_2)_x\text{SH}$, with $x = 2, 3, 5$ and 6 initiated by peroxides is presented.

From these dithiols, the diols which were obtained selectively and quantitatively have been characterized by both ^1H and ^{13}C -NMR spectroscopy.

Introduction

The great importance of telechelic diols has been shown by the wide range of recent applications (1-5). They are important precursors for polycondensates such as polyesters, polyurethanes and silicones, and can be used to introduce photocrosslinkable functionality into polymer systems.

Harell (6) and Boutevin (7) demonstrated the importance of their monodispersity by showing the improvement which the diols gave in mechanical properties of derived polymers when compared with those from polydispersed analogues.

Harell (6), Bill (8) and Eisenbach (9) developed the synthesis of monodispersed telechelic intermediates using reactions which gave only moderate overall conversion and were unsuitable for the production of large batches of material. Nevertheless, telomerization (10-24) remains an interesting route to α, ω functionalised intermediates as other workers have reported. For example, the redox telomerization of functional monomers with

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trichloromethyl-terminated telogens can be used to produce α, ω -diols (11-14). Similarly, the reaction of telogens with monoconjugated dienes (15-20) and the bismonoaddition of functional monomers with α, ω -bis(trichloromethyl) telogens (21-24) followed by end-group transformation have been noted in the literature. But yields are only medium and in several cases the product of monoaddition limits their usefulness.

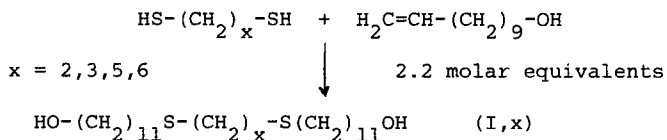
However, very good yields are obtained when functional monomers are added onto thioalcohols (26-27) or dithiols and catalyzed by either basic (26) or acidic (28) species ; or initiated by diazoic (27) compounds or peroxides (7). The products are monodispersed telechelic diols.

The authors are unaware of any previous reports of polymethylene dithiols being used as telogens in such syntheses.

This paper, then, reports the synthesis of monodispersed telechelic diols prepared from the radical telomerization of undecylenol with α, ω -(polymethylene)dithiols.

Results and Discussion

Poly(methylene) dithiol and an excess of undecylenol were used as reactants. In the presence of initiator the reaction proceeds according to the following scheme :



In this paper, we describe the reaction involving the pentanedithiol. This reaction was carried out in the presence of several initiators with a $R = [\text{dithiol}]/[\text{monomer}]$ molar ratio of 0.45 and various $C_o = [\text{initiator}]/[\text{monomer}]$ molar ratio. Three initiators were used separately at a temperature chosen at which their half life time was close to one hour : AIBN, benzoyl peroxide and tertio-butyl peroxyvalate.

In table I we have listed the results obtained after 5 hours reaction time and we note that although each initiator produced very good yields, t-butyl peroxyvalate gave the best results.

Table 1 : Experimental conditions and yields of the radical telomerization of undecylenol with pentanedithiol ($R_o = 0.45$ for 5h).

| Initiator | C_o (10^{-1}) | T(°C) | Yield (%) |
|----------------------|---------------------|-------|-----------|
| AIBN | 1.0 | 85 | 85 |
| Benzoyl peroxide | 1.0 | 93 | 90 |
| t-butyl peroxyvalate | 0.5 | 80 | 96 |

According to classical general mechanisms, we may expect to obtain the monoadduct, the telechelic product and higher adducts. However, it is well known that with allylic olefins the product of monoaddition is selectively produced but that does not exclude the monoaddition on one side only. To avoid this, we used an [undecylenol]/ [dithiol] molar ratio of 2.2 and we note on the GPC chromatogram only the presence of the monomer, dithiol and one product which is the α, ω -difunctional telomer as we show below.

After reaction, the telechelic diol was precipitated and then recrystallized from acetonitrile, to eliminate residual starting materials.

The diol was characterized by both ^1H and ^{13}C -NMR.

