

polymer communications

Synthesis of narrow molecular weight distribution α,ω -hydroxy telechelic polyoxetane by the activated monomer mechanism

Hemant Desai*, Anthony V. Cunliffe and Malcolm J. Stewart

Defence Research Agency, Fort Halstead, Sevenoaks, Kent, TN14 7BP, UK

and Allan J. Amass

Department of Chemical Engineering and Applied Chemistry, University of Aston, The Triangle, Birmingham, B4 7ET, UK

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The cationic activated monomer mechanism has been used to prepare polyoxetane (poly(trimethylene oxide)) with low dispersities, hydroxy functional end groups and without significant oligomer contamination. Tetrafluoroboric acid and 1,4-butanediol were used as the catalyst system. The polymer has been characterized by n.m.r. and s.e.c.

(Keywords: cationic polymerization; activated monomer mechanism; α,ω -hydroxy telechelic; nuclear magnetic resonance)

Introduction

The polymerization of oxirane and substituted oxiranes, such as epichlorohydrin, by the activated monomer mechanism (AMM) has been well reported in the literature¹⁻³. As far as the authors are aware the preparation of polyoxetane (poly(trimethylene oxide)) by AMM has not been reported, even though oxirane (ethylene oxide) and oxetane have similar ring-strains⁴. The ring-strains for oxirane, oxetane and oxolane (tetrahydrofuran (THF)) are, respectively, 114, 107 and 23 kJ mol⁻¹. Hence, it seemed reasonable to expect that careful control of reaction conditions would yield a predominantly oligomer-free hydroxy telechelic polyoxetane. Here, we present an account of the synthesis of polyoxetane by AMM.

Experimental

The oxetane was obtained from Lancaster Synthesis. An 85% solution of tetrafluoroboric acid (HBF₄) in diethyl ether and 1,4-butanediol were purchased from Aldrich Chemical Co. All these chemicals were used as received but dichloromethane (Romil Chemical Co.) was distilled over CaH₂ before use. High purity nitrogen was used to provide an inert atmosphere over all the reactions carried out.

An oven-dried 100 cm³, two-necked jacketed vessel with a magnetic stirrer bar was cooled by passing nitrogen through it. The vessel was then connected to a Haake temperature controller and further cooled to 10°C. The flask was charged with 1,4-butanediol (0.0207 mol) and tetrafluoroboric acid (1.279 × 10⁻³ mol) by syringe, to give an overall [-OH]:[HBF₄] mol ratio of 32:1. The mixture was stirred for 15 min before a 35% solution of oxetane in CH₂Cl₂ (w/v) was pumped in at a rate of 0.069 cm³ min⁻¹ for 24 h. Therefore, a total of 35 g (0.60 mol) of oxetane was added to the vessel. A further 2 h of stirring was allowed before the reaction was

stopped by pouring the reaction mixture into 200 cm³ of 5% aqueous NaHCO₃ solution. The mixture was separated and the CH₂Cl₂ evaporated to leave a colourless viscous liquid. This was analysed by size exclusion chromatography (s.e.c.)—using a Waters System with four Polymer Laboratories 10 μm columns of 10⁵, 10⁴, 10³ and 10² Å arranged in series—and n.m.r.

¹H n.m.r. spectra at 300.13 MHz and ¹³C n.m.r. spectra at 75.46 MHz were recorded on a Bruker MSL-300 FT n.m.r. spectrometer at ambient temperature (~22°C). All samples were recorded as solutions in CDCl₃, with tetramethylsilane (TMS) as internal reference, at a concentration of about 3% for ¹H and 15% for ¹³C measurements. For the ¹H spectra, 16 scans were recorded with a delay between pulses of 5.0 s. For broadband decoupled ¹³C spectra, typically 5000 scans were accumulated, with a delay between pulses of 3.0 s. For semiquantitative runs, a gated decoupling pulse sequence was used to suppress the nuclear Overhauser enhancement, with a pulse delay of 5.0 s.

