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Synthesis of Polytetrahydrofurane Macromers by Cationic Deactivation

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A new method to synthesize polytetrahydrofurane macromers is described. The cationic "living" polymerization of oxolane is stopped at a given stage by addition of an effective unsaturated nucleophile. It was established, by means of accurate characterization techniques, that the macromers obtained exhibit the structure, molecular weights and polydispersity expected.

Ionic "living" polymerizations are well suited for the synthesis of macromers (1). Such processes allow an adequate control of molecular weight and provide for narrow molecular weight distribution. The end-standing unsaturation can be introduced either upon initiation or upon deactivation of the "living" sites.

In a recent paper (2) we have described a method to synthesize polytetrahydrofurane macromers by means of an efficient unsaturated cationic initiator: methacrylylhexafluoroantimonate.

We are presenting here results obtained with the alternate method: The polymerization of oxolane (THF) is initiated; once the chains have reached the average length that is desired, an efficient unsaturated nucleophile is added, whereupon deactivation occurs, and terminal double bonds are introduced. A method similar to ours has been published recently by Asami et al. (3). A detailed characterization was performed on the samples obtained to establish whether the samples exhibit the structure expected.

EXPERIMENTAL PART

All reagents and solvents are carefully purified according to classical procedures (4).

The experiments are carried out in reactors fitted with efficient stirring, temperature control, and dropping funnels, under a slight argon overpressure.

Initiator : Propionylhexafluoroantimonate was chosen as initiator. It is made in situ by reacting stoichiometric amounts of propionylchloride and silver hexafluoroantimonate, in THF solution. AgCl precipitates and polymerization starts at once.

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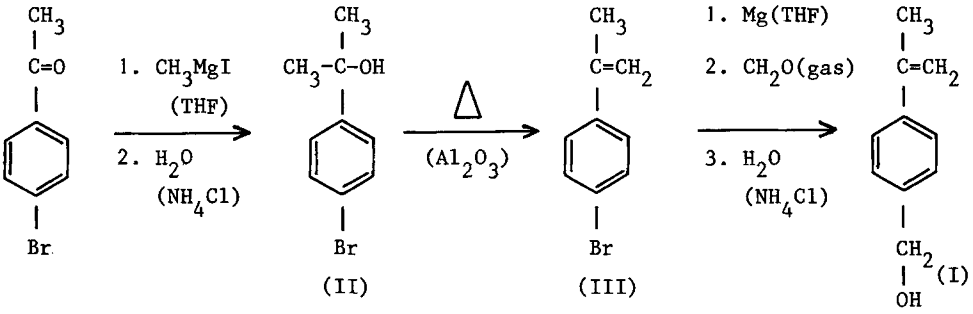
Deactivating agent : p.isopropenylbenzylalcohol, a compound only briefly mentioned before (5,6) was synthesized in the laboratory by a pathway that involves three steps:



No major difficulty impeded this synthesis. Dehydratation of the tertiary alcohol (II) occurs quantitatively upon heating to 250°C over alumina in an oven. The Grignard derivative of (III) is formed easily in THF solution, and gazeous formaldehyde (originating from the thermal decomposition of polyoxymethylene) is bubbled through the solution. The hydrolysis is performed at room temperature by means of an aqueous NH_4Cl solution. The raw product is distilled under vacuum (Bp : 92°C/0.2 mm Hg) and it is recrystallized from heptane. Melting point is 36.4°C. The overall yield is of the order of 60%. No impurities could be detected by GLC, nor by VPC. The ^1H-NMR spectrum exhibits peaks at :

6.8 - 7.2 ppm : aromatic protons
4.8 and
5.1 ppm : protons on double bonded carbon
4.2 ppm .... : methylene protons
4.0 ppm .... : hydroxyl proton
1.9 ppm .... : methyl protons

The potassium alkoxide of (I) was made by slowly adding a diphenylmethylpotassium solution in THF to a solution of (I) in the same solvent. The reaction is carried out under inert atmosphere. Once the alcohol is converted into alcoxide the solution turns slightly red and the addition of $\emptyset_2$CHK is stopped. Efficient stirring is advisable as the potassium alcoxide is insoluble. However it is not really necessary for the present purpose to have the reaction go to completion. A mixture of alcohol and alcoxide will do, just as well, and thus the heterogeneity of the reaction medium can be avoided.

EXPERIMENTAL PROCEDURE

The polymerization of THF is carried out in the bulk, at 0°C. At this temperature the rate constant of propagation is 3×10^{-3} $l.mol^{-1}.sec^{-1}$ (7) and the chains of poly-THF need 5-20 minutes to reach the average molecular weights in the range required. The growth is then stopped by addition of the THF solution (or suspension) of the potassium alcoxide. This reaction is exothermic; nevertheless in order to achieve rapid and quantitative deactivation, an excess of about 10% of potassium alcoxide was used.

