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Synthesis of telechelic monodispersed dithiols

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Summary

The synthesis of novel telechelic monodispersed dithiols from a nonconjugated diene and an α , ω -dithiol is presented. The batch reaction produced a polydispersed mixture of dithiols separable with difficulty whereas a dropwise addition of diene onto an excess of dithiol in the presence of peroxide led selectively and quantitatively to the addition product : dithiol-diene-dithiol.

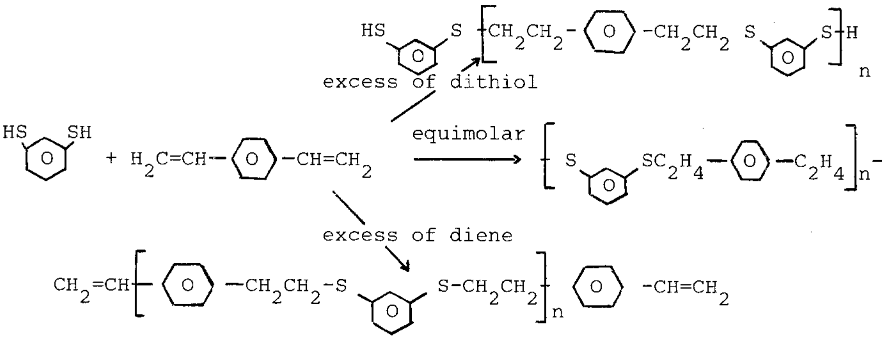
Introduction

The importance of monodispersed telechelic dithiols has been greatly increasing as evidence by the wide range of applications. For instance, these compounds are interesting forerunners of multiblock copolymers (1,2), prepolymers (3), polyurethanes (4) and elastomers (5).

Numerous publications and patents have been published showing further novel applications : in optic materials (6), in textile (7), and in photocuring coatings produced by the thiol-ene process (8,9).

Each of these above examples exploits the enhanced reactivity of two mercapto end-group.

Since 1857 (10) , it has been well known that the addition of the -SH end-group onto an ethylenic double bond occurs by a radical mechanism (11,12) giving the anti-Markovnikov product. The reaction between an α , ω dithiol and a nonconjugated diene is a polyaddition (13) in which the end groups and the molecular weight of the products are controlled by the stoichiometry of the reaction according to the following chemical scheme, in the case of 1,3-benzenedithiol and 1,4-divinylbenzene (14):



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Thus, an excess of dithiol produces a mixture which exhibits predominantly mercapto chain ends, whereas an excess of diene leads to ethylenic functionality, mainly (14).

Nuyken et al. (14) showed that the end-group titration can be used to determine the molecular weights below 5,000.

Usually, they used a system in which reactants were aromatic (14-19), or in which the dithiol, itself, was either aliphatic (20) or aromatic (21).

Similarly, the German team carried out polyadditions of aromatic dithiols onto triple bonds (14,17,22) (1,4-diethynyl-benzene instead of divinylbenzene as scheme above).

Moreover, the only study involving both aliphatic reactants was performed in 1951 in which the authors wished to obtain polydispersed oligomers (of molecular weights below 1,000) which had unsaturated and mercapto end-groups (13). So far, no dithiol containing a heteroatom has been used in these addition reactions.

This article pesents an effective synthesis of novel telechelic monodispersed dithiols obtained from aliphatic dienes and dithiols.

Results and Discussion

1,5-hexadiene or 1,9-decadiene and an excess of 2-mercapto ethyl ether were used as reactants in the presence of peroxides, the reaction proceeding according to the following scheme :

$$H_2C{=}CH{-}(CH_2)_x{-}CH{=}CH_2 \ + \ HSCH_2CH_2OCH_2CH_2SH$$

$$x{=}2 \text{ or } 6 \qquad \Big\downarrow \text{radical} \qquad \text{(excess)}$$

$$HS(CH_2)_2O(CH_2)_2S(CH_2)_{x+4}S(CH_2)_2O(CH_2)_2SH$$

<u>A, x</u>

1°) Batch-reaction

We chose several initial molar ratios (R_o) in which [dithiol]/[1,5-hexadiene] = R_o = 2.0 or 3.0 or 4.0 .

After 3 h reaction, we noted the GPC chromatogram (figure 1) of the reaction medium exhibited a polydispersed behavior.

We observe logically that the lower the R_o, the higher the molecular weight of the telomers obtained. Whatever R_o, the medium is composed of a mixture of several dithiols $T(DT)_n$:.

