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Synthesis of novel telechelic monodispersed nonconjugated dienes

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Summary

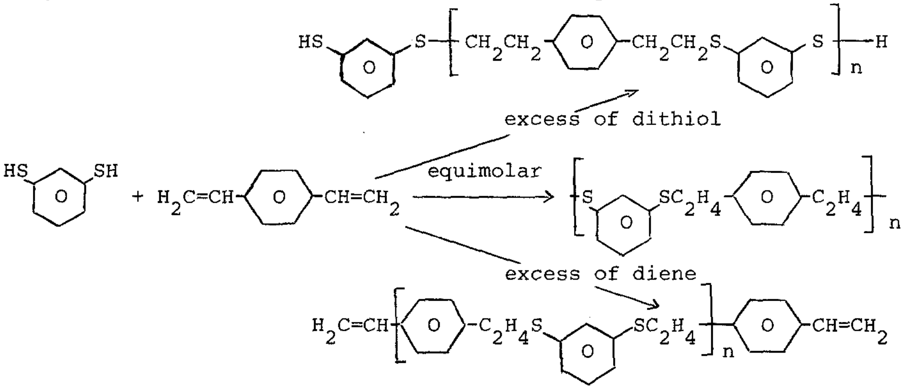
The synthesis of novel telechelic monodispersed nonconjugated dienes from commercially available α, ω- dithiols and dienes is presented. The batch reaction produced a polydispersed mixture separable with difficulty whereas a dropwise addition of dithiol onto an excess of α, ω-diene in the presence of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

Introduction

The importance of α, ω -unsaturated oligomers has been recently increased as evidenced by the wide range of applications claimed for them. For instance, these compounds are interesting precursors of diols (1-3) diesters (3,4) dialdehydes (5), diepoxides (5), disulfonates (6) or multibloc copolymers (7).

Numerous applications and patents have been published showing further novel speciality polymer applications (8,9) : coatings for optical fibers (10), silicon-containing polymers (11), crosslinked networks (12), photocrosslinkable products for thiol-ene systems (13) or polymers having water, fuel, solvent and temperature resistance (14).

Several investigations led to the introduction of unsaturations on both extremities of poly(methyl methacrylate) (15,16), poly(N-vinylpyridine) (17), poly(isobutylene) (18), poly(alkelene glycol) (19). Others produced α, ω-distyrenic derivatives (19,21). Furthermore, nonconjugated dienes can be prepared by metathesis (22), by coupling of allylic halogenides (23) or by direct reaction between an α, ω-dithiol and an α, ω-diene : strictly speaking, this latter process is a polyaddition (24) in which the end-groups and the molecular weights of the products are controlled by the stoichiometry of the reaction as in the following chemical scheme, (e.g. case of 1,3-benzenedithiol and 1,4-divinylbenzene (25)) :



Usually, such a system involves a reaction in which both components are aromatic (25-30), or in which the dithiol, itself, is either aliphatic (31,32) or aromatic (33).

This article presents an effective synthesis of novel telechelic monodispersed dienes obtained from aliphatic, commercially available dienes and dithiols.

Results and discussion

2-mercaptoethyl ether (or 1,9-nonanedithiol) was reacted with an excess of 1,5-hexadiene (or 1,9-decadiene, respectively) in the presence of peroxides, to give dienes representated by the following scheme :

$$\begin{array}{lcl} H_2C{=}CH{-}(CH_2)_x{-}CH{=}CH_2 & + & HS\ C_2H_4{-}R{-}C_2H_4SH \\ x = 2 \text{ or } 6 & & R = \text{oxygen or } (CH_2)_5 \\ \text{(excess)} & \Big\downarrow \text{radical} & \end{array}$$

$$H_2C{=}CH{-}(CH_2)_{x+2}SC_2H_4{-}R{-}C_2H_4S(CH_2)_{x+2}CH{=}CH_2 \qquad \text{DTD}$$

	R	x
1	O	2
2	$(CH_2)_5$	6

Two reactions were thus performed, and we detail them below.