Thereafter the precipitate (AgCl and $KSbF_6$) is filtered off. In some cases a centrifugation is necessary to separate quantitatively the insoluble salts. The solution is concentrated in a Rotavapor, and subsequently poured into a large excess of cold methanol (-30°C). The macromer precipitates out. Low temperature filtration is not easy. The macromer obtained is dissolved in benzene and freeze-dried.

CHARACTERIZATION OF THE MACROMERS FORMED

Various characterization techniques were used to establish whether the structure of the macromer conforms with that expected.

- Light scattering and vapor pressure osmometry yield the true $\bar{M}_w$ and $\bar{M}_n$ values, respectively.
- Gel permeation chromatography was used to evaluate the polydispersities. Some GPC experiments were run with both refractometric and UV detection, to establish whether the isopropenylphenyl chromophore is attached to the polymer chain (Fig. 1).

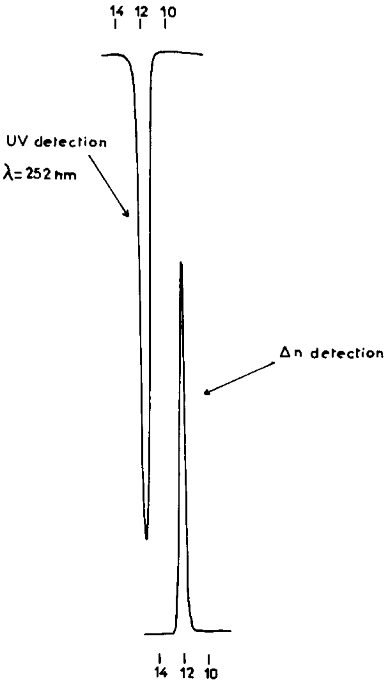


Fig. 1 : GPC diagram of a poly-THF macromer

- Proton NMR can be used for molecular weight determination provided the chains are short enough. The 4 aromatic protons originating from the deactivator appear at 7.2 ppm. The poly-THF chain exhibits two separate peaks located at 3.4 ppm (H_α protons) and 1.5 ppm (H_β protons). Fig. 2 shows a typical spectrum.

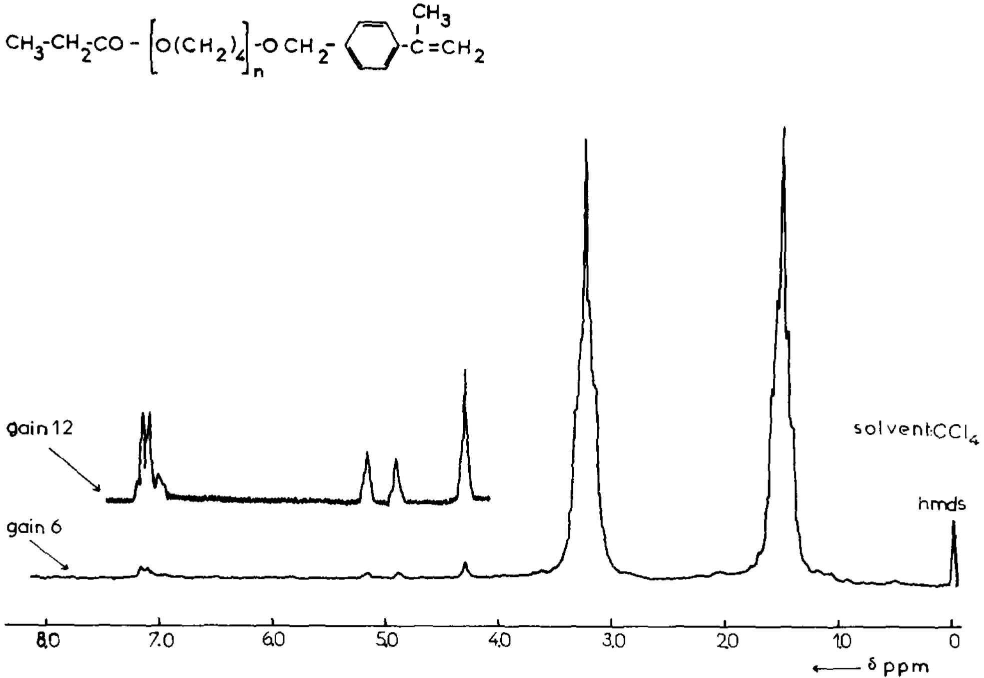


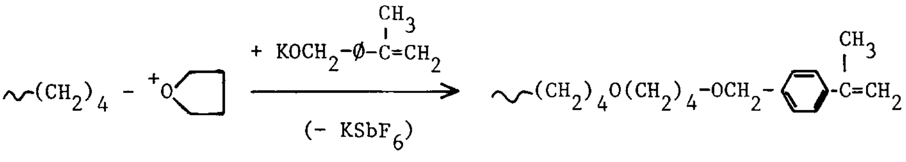
Fig. 2 : ^{1}H-NMR spectrum of a poly-THF macromer

