Polymer Bulletin 31, 1–7 (1993)

Polymer Bulletin

Synthesis of a telechelic monodispersed mercapto-alcohol

Bruno Ameduri[1], Khalid Berrada[1], Bernard Boutevin[1], and Roy D. Bowden[2]

[1]URA D11930 CNRS, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'Ecole Normale, F-34053 Montpellier Cédex 1, France
[2]I.C.I., Materials, Research and Technology Department, The Heath, Runcorn, Cheshire WA7 4QD, UK

Summary

The synthesis of a novel telechelic monodispersed mercapto-alcohol produced from the radical addition of 10-undecenol onto a large excess of 2-mercaptoethyl ether, initiated by peroxides is presented. The yield was quantitative and this product was characterized by both ^1H and ^{13}C-NMR.

Introduction

Telechelic monodispersed oligomers are important intermediates for building materials of controlled architecture (1-6) such as polyesters, polyurethanes, polyamides and polyimides. They have also been used in rocket propellants, as chain extenders, prepolymers and in high solid resins coatings.

However, their use is restricted by their limited availability. Of the α,ω-diols, some are available from poly (THF) (7, 8) or can be prepared from organic syntheses (9) or from telomerization (10-14).

Some monodispersed α,ω-dithiols are available commercially or can be synthesized either from commercially available dithiols and dienes (15-18), from diols (19-20) from divinylsiloxane (21), from α,ω-dihalogenated compounds (4, 19-22) or from dilithiated compounds (23). Like the diols, the dithiols are also interesting precursors for multiblock copolymers (24, 25), prepolymers (26), polyurethanes (27), elastomers (28) and lead to many applications in optical materials (29), in textile (30), and in photocurable coatings produced by the thiol-ene process (31).

Telechelic monodispersed oligomers in which the α- and ω- functional groups differ are important synthons since they allow for further controlled stepwise build-up of higher molecular weight prepolymers. Mercapto-alcohols are little-known. In 1948, Woodwards (32) obtained the monothioethylene glycol by bubbling hydrogen sulfide into sodium sulfide and then adding ethylene oxide. The product was obtained by ring opening of the epoxide by nucleophilic attack of the $^{\ominus}$SH anion (33). Similarly, Arretz et al. (34) obtained novel mercapto-alcohols in high yields. The H_2S adduct with hexafluoroacetone is a mercapto-alcohol (35) but if addition is carried out at high temperatures reductive thiolation gives hexafluoroisopropyl mercaptan (36). Aromatic thio-alcohols have also been prepared by Nuyken (15) who synthesized 4-(2-methyl-2-hydroxymethyl) benzene thiol. More recently, Schwar and Voss have obtained an interesting α,ω-mercapto-alcohols which exhibits a central carbonyl group (37).

However, these investigations were performed on short chain molecules, only. The subject of this paper concerns the synthesis of longer chain monodispersed telechelic mercapto-alcohol using a method of general applicability and exemplified by one particular product.

Results and Discussion

Previous works have shown that it was crucial to perform a dropwise addition of a difunctional reactant (e.g. α,ω-dithiol (18) or nonconjugated diene (38) onto a substrate which contained the initiator to give the 1:1 compound since higher adducts may be produced when all the starting materials are stirred together in a batch-vessel.

Consequently, by dropwise addition of the 10-undecenol into an excess of 2-dimercaptoethyl ether, the mercapto-alcohol 1 was prepared as follows :

$$\begin{array}{c} H_2C{=}CH{-}(CH_2)_9\,OH \\ + \\ HS\,(CH_2)_2\,O\,(CH_2)_2\,SH \end{array} \xrightarrow{\text{rad.}} \underset{\underline{1}}{HS\,(CH_2)_2\,O\,(CH_2)_2\,S\,(CH_2)_{11}\,{-}\,O}$$

Furthermore, previous investigations (12, 38-41) about the nature and the quantity of the initiator concluded that tertiobutyl-peroxypivalate was to be preferred and, since it exhibits at low temperature (70°C) a half life of one hour, it is obviously convenient for use in low boiling solvents.

The reaction was monitored by GPC and it was observed that one hour after the total addition of the hydroxylated olefin onto the α,ω-dithiol, the reaction was complete as shown by the absence of the peak of the 10-undecenol (41). The GPC chromatogram (Figure 1) exhibits, besides the band assigned to the dithiol, the presence of another signal, the elution volume of which was smaller than those of both the reactants.

After evaporation of the solvent and rectification of the excess of the 2-dimercapto ethylether, the residue was characterized by ^{1}H and ^{13}C-NMR.