Results and discussion

Figure 1 shows the s.e.c. trace of the polymer obtained. Although a very small amount of oligomer is detected (<2%) it is much less than that usually observed for polymers prepared via the active chain-end (ACE) type mechanism. This, allied to the fact that the dispersity of the polymer is less than 1.2, suggests that the dominant mode of propagation is not through the ACE mechanism; although narrow dispersity polymers may be prepared by the ACE mechanism, card-ice/acetone temperatures are normally required and/or living systems. Moreover, the conditions used in this preparation are not suitable for ACE type propagation due to the large excess of hydroxyl concentration relative to the active cationic species, which hinders all monomer in ACE propagation.

The number average molecular weight (M_n) of the polymer is 1200 and the peak molecular weight (M_p) is 1300. However, the expected M_n is 1800, assuming that

* To whom correspondence should be addressed

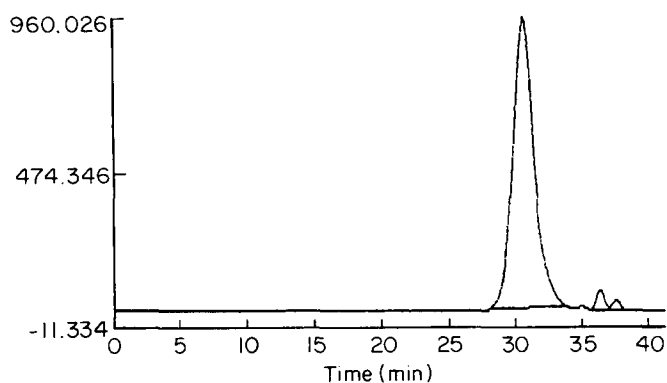


Figure 1 S.e.c. trace of a narrow molecular weight polyoxetane ($M_n=1200$, $M_p=1300$, $D=1.17$) using a refractive index detector

Peak retention time (min)	Area (%)	Height (%)
30.51	95.23	90.40
36.40	2.40	6.20
37.63	1.14	3.25

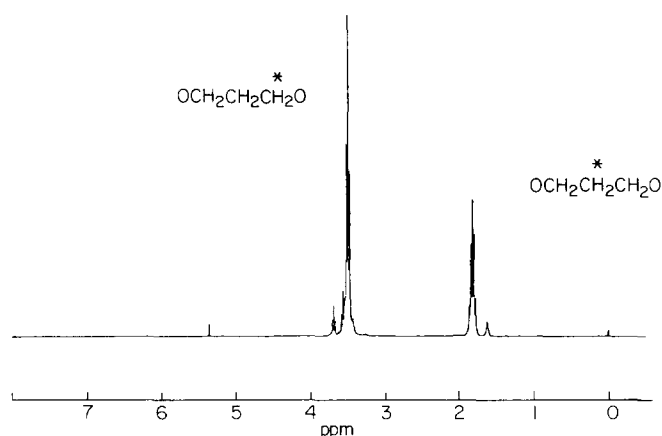


Figure 2 ^1H n.m.r. spectrum (300 MHz) of polyoxetane

all the monomer is incorporated into a polymer growing from the 1,4-butandiol. That is:

$$M_n = \frac{(\text{wt of monomer used})}{(\text{mol initiator})} + M_w \text{ of initiator} \quad (1)$$

This anomaly could be due to a number of factors: for example, the presence of hydroxy species in the reaction, particularly water, which is known to initiate AMM polymerization of oxiranes⁵; the evaporation of the monomer during the addition process; insufficient stirring time, which may result in the yield of polymer recovered being about 90%; and inaccuracies in the molecular weight measurements. Further work is in progress to investigate this effect.

N.m.r. spectroscopy was used to establish the overall structure of the polymer, the types of end group present and the way in which the 1,4-butandiol coinitiator was incorporated into the polymer chain. The latter two features are dependent on the polymerization mechanism and therefore provide useful information about this.

The polymer was identified as linear polyoxetane from its ^1H and ^{13}C n.m.r. spectra. The 300 MHz ^1H

spectrum (Figure 2) shows bands at 3.49 ppm (triplet), and 1.81 ppm (pentet), in the ratio 2:1, assigned to the $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$ and $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$ groups, respectively. The spectrum also shows peaks of equal intensity at 3.41 ppm and 1.61 ppm. These peaks, with the characteristic multiplet lineshape found in polyTHF, are assigned to $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ and $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ groups, respectively, arising from the 1,4-butandiol coinitiator fragments. The symmetry of the resonances indicates that they are present in symmetrical environments (i.e. $\text{C}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}$ rather than $\text{C}-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$). The observed shifts agree well with literature values for poly(oxetane-co-THF) copolymers⁶.

