Cationic Synthesis of Macromers

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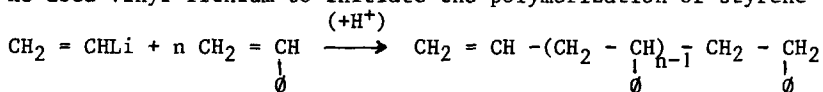
SUMMARY

Unsaturated oxocarbenium salts were used to initiate the polymerization of THF. The macromers obtained were characterized carefully, and it was found that these species are well defined, of narrow molecular weight distribution, and fitted quantitatively with end standing polymerizable double bonds.

INTRODUCTION

Macromers are short polymer molecules carrying an end-standing unsaturation, that is polymerizable in turn. Copolymerization of a vinylic (or acrylic) monomer with a macromer should result in a graft copolymer, the macromer units constituting the grafts.

Until recently little interest has been paid to the synthesis of macromers, to their properties and to their potential applications as intermediates for an easy synthesis of graft copolymers. Though macromers were mentioned in recent reviews (1,2), most of the work that has been done along this line was carried out in industrial laboratories and published in the patent literature.

To our knowledge, WAAK (3,4) was the first to prepare macromers. He used vinyl lithium to initiate the polymerization of styrene

$$CH_2 = CHLi + n\ CH_2 = CH \xrightarrow{(+H^+)} CH_2 = CH -(CH_2 - CH)_{\overline{n-1}}\ CH_2 - CH_2$$
$$\qquad\qquad\qquad\quad \phi \qquad\qquad\qquad\qquad\qquad \phi \qquad\qquad \phi$$

However the initiation rate is low and the molecular weights obtained are far above the expected ones. Incidently, the same ω-allyl polystyrene can be obtained more easily by reacting a "living" anionic polystyrene with allyl bromide (5).

MILKOVICH (2,6,7) has generalized the synthesis of macromers, by fitting various anionically obtained vinyl polymers with unsaturated functions at chain end, either upon initiation or upon deactivation.

Attempts were also made (8) to obtain macromers by means of radical polymerization using a functional initiator, and subsequent chemical reactions to provide for the endstanding double bond. Cationic methods were used by WATANABE (9), who polymerized alkylene oxides in the presence of hydroxyethylmethacrylate, by means of a

Lewis acid. Similar work was performed recently by KENNEDY (10) on isobutene, that was polymerized in the presence of chloromethyl-styrene to yield polyisobutene macromers. All these macromers co-polymerized readily with various vinyl monomers.

In the present paper we shall describe the cationic synthesis of polytetrahydrofurane macromers. The systems we have used enable to choose the molecular weights of the macromers, and the samples obtained have been submitted to a detailed characterization to ascertain their structure.

PRINCIPLE OF THE METHOD USED

Ionic "living" polymerizations - characterized by the absence of spontaneous transfer or termination reactions - are well suited for the synthesis of macromers of known molecular weight and of low polydispersity. Provided the initiator used is efficient the number of active sites (i.e. of growing chains) remains constant throughout the process. Two different routes can be employed to fit the macromolecules with a terminal double bond :

- either, use is made of an initiator bearing an unsaturation. Attention must be paid to avoid side reactions involving this double bond during the growth of the macromer ;
- or, the unsaturation is introduced upon deactivation of the "living" sites, by means of an unsaturated electrophile, if the polymerization proceeds anionically, or by means of an unsaturated nucleophile, if a cationic process has been chosen.

Oxolane is known to polymerize cationically to "living"polymers(11). The propagation reaction is reversible, and at each temperature corresponds an equilibrium monomer concentration $|M|_e$. The monomer consumption follows a first order law :

$$- \frac{dM}{dt} = k_p \ |M^+| \ |M| \ - k_d \ |M^+|$$

Here k_p is the propagation rate constant, $|M^+|$ is the concentration of growing sites and $|M|$ is the monomer concentration. The equilibrium monomer concentration is given by
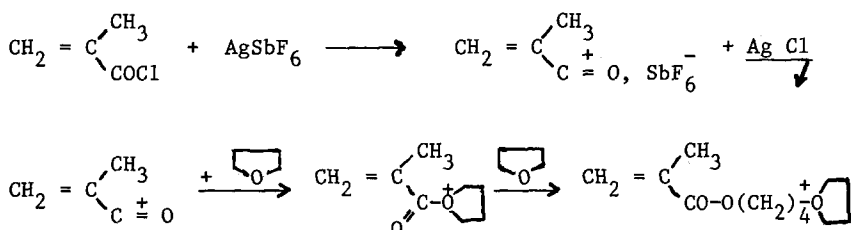
$$|M|_e \ = \ k_d \ / \ k_p$$

If the initiation reaction is rapid and quantitative the value of $|M^+|$ is constant, and equal to the initiator concentration, whereby the integration of equation (1) yields the following expression

$$\log \left[\frac{|M|_o - |M|_e}{|M| - |M|_e} \right] \ = \ k_p \ |M^+| \ t$$

where $|M|_o$ is the initial monomer concentration.