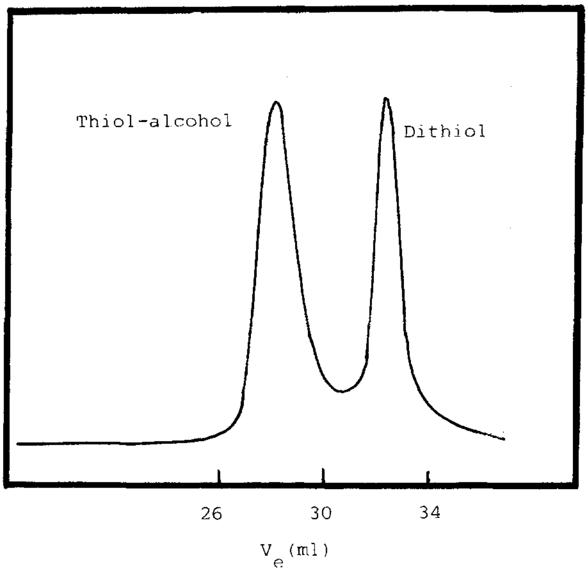

Figure 1 : GPC chromatogram of the product of the reaction one hour after dropwise addition of 10-undecenol onto an excess of 2-mercaptoethyl ether.

1	HO	CH_2	CH_2	CH_2 $(CH_2)_6$ CH_2	CH_2S	CH_2 CH_2 O CH_2 CH_2	SH
^1H	1.85 (s)	3.4-3.6 (m)	1.4-1.6 (m)	1.2 (m) 1.4 1.4-1.6 (m)	2.5 (t)	2.7 (t) 3.4 — 3.6 (m) 2.7 (m)	1.4-1.6 (m)
^{13}C	-	62.5	32.2	26.2 28.1 30.0	32.6	33.1 70.5 72.2 24.5	-

Table 1 : Chemical shifts (10^{-6}) of thio-alcohol 1 in ^1H and ^{13}C-NMR (the shape of the signal is given in parentheses).

The ^1H-NMR spectrum (Figure 2) shows the absence of the ethylenic protons in the 4.5-6.0•10^{-6} range and this confirms the total addition of the olefin. Furthermore, the triplet at 2.5•10^{-6} (J=7.0 Hz) and a complex signal at 2.65•10^{-6} are assigned to both the methylene groups in the α position about the sulfur atom (Table 1), respectively. Whereas that in the α position of the mercapto end-group gives a signal at 2.65•10^{-6} . Moreover, the peak at 1.90•10^{-6} and the triplet centered at 1.60•10^{-6} are characteristic of the hydroxyl and the mercapto end-groups, respectively. The methylenic chain and the three methylene groups adjacent to the oxygen atoms, appear as a broad signal at about 1.2•10^{-6} and a mixture of triplets centered at about 3.55•10^{-6}, respectively.

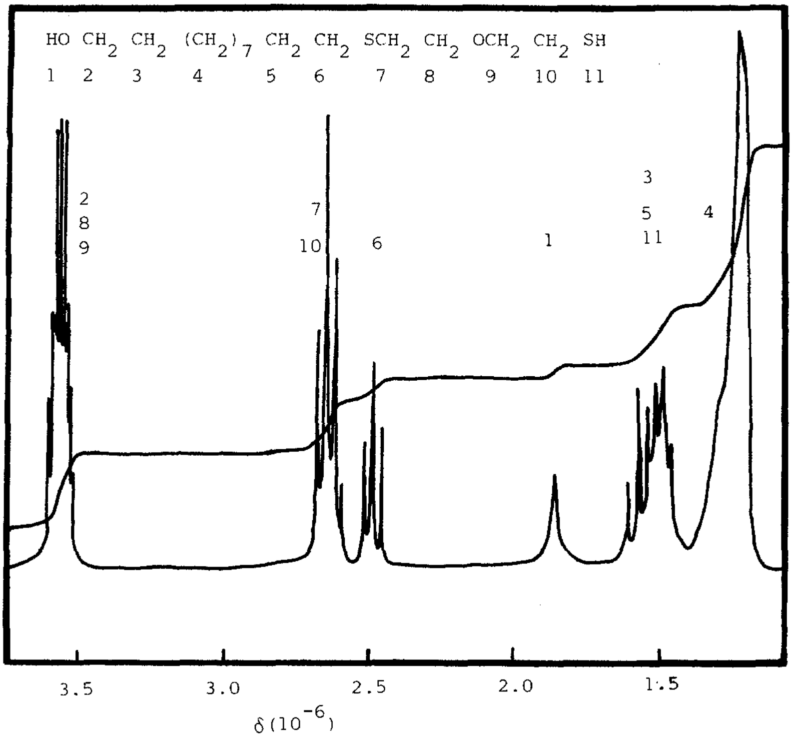

Figure 2 : ^{1}H-NMR spectrum of the mercapto-alcohol 1.