TDT : $HS(CH_2)_2O(CH_2)_2S(CH_2)_6S(CH_2)_2O(CH_2)_2SH$

$T(DT)_2$: $HS(CH_2)_2O(CH_2)_2S\left[(CH_2)_6S(CH_2)_2O(CH_2)_2S\right]_2H$

$T(DT)_3$: $HS(CH_2)_2O(CH_2)_2S\left[(CH_2)_6S(CH_2)_2O(CH_2)_2S\right]_3H$

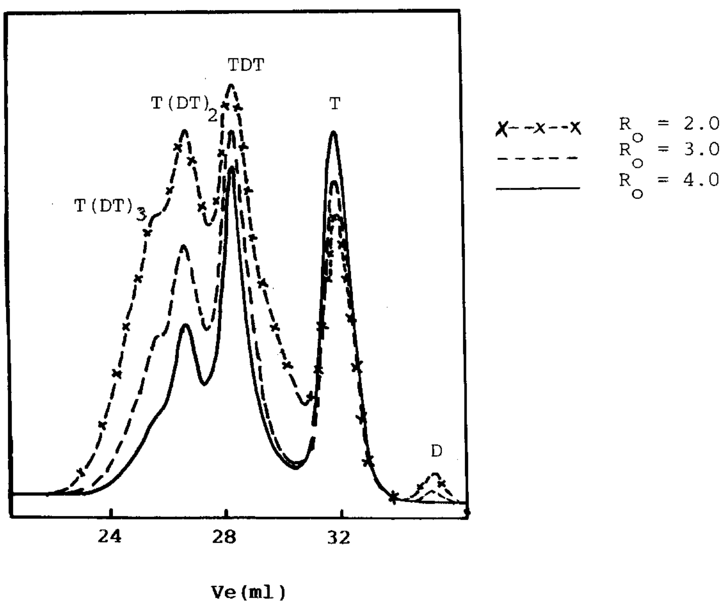

Figure 1 : GPC chromatogram of the product of the addition of 2-mercaptoethyl ether (T) onto 1,5-hexadiene (D) (batch reaction)

which can only be separated with difficulty using conventional methods.

Such a polydispersed product did not represent the goal we wished to reach ; thus, this method of obtaining monodispersed telechelic dithiols selectively is not valid. The same conclusion is reached when 1,9-decadiene is used.

2°) By dropwise addition of diene

This method consists of a slow dropwise addition of the 1,5-hexadiene into a large excess of α, ω dithiol containing the initiator (peroxide). 30 minutes after the total addition of the diene, the GPC chromatograph of the medium (figure 2) exhibits one peak only which corresponds to a product, the molecular weight of which is greater than those of the reactants. The reaction is quantitative.

The ^1H NMR spectrum (figure 3) of the obtained dithiol shows:

* the signal at $1.55\ 10^{-6}$ assigned to the presence of the -SH end-group ;
* the absence of the signal of the ethylenic protons in the $5.5\text{-}7.0\ 10^{-6}$ range which is evidence that the reaction of 1,5-hexadiene is total ;
* a signal at $1.35\ 10^{-6}$ due to the inner methylene groups between both thioether bridges. This comes from the addition product of the thiol accross the double bonds.

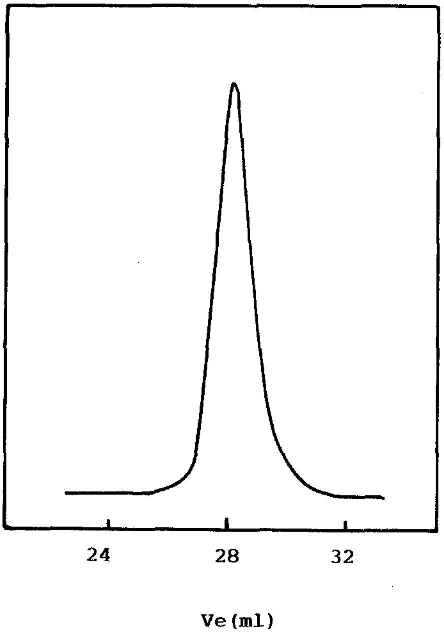

Figure 2 : GPC chromatogram of the product obtained 30 min after complete dropwise addition of 1,5-hexadiene onto 2-mercaptoethyl ether