1) **Addition of 2-mercaptoethyl ether onto 1,5-hexadiene**

a) Batch reaction

The following initial molar ratios (R_o) were chosen : R_o = [diene]/[dithiol] = 0.50 ; 0.33 and 0.25. After 3 hours of reaction, we noted that the GPC chromatogram (Figure 1) of the reaction medium exhibited a polydispersed behaviour.

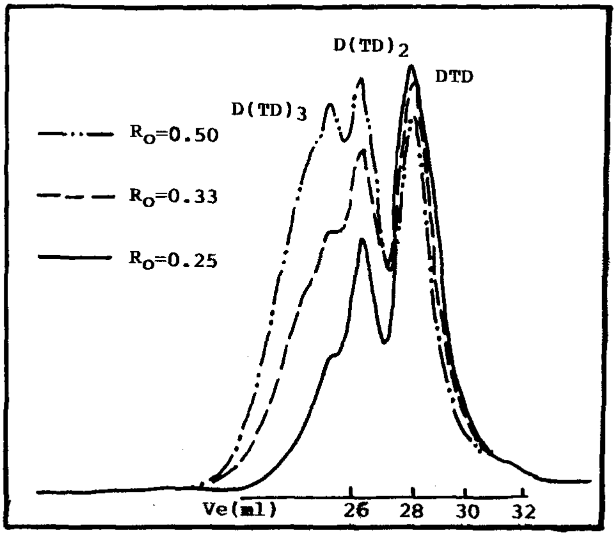


Figure 1 : GPC chromatogram of the product of the addition of 2-mercaptoethyl ether (T) onto 1,5-hexadiene (D) in excess (batch-reaction).

As expected it is observed that the higher the R_o, the higher the molecular weight of the telomers obtained. In respective of the value of R_o, the medium is composed of a mixture of several dienes which is schematically represented by $D(TD)_n$ with n = 1,2,3 and 4. This mixture can only be separated with difficulty using conventional methods. Consequently such a method is not effective for obtaining monodispersed telechelic dienes selectively.

b) By dropwise addition of dithiol onto the diene

As we previously described (32), this method exploits a slow dropwise addition of the 2-mercaptoethyl ether into a large amount of 1,5-hexadiene which contains the peroxidic initiator diluted in acetonitrile. Forty minutes after the total addition of the dithiol and evaporation of the volatile reactants, the GPC chromatogram of the medium (Figure 2) exhibits only one peak. This peak corresponds to a product having a molecular weight greater than those of the reactants. The yield is quantitative.

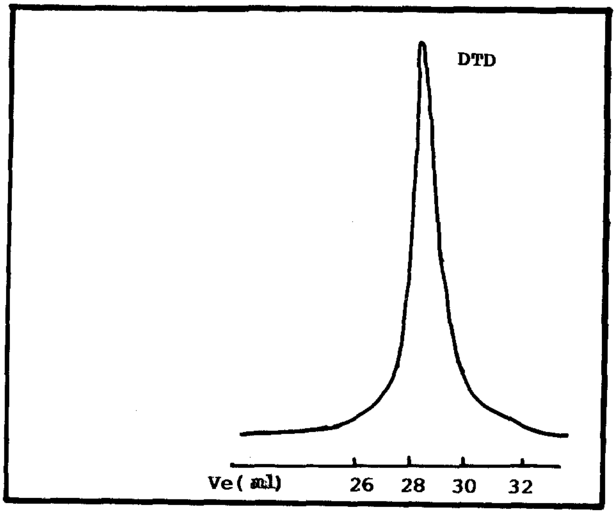


Figure 2 : GPC chromatogram of the product obtained 40 minutes after complete dropwise addition of 2-mercaptoethyl ether onto 1,5-hexadiene.