On the ^{13}C-NMR spectrum (Figure 3), it is noted the absence of the ethylenic carbons in the 110-140•10^{-6} range, whereas the three methylene groups in α of the oxygen atoms give three peaks in the 62-73•10^{-6} region. The two high fields shifted peaks are characteristic of the methylene groups adjacent to the mercapto group and in γ about the hydroxyl one whereas the methylene groups in α of the thioether one appears at 32.6 and 33.1•10^{-6}. The assignement of the other signals are shown in the Table 1 and are in a good agreement with Robert's law (42).

It was obtained a total conversion of the 10-undecenol and a quantitative yield of the product.

Conclusion

The method presented gives telechelic monodispersed mercapto-alcohols selectively, easily and in excellent yield.

In a further paper, it will be demonstrated the use of such a compound as precursor of original monodispersed telechelic diols, which are useful intermediates for producing well-defined structured polymers.

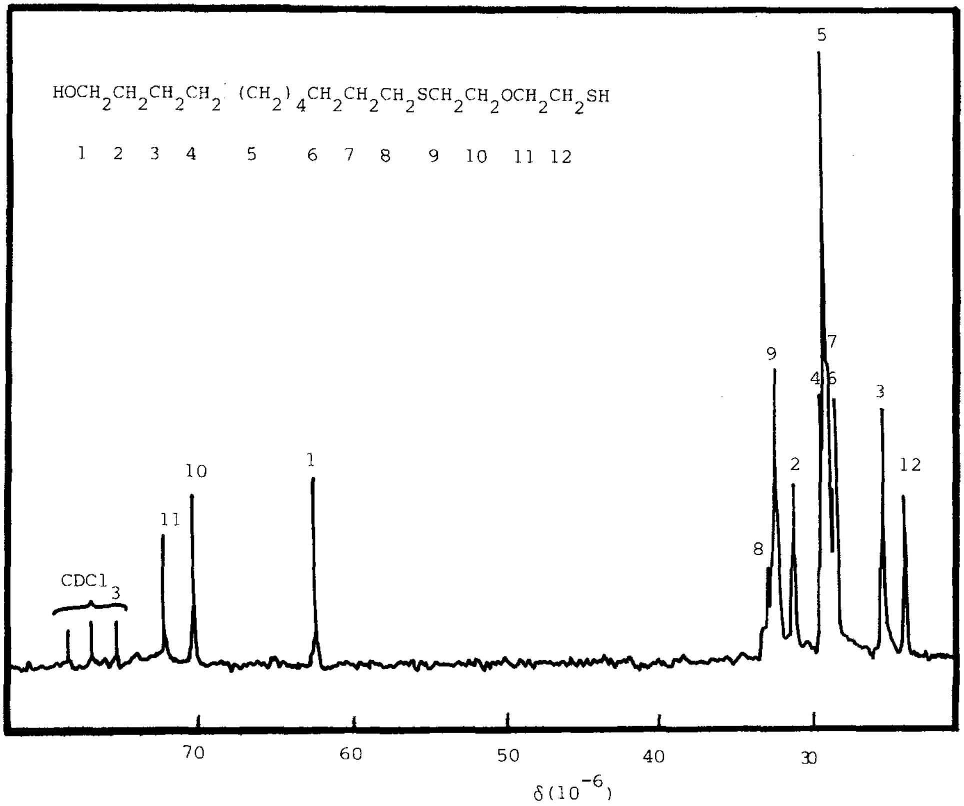

Figure 3 : ^{13}C-NMR spectrum of the thio-alcohol 1.

Acknowledgements

We are grateful for I.C.I. Materials (Runcorn) for its financial support.