The ^1H -NMR spectrum (figure 1) of the diol obtained (I,5) shows :

a triplet centered at 3.62×10^{-6} , characteristic of the methylene groups in the position α to the oxygen atom ;

two triplets at 2.50×10^{-6} assigned to those in the position α to the sulfur atoms ;

a broad peak in the $1.20\text{-}1.40 \times 10^{-6}$ range corresponding to the methylenic chain ;

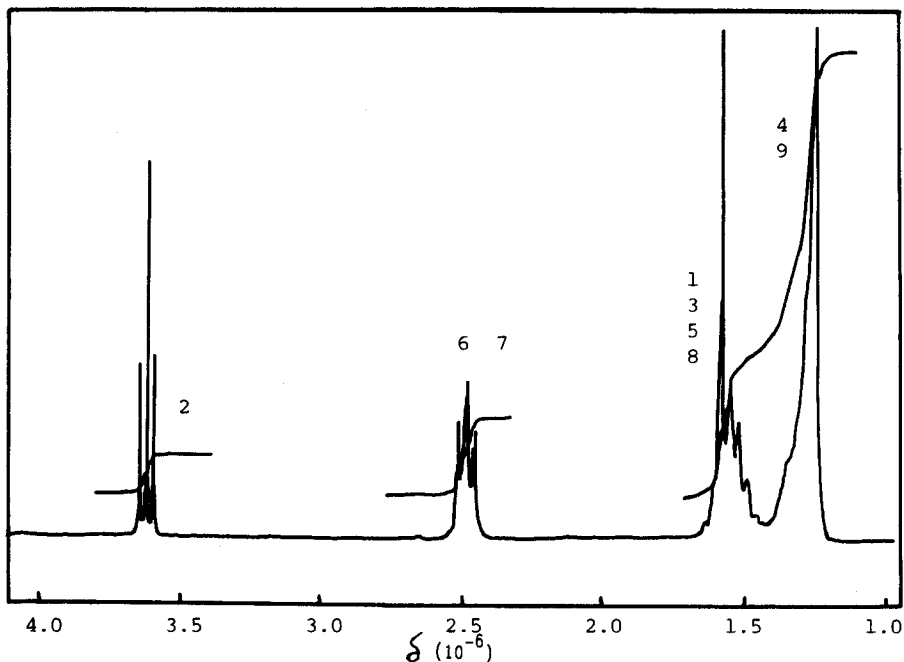


Figure 1 : ^1H NMR spectrum of the diol (I,5)

However, the absence of the triplet at 1.55×10^{-6} assigned to the -SH end-group (29), of the ethylenic protons of undecylenol (absence of peak in the $4.5-6.0 \times 10^{-6}$ range) and the absence also of allylic protons $\text{CH}_2-\text{CH}=\text{CH}_2$ (which appear at 2.0×10^{-6} on the $^1\text{H-NMR}$ spectrum of undecylenol), evidences of the purity of the diols.

The $^{13}\text{C-NMR}$ spectrum (figure 2) exhibits the expected singlets assigned to the different carbon atoms of the diol (I,5) (table 2). We note the absence of the signals at about 24, 120 and 140 10^6 characteristic of the carbon atoms of the $-\text{CH}_2-\text{SH}$ of the dithiol, and the ethylenic carbon atoms of the undecylenol.

We note also the observed chemical shifts of the different peaks are in a good agreement with those predicted by Roberts' law (30).

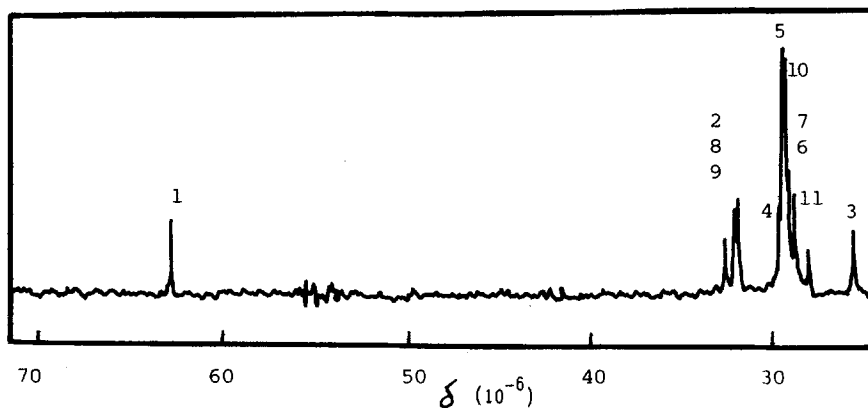


Figure 2 : $^{13}\text{C-NMR}$ spectrum of the diol (I,5).