The ^{13}C-NMR spectrum (Figure 3) of the obtained monodispersed α , ω-diene exhibits 8 peaks assigned to the 8 different carbon atoms of 1 and the assignments are detailed in table 1. The absence of any signal in the $24\text{-}25x10^{-6}$ zone is evidence of the absence of the CH_2-SH group. The allylic methylene group is shifted toward low fields ($\delta = 32.5x10^{-6}$) about the CH_2 adjacent to the sulfur atom ($\delta = 31.6x10^{-6}$) because the double bond is more electronegative. For the same reason, the peaks at 28.1 and 29.0 10^{-6} are assigned to the methylene groups located in β and in γ positions about the S heteroatom, respectively.

Table 1 : Chemical shifts δ of the dienes 1 and 2 in ^{13}C-NMR.

	$[H_2C$ =	CH -	CH_2 -	CH_2 -	CH_2 -	CH_2 - S -	CH_2 -	$CH_2]_2$ O
1 (10^{-6})	114.9	138.5	31.5	28.5	28.9	32.6	33.2	70.4
	$[H_2C$ =	CH -	CH_2 -	$(CH_2)_6$ -	CH_2 - S -	CH_2 -	$(CH_2)_3]_2$	CH_2
2 (10^{-6})	114.9	139.6	30.3	28-30	33.4	32.5	28-30	28-30

The ^1H-NMR characteristics of the obtained dienes are shown in Table 2.

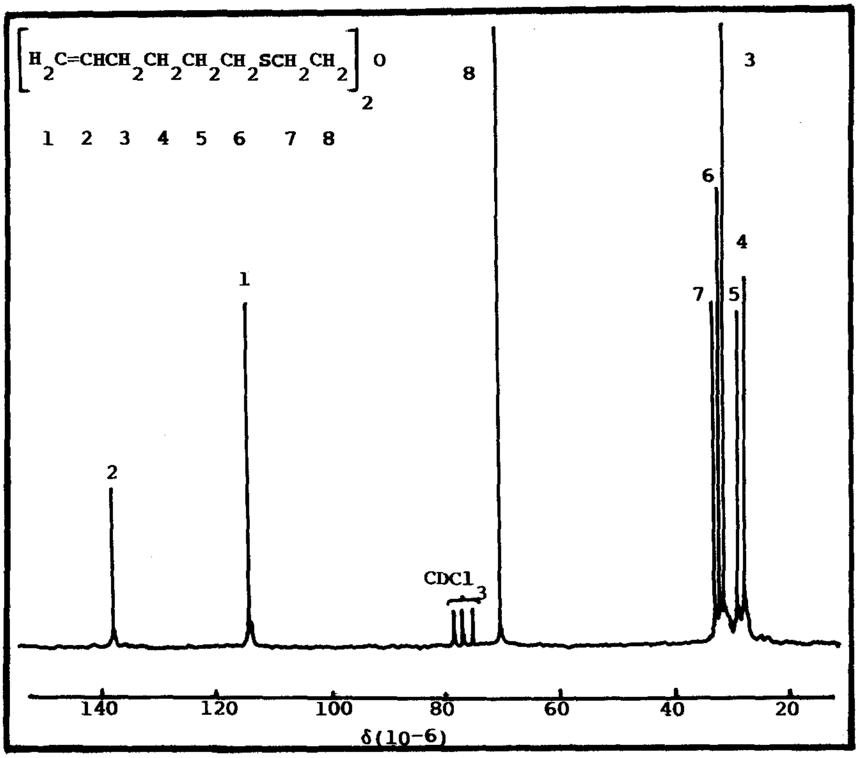


Figure 3 : ^{13}C-NMR spectrum of $H_2C{=}CH-(CH_2)_4S(CH_2)_2O(CH_2)_2S(CH_2)_4CH{=}CH$