FRANTA (12,13) showed recently that oxocarbenium salts are efficient initiators for the cationic polymerization of THF. They can be made readily, in situ, by reacting silver hexafluoroantimonate onto an acid chloride. They react fast, and by addition onto THF.

A reaction path that seemed appropriate for the synthesis of poly-THF macromers was to use methacrylyl hexafluoroantimonate as the unsaturated initiator. It can be formed easily and it initiates the THF polymerization according to :

$$CH_2 = C \overset{CH_3}{\underset{COCl}{}} + AgSbF_6 \longrightarrow CH_2 = C \overset{CH_3}{\underset{C = O, \; SbF_6^-}{\overset{+}{}}} + \underline{Ag \; Cl} \downarrow$$

$$CH_2 = C \overset{CH_3}{\underset{C \overset{+}{=} O}{}} + \overset{\frown}{O} \longrightarrow CH_2 = C \overset{CH_3}{\underset{O \diagdown C - \overset{+}{O}}{}} \overset{\frown}{O} \longrightarrow CH_2 = C \overset{CH_3}{\underset{CO-O(CH_2)_4 \overset{+}{\overline{}} O}{}}$$

The presence of ester functions in the polymer - once isolated and purified - is a good evidence that initiation occurs by addition onto the monomer.

The methacrylic double bond is insensitive to attack by cationic initiators, and it should remain untouched.

A kinetic investigation of the polymerization of THF with metha-crylyl hexafluoroantimonate as initiator was necessary to establish whether initiation is fast and quantitative. This condition is re-quired for an adequate control of the molecular weight of the macromers.
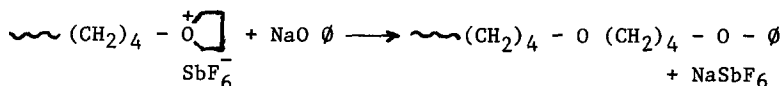
SYNTHESIS OF MACROMERS

The experiments were carried out under inert atmosphere. Pure THF was introduced first, then stoichiometric amounts of methacrylyl chloride and of $AgSbF_6$ (in THF solution) were added under efficient stirring, at a well controled temperature. After a given time (1 to 3 minutes) deactivation was performed by addition of sodium phe-nate. The macromer was recovered after centrifugation and evapora-tion of some of the solvent, by precipitation in methanol at-30°C.

CHARACTERIZATION OF THE MACROMERS

A detailed characterization of the macromers obtained was carried out in order to establish whether the structure of the molecules formed conforms with that expected. The following techniques were used for that purpose :

1- Gel permeation chromatography is meant to determine the polydis-persity of the samples, rather than to get the absolute values of the molecular weights.
2- UV Spectroscopy can be used as a convenient method to measure number average molecular weights, when deactivation of the "li-ving" oxonium ions is performed by SAEGUSA's method (14), i.e. addition of sodium phenoxide.

$$\sim\!\!\sim\!\!\sim (CH_2)_4 - \overset{+}{O} \underset{SbF_6^-}{} + NaO \; \emptyset \longrightarrow \sim\!\!\sim\!\!\sim (CH_2)_4 - O \; (CH_2)_4 - O - \emptyset$$
$$+ \; NaSbF_6$$

The end-standing phenoxy group exhibits a strong absorption at 272 nm. Knowing the extinction coefficient and assuming each molecules contains <u>one</u> phenoxy group, the value of M_n results.

The UV detection of the methacrylic ester function sitting at the other end of the molecule is not possible, as the corresponding absorption is located around 200 nm.