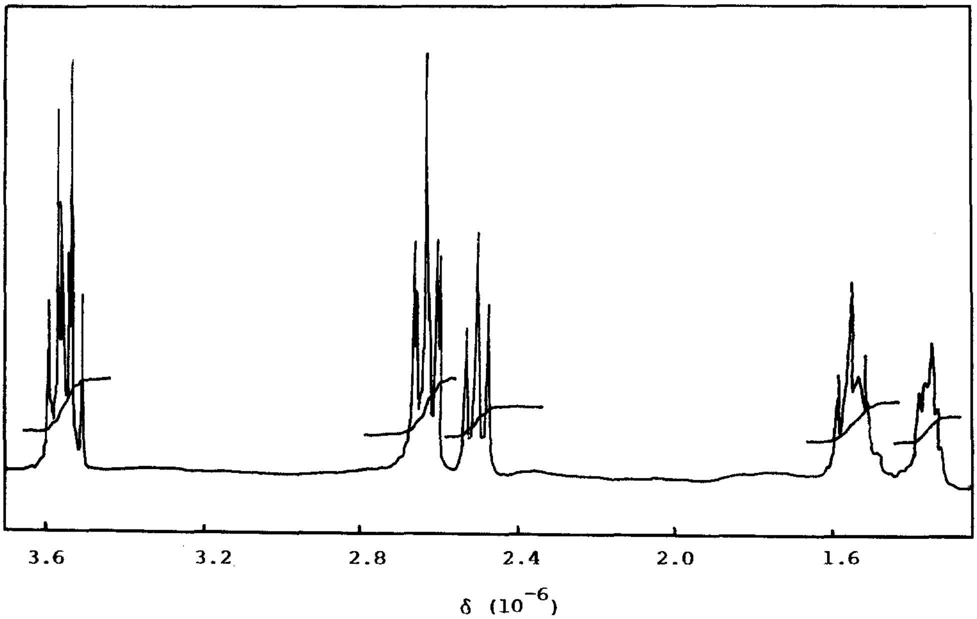

Figure 3 : ^{1}H NMR spectrum of A,2

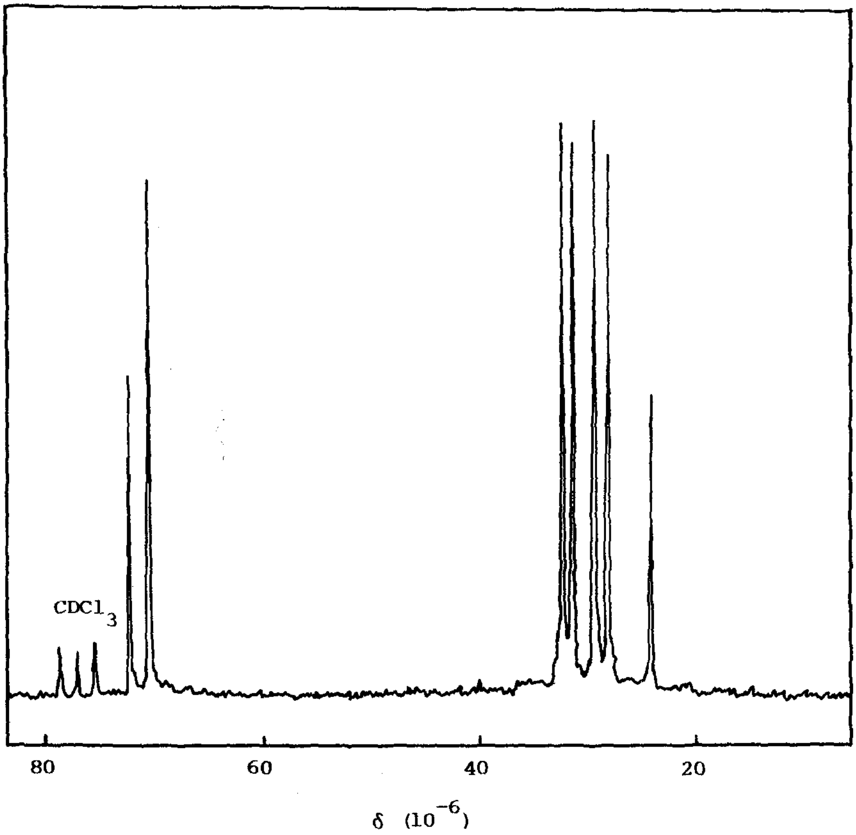

Figure 4 : ^{13}C NMR spectrum of A,2

The ^{13}C NMR spectrum (figure 4) exhibits 7 singlets assigned to the different carbon atoms of the dithiol A,2 (table 1).

The methylene groups located in the position α to the oxygen atom (70.37 and 72.21 10^{-6}) are shifted further towards high fields than are those in α position either to the thioether bridge (31.31 and 32.24 10^{-6}) or the end-groups. This peak appears at 24.02 10^{-6} which is characteristic of the thio group.

	HS CH$_2$	CH$_2$ O	CH$_2$	CH$_2$ S	CH$_2$	CH$_2$	CH$_2$	CH$_2$	CH$_2$
A,2 (Fig.4)	24.02	72.21	70.37	32.24	31.31	29.30	28.02	-	-
A,6	24.25	72.48	70.66	32.61	31.52	29.70	29.34	29.09	28.73

Table 1 : ^{13}C NMR characteristics of A,2 and A,6

A similar dropwise addition of 1,9-decadiene into the 2-mercaptoethyl ether produces the expected α, ω dithiol quantitatively A,6. Its ^{13}C NMR characteristics are also listed in table 1.

Conclusion

The synthesis of long chain monodispersed telechelic dithiols can be acheived by slow dropwise addition of a nonconjugated diene into an excess of α, ω dithiols with peroxidic initiation. This synthesis is very simple and quick and produced the expected telechelic dithiols selectively and quantitatively. Such new dithiols are interesting intermediates for the production of precursors of well-defined structured polymers.

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