Table 2 : $^{13}\text{C-NMR}$ characteristics of (I,2) (I,3), (I,5) and (I,6).

| Diols | HOCH_2 | CH_2 | CH_2 | CH_2 | (CH_2) | CH_2 | CH_2 | CH_2S | CH_2 | CH_2 | CH_2 |
|-------|-----------------|---------------|---------------|---------------|-----------------|---------------|---------------|-----------------------|---------------|---------------|---------------|
| (I,2) | 63.11 | 32.45 | 25.79 | 29.79 | 29.53 | 28.91 | 29.26 | 32.46 | 32.87 | - | - |
| (I,3) | 62.99 | 31.07 | 25.74 | 29.69 | 29.48 | 28.89 | 29.21 | 32.25 | 32.80 | 29.48 | - |
| (I,5) | 62.89 | 31.99 | 25.66 | 29.66 | 29.41 | 28.83 | 29.16 | 32.19 | 32.74 | 29.34 | 28.12 |
| (I,6) | 63.11 | 32.33 | 25.79 | 29.55 | 29.54 | 28.98 | 29.27 | 32.33 | 32.87 | 29.33 | 28.56 |

Similar radical telomerization of undecylenol with the other dithiols $\text{HS}(\text{CH}_2)_x\text{SH}$, where $x = 2,3,6$ initiated with t-butyl peroxyvalate ² afforded the expected α, ω -diols in excellent yields (> 90%). Their ¹³C-NMR characteristics are listed in table 2.

Conclusion

The synthesis of new monodispersed telechelic diols can be achieved by the addition of an excess of undecylenol onto α, ω -dithiols with peroxidic initiation. Such a preparation is quick, very simple and leads to the expected telechelic monodispersed diols selectively and in excellent yields. Such new diols are interesting intermediates for the production of well-defined structured polymers (polyurethanes, polyesters etc...).

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References

- 1 Athey RD Jr (1982) J Coat Technol 54(690):47
- 2 Brossas J (1974) Inf Chim 128:185
- 3 Heitz W (1978) Makromol Chem Macromol Symp 10/11:297
- 4 Nguyen MA, Maréchal E (1988) Rev Macromol Chem Phys C28(2):187
- 5 Goetals EJ in Telechelic Polymers and Their Applications, Ed CRC Press (1989)
- 6 Harell LL (1969) Macromolecules 2 : 607
- 7 Boutevin B, Chaib M, Robin JJ (1990) Makromol Chem 191:737
- 8 Bill R, Droscher M, Wegner G (1981) Makromol Chem 182:1033
- 9 Eisenbach CD, Gunter CL (1983) ACS Org Coat Appl Polym Sci Proc 49:239
- 10 Boutevin B, Pietrasanta Y (1989) Comprehensive Polymer Science Vol III:14:185 "Telomerization", Ed Pergamon Press
- 11 Bertrais H, Boutevin B, Maliszewicz M, Pietrasanta Y, Vernet JL (1982) Eur Poly J 18:791
- 12 Améduri B, Bowden RD, Conti-Ramsden J, Thomas NL (ICI) Patent in preparation
- 13 Battais A, Boutevin B, Hugon JP, Pietrasanta Y (1980) J Fluor Chem 16:397
- 14 Améduri B, Boutevin B (1991) Macromolecules 24:2475
- 15 Piccardi P, Massardo P, Modena M, Santoro E (1973) J Chem Soc Perkin Trans 1:982
- 16 Corallo M, Pietrasanta Y (1977) Phosphorous Sulfur 3:359
- 17 Ciba Ltd, British Pat 1,000,389 (1965) Chem Abst 1967 64:p2053e
- 18 Matsumoto A, Nakame T, Diva M (1983) J Appl Poly Sc 28:1105
- 19 Boutevin B, Dongala EB, Pietrasanta Y (1977) Eur Poly J 13:939
- 20 Améduri B, Boutevin B (1990) Macromolecules 23:2433
- 21 Boutevin B, Dongala EB, Pietrasanta Y (1977) Eur Poly J 13:935

- 22 Améduri B, Boutevin B, Lecrom C, Pietrasanta Y, Parsy R (1988) Makromol Chem 189:2545
- 23 Améduri B, Boutevin B, Lecrom C, Garnier L, J Poly Sc (in press)
- 24 Battais A, Boutevin B, Pietrasanta Y, El Sarraf T (1982) Makromol Chem 183:2359
- 25 Belbachir M, Boutevin B, Pietrasanta Y, Rigal G (1982) Makromol Chem 183:2347
- 26 Singh H, Hutt JW, Williams ME (Products Research and Chemical) Eur Pat Appl 81305695.9 (March 12th 1981)
- 27 Boutevin B, El Idrissi A, Parisi JP (1990) Makromol Chem 191:445
- 28 Nuyken O, Völker T (1990) Makromol Chem 191:2465
- 29 Berrada K, PhD thesis (1991) Ecole N.S. Chimie Montpellier
- 30 Robert JD, Weigert FJ, Kroschwitz JI, Reich H J (1970) J Am Chem Soc 92:1338

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