3- Infrared spectroscopy. The $C = C$ and the $C = O$ double bonds of the methacrylic ester moiety absorb at 1640 and 1730 cm^{-1}, respectively, and these absorptions were shown to obey BEER's law. Butylmethacrylate was used to get the values of the extinction coefficients :

$$\varepsilon_{1730}^{C=O} = 702 \ cm^{-1} mol^{-1} l \quad ; \quad \varepsilon_{1640}^{C=C} = 75 \ cm^{-1} mol^{-1} l$$

The concentrations should thus be above 0.14 mol l^{-1} to get an acceptable accuracy ; this implies that molecular weights higher than 3000 cannot be measured by this method.

4- Proton NMR. The number average molecular weights of the samples deactivated by sodium phenoxide can be determined from the ratio of the peak areas of the aromatic protons (~ 7 ppm) and of the methylene protons of the poly THF chain (1.5 ppm for H_β and 3.3 ppm for H_α) (fig.1). In addition, it is possible to detect the methacrylic protons ($\underline{H}_2C=$) by NMR, but for good accuracy a calibration is necessary. Again butylmethacrylate was used for that purpose.

5- Vapor pressor osmometry is an efficient method of determination of number average molecular weights, provided the calibration substance is extremely pure, and its molecular weight is as close as possible to that studied. The results are accurate in the 1000 to 5000 range of M_n.

6- Functional analysis. The methacrylic double bonds were determined iodometrically, using WIJS'method.

<u>DISCUSSION OF THE RESULTS</u>

1) Kinetic investigation of the initiator efficiency
A first order plot showing the monomer consumption upon cationic polymerization initiated with methacrylyl hexafluoroantimonate is shown on fig 2. The experimental points are on a straight line that passes through the origin. It can be concluded that initiation is fast, and that the number of active sites remains constant. Knowing that the rate constant of propagation k_p is $30.10^{-3} \ l \ mol^{-1} s^{-1}$ at 25°C, the concentration of active sites $|M^+|$ can be calculated from the slope of the line. The value found ($4.5 \times 10^{-3} \ mol \ l^{-1}$) is very close to the actual initiator concentration (4.55×10^{-3}) used, thus demonstrating that the initiator efficiency is quantitative.

2) Macromer characterization
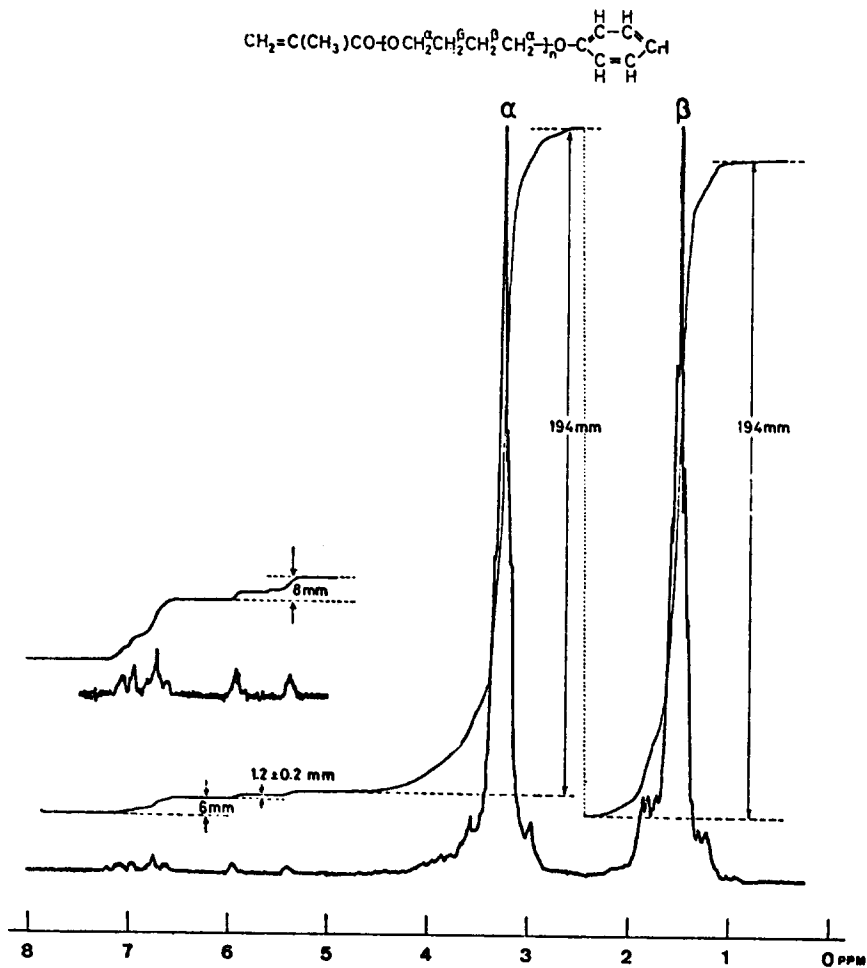The data obtained upon charaterization of the macromers are collected on table 1.