- UV spectroscopy was used to characterize the isopropenylphenyl groups at chain end. This group absorbs at 252 nm and the absorptivity ε was determined from measurements on p(ethoxymethyl) isopropenylbenzene, specially synthesized for that purpose. ε was found to be 12 700 $l.mol^{-1}.cm^{-1}$. Using this value the molecular weights of the macromers can be evaluated from measurements of the optical density at 252 nm.
- Double bond titrations were performed by the mercury acetate method (8), and they also yield number average molecular weights, assuming one double bond per molecule.

DISCUSSION OF THE RESULTS

It has been established (9) that oxocarbenium ions are efficient initiators for the cationic polymerization of THF. Initiation is fast and quantitative and it proceeds by addition onto the monomer. Propionylhexafluoroantimonate was chosen rather than the benzoyl salt, because the latter would have introduced one additional benzene ring into the macromer molecule.

The reaction of an unsaturated alcoxide with the oxonium site of "living" poly-THF was chosen as the deactivation process. Alcoxides are good nucleophiles, and should react fast and quantitaticely.



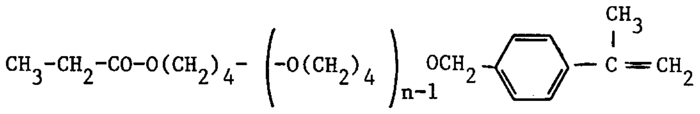
The molecular weight distribution of the macromers is rather sharp, the polydispersity index is of the order of 1.15 .

The experimental data are gathered in Table 1.

[I] (Mol/1)	$t^{a)}$ (min)	THF conv. (%)	$\bar{M}_w$ (LS)	$\bar{M}_n$ $\rangle=\langle$	$\bar{M}_n$ (UV)	$\bar{M}_n$ (NMR)
$3 . 10^{-2}$	17	-	-	$2300^{b)}$	2300	2200
$5 . 10^{-2}$	14	17	4500	4400	3900	-
$1.5.10^{-2}$	28	14	8000	8000	7100	-
$5 . 10^{-2}$	11.5	15	4200	3700	3200	-

a) reaction time
b) by vapor pressure osmometry

The characterization results are consistent with the structure expected for the macromers. Each molecule contains one phenyl ring and one double bond arising from the alcoholate used as nucleophilic deactivator. The satisfactory fit between the molecular weights obtained by light scattering, and those calculated from the proportion of aromatic protons (by NMR), from the optical density at 252 nm, and from the double bond content are in satisfactory agreement. The ester function originating from the initiation reaction can also be detected(though we did it only qualitatively) by its IR absorption near 1730 cm^{-1}. These results strongly support the structure expected for the macromer:



These macromers are sensitive to the attack by radicals andthey can undergo copolymerization with other monomers.

CONCLUSION

Ionic polymerization methods are versatile techniques for the synthesis of macromers, of known molecular weight, of low polydispersity, and of well established structure. The unsaturation can be introduced quantitatively upon deactivation of the "living" sites. These conclusions meet with those of Asami (3), and can be considered as an extension of our previous results on the anionic synthesis of polyoxyethylene macromers (10).

REFERENCES

1) P.REMPP, P. MASSON, J. SIERRA-VARGAS, E. FRANTA
Plaste und Kautschuk 28, 365 (1981)

2) J. SIERRA-VARGAS, J.G. ZILLIOX, P. REMPP, E. FRANTA
Polym.Bull. 3, 83 (1980)

3) R. ASAMI, M. TAKAKI, K. KITA, E. ASAKURA
Polym.Bull. 2, 713 (1980)

4) F. AFSHAR-TAROMI, M. SCHEER, P. REMPP, E. FRANTA
Makromol.Chem. 179, 849 (1978)

5) L. TOMASZEWSKA, W. ZACHAREWIEZ
Roczniki Chem. 35, 1597 (1961)

6) I.I. BARDYSHEV, V.S. SHAVYRIN, V.V. BUDYLINA
Khim.Prom. 21, 25 (1971)
Chem.Abst. 80 70973 V (1974)

7) M. SCHEER, E. FRANTA
Unpublished Results

8) J.B. JOHNSON, J.P. FLETCHER
Analyt. Chem. 31, 1563 (1959)

9) E. FRANTA, L. REIBEL, L. LEHMANN, S. PENCZEK
J.Polym.Sci. (Polym.Symp.) 56, 139 (1976)

10) P. MASSON, G. BEINERT, E. FRANTA, P. REMPP
Polym.Bull. 7, 17 (1982)

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