Table 2 : Chemical shifts δ of the dienes 1 and 2 in ^{1}H-NMR

1	$[H_2C =$	$CH -$	$CH_2 -$	$CH_2 -$	$CH_2 -$	$CH_2S -$	$CH_2 -$	$CH_2]_2\ O$	
	4.90	5.80	2.10	1.10-1.40	1.40-1.70	2.55	2.75	3.60	
(10^{-6})	(t)	(m)	(m)	(m)	(m)	(t)	(t)	(t)	
2	$[H_2C =$	$CH -$	$CH_2 -$	$(CH_2)_5 -$	$CH_2 -$	$CH_2 -$	SCH_2	CH_2-	$(CH_2)_2]_2CH_2$
	4.90	5.80	2.05	1.10-1.40	1.50-1.80	2.50	2.50	1.50-1.80	1.10-1.40
(10^{-6})	(t)	(m)	(q)	(m)	(m)	(t)	(t)	(m)	(m)

We note the ethylenic protons $H_2C{=}CH-$ appear at 4.9 and 5.8×10^{-6}, respectively ; whereas the allylic methylene $\underline{CH_2}-CH{=}CH_2$ gives a multiplet at 2.1×10^{-6}. Furthermore, the absence of a signal at 1.55×10^{-6} is evidence that the dithiol has reacted completely.

In compound 2, the triplet at 2.50x10^{-6} is assigned to the methylene groups adjacent to sulfur. In compound 1, where the two methylene groups in the β position are in different environments, the methylene groups appear at 2.55 and 2.75x10^{-6}.

2) Synthesis of a nonconjugated diene from the bismonoaddition of 1,9-decadiene onto 1,9-nonanedithiol

A similar dropwise addition of 1,9-nonanedithiol into the 1,9-decadiene produced the expected α,ω-nonconjugated diene 2 quantitatively. Its ^{13}C and ^{1}H NMR (Figure 4) characteristics are also listed in table 1 and 2, respectively.

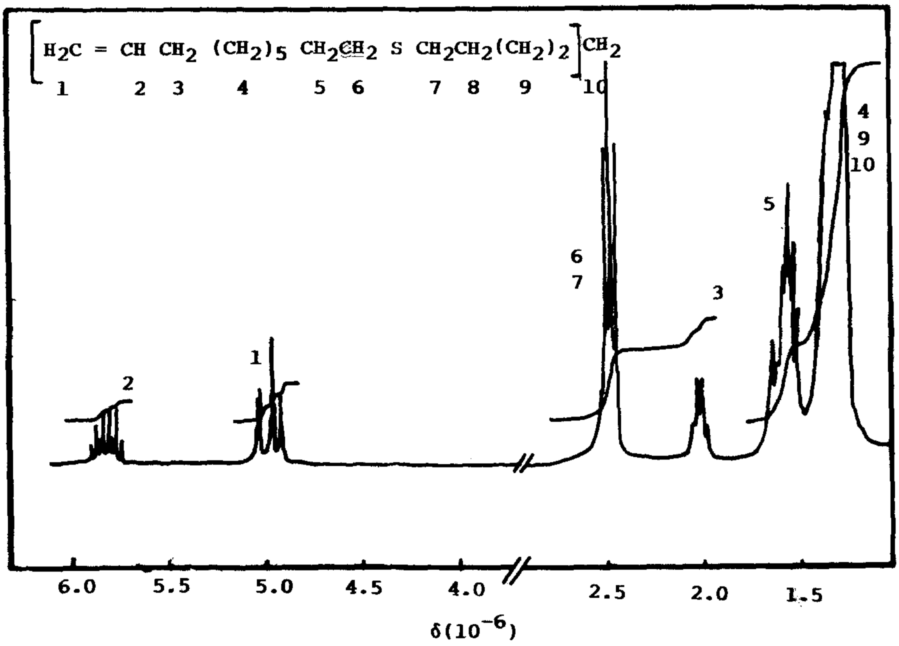


Figure 4 : ^{1}H-NMR spectrum of the diene 2

Conclusion

The synthesis of novel telechelic dienes can be acheived by slow dropwise addition of a commercially available dithiol into an excess of commercially available α,ω-diene with peroxidic initiation. This synthesis is simple, fast and produced the expected nonconjugated dienes selectively and quantitatively. Such new dienes are interesting intermediates for the production of precursors of well-defined structured polymers.

Acknowledgements

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