References

1. Brossas J (1974) Inf Chimie 128 : 185

2. Heitz W (1978) Makromol Chem Macromol Symp 10/11 : 297

3. Athey RD Jr (1982) J Coat Technol 54 (690) : 47

4. Goethals EJ (1989) in Telechelic Polymers : Synthesis and Applications, Edition CRC Press

5. Percec V, Pugh C, Nuyken O, Pask SD (1989) "Macromonomers, Oligomers and Telechelic Polymers" in Bevington (ed) "Comprehensive in Polymer Science", vol 6 : 9 : 281

6. Jerome R, Henrouille-Gronville M, Boutevin B, Robin JJ (1991) Prog Polym Sci 16 : 837

7. Harell LL (1969) Macromolecules 2 : 607

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) "Telomerization" in Allen G, Bevington JC (ed) Comprehensive in Polymer Science", vol 3 : 14 : 185 Pergamon Press, Oxford

11. Gordon G, Loftus J (1989) "Telomerization" in Kirk Othmer (ed) "Encyclopedia of Polymer Science and Engineering", 2nd Edition, John Wiley, New-York, Vol 16 : 533

12. Améduri B, Berrada K, Boutevin B, Bowden R submitted to Poly Bull

13. Améduri B, Boutevin B (1990) Macromolecules 23 : 2433

14. Améduri B, Boutevin B (1991) Macromolecules 24 : 2475

15. Nuyken O, Reuschel G, Siebzehnrübl F (1989) Makromol Chem Macromol Symp 26 : 313

16. Kabayashi E, Ohashi T, Furukawa J (1986) Makromol Chem 187 : 2525

17. Duda A, Penczek S (1989) Sulfur-containing Polymers. In : Kirk Othmer (ed) "Encyclopedia of Polymer Science and Engineering", 2nd Edition, John Wiley, New-York vol 16 : 280

18. Améduri B, Berrada K, Boutevin B, Bowden R, Pereira L (1991), Poly Bull 26 : 377

19. Klemm E, Stockl C (1991) Makromol Chem 192 : 153

20. Singh H, Hutt JW, Williams ME (Products Research and Chem Corp) Eur Patent Appl 0,054,379 (03/12/81)

21. Klemm E, Beil U (1991) Die Angew Makromol 188 : 189

22. Kobayashi H, Ohashi T, Miyabayashi (Mitsubishi Petrochemical Co Ltd) Jap Patent 62,195,023 (08/27/87) Chem Abst 108 : 56808 k

23. Robson P, Stacey M, Stephens R, Tatlow JC (1960) J Chem Soc 4754

24. Crivello J, Juliano PC (1975) J Polym Sc Poly Chem Ed 13 (8) : 1819

25. Fujisawa T, Tanaka A, Yosoyima R (1982) Makromol Chem 183 : 2923

26. Nishino H, Hattori T, Kushida T, Kumatra M (Honda Motor Co) Eur Patent 346,094 (12/13/89) Chem Abstr 112 : 199375 k

27. Kanemura Y, Sasagawa K, Imai M (Mitsui Toatsu Chemicals Inc) Jap Patent 0190,167 (04/06/89) Chem Abstr 111 : 196007 k

28. Nippon Mekton KK Jap Patent 57,170,910 (10/21/82) Chem Abstr 98 : 144806 p

29. Asuke T, Saeda S, Takenoshita Y, Yoshida H (Showa Donko KK) Jap Patent 63,234,032 (09/29/88) Chem Abstr 110:25168 p

30. Minnesota Minning Manufacturing, French Patent 1,562,070 (01/24/68)

31. Morgan CR, Magnotta F, Ketley AD (1977) J Poly Sc Poly Chem Ed 15 : 627

32. Woodwards FN (1948) J Chem Soc 1892

33. Wardell (1974) in Patai (ed) The Chemistry of thiol group, Wiley, New-York part 1 : 179

34. Arretz E, Auge P, Mirasson A, Landoussy C (SNEA) French Patent 2,609,027 (07/01/68)

35. Harris Jr JF (1965) J Org Chem 30 : 2190

36. Harris Jr JF (1960) (EI du Pont de Nemours Corp) US Patent 2,965,677

37. Schwar G, Voss J (1992) 15 th Inter. Symposium on the Chemistry of Sulfur, Caen (France) June 28 th - July 3rd (poster PA16)

38. Améduri B, Berrada K, Boutevin B, Bowden R, Polym Bull, 28,351 (1992)

39. Améduri B, Boutevin B, Nouiri M, J Poly Sc Poly Chem Ed (in press)

40. Boutevin B, Cersosimo F, Youssef B, Kappler P (1991) J Fluor Chem 52 : 403

41. Berrada K (1991) PhD thesis. Ecole Nationale Supérieure de Chimie de Montpellier

42. Robert JD, Weigert FJ, Kroschwitz JI, Reich HJ (1970) J Am Chem Soc 92 : 1338

Accepted May 19, 1993 C