$$CH_2=C(CH_3)CO+OCH_2^{\alpha}CH_2^{\delta}CH_2^{\beta}CH_2^{\alpha}+_n O-C \begin{array}{c} H \quad H \\ C-C \\ C=C \\ H \quad H \end{array} CH$$

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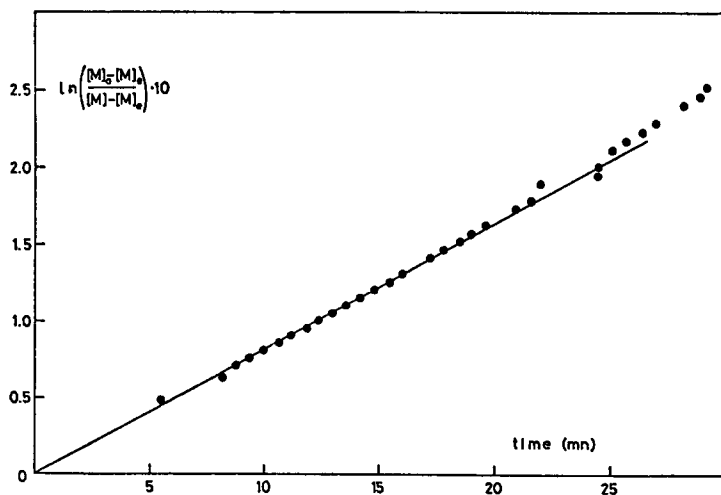

Fig. 2. Kinetics of THF polymerization with methacrylyl hexa-
fluoroantimonate as initiator

Table 1

Characterization Data of poly THF Macromers

	M_n th.	M_n UV	M_n IR	M_n RMN	M_n osm.	M_n Iodometry	M_w/M_n GPC
6.1		2800	2800	3000			1.2
6.2		3900	3360	3400			1.2
7.1		1900	1700	2100			1.2
M 1	1400	1550	2200	1650	1130	1500	1.2
M 3	2400	2600	2400	1800	2000	1850	1.2
M 2	2700	3000	2800	3000	2500	2600	1.2

It can be seen that the cationic synthesis of macromers fitted at chain end with a methacrylic ester function is possible. The molecular weights of the samples can be set at will, by choosing the reaction time, knowing the rate constant of propagation at the temperature used. The polydispersity is narrow, as it usually is for "living" polymers.

The interesting feature is the satisfactory agreement between the number average molecular weights obtained from UV spectroscopy, from IR spectroscopy, from NMR data, from vapor pressure osmometry and from double bond determinations as well as from kinetics. None of the methods is of high accuracy, but the agreement between the individual values proves that the molecules formed are fitted at one chain end with a methacrylic ester function. This result clearly demonstrates that initiation proceeds by addition onto the monomer. The other end of the macromer chain carries a phenoxide function, which is quite useful because of its UV absorption, that gives access to molecular weight. The macromers obtained can thus be represented by the formula

$$CH_2 = \overset{CH_3}{\underset{}{C}} - CO - O \, (CH_2)_4 - \left[O \, (CH_2)_4 \right]_{n-1} - O -\bigcirc$$
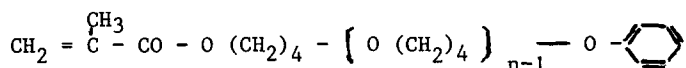
CONCLUSION

The cationic "living" polymerization techniques of oxolane (THF) can be used for the synthesis of well defined macromers, of low polydispersity and of known average molecular weight. The unsaturation can be introduced efficiently, upon initiation, by using an unsaturated oxocarbenium salt as initiator.

The copolymerization of such macromers with various vinyl monomers was investigated, and the resulting novel synthesis of graft copolymers will be described in another paper.

Instead of introducing the unsaturation upon initiation one can also do it upon deactivation of the "living" poly THF chains. An efficient initiator is used, and the polymerization is stopped, at a given time, by addition of an unsaturated nucleophile. Experi-

ments carried out along this line were successful, too. The re-
sults obtained will be published in the near future.

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