More structural details were obtained by ^{13}C n.m.r. spectra at 75.46 MHz (Figure 3). In order to understand the relationships of the end group resonances to the in-chain ones, and the expected positions of the resonances due to the 1,4-butandiol fragments, use is made of the additive nature of ^{13}C n.m.r. chemical shifts⁷. On the basis of simple additive parameters it is possible to calculate chemical shifts to an accuracy of about 1 ppm. This is often very useful in distinguishing between alternative assignments, particularly when comparing end groups with similar in-chain units. The fragments to be considered, together with their calculated chemical shifts⁷, are given in Table 1.

The main in-chain resonances are observed at 67.7 ppm (relative area 2) and 30.1 ppm (relative area 1), assigned to

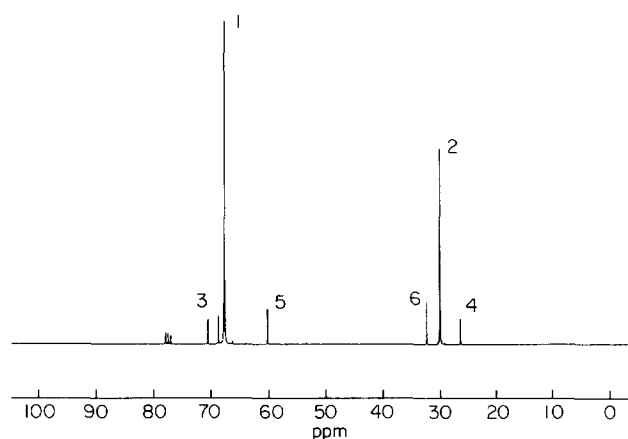
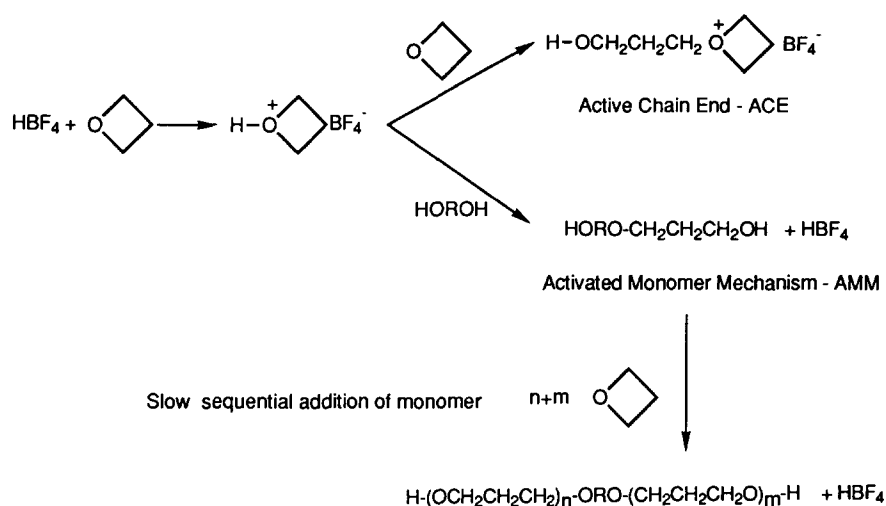


Figure 3 ^{13}C n.m.r. spectrum (75.46 MHz) of polyoxetane

Table 1 Calculated ^{13}C chemical shifts for in-chain and end group polymer structures. The shifts were calculated using the additive shift parameters given by Stothers⁷

Structure and ^{13}C shift (ppm from TMS)	Group
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}$ 2 1 31.2 66.9	I
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}$ 4 3 27.3 69.5	II
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 6 5 33.3 59.6	III
$-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ 8 7 29.8 62.2	IV



Scheme 1 Competing modes of propagation in cationic ring-opening polymerization of oxetane

Table 2 Comparison of calculated and observed ^{13}C chemical shifts for the various carbon atoms expected in the polyoxetane prepared with 1,4-butanediol cointiator

Carbon atom	Calculated shift (ppm from TMS)	Observed shift (ppm from TMS)
1	66.9	67.7
2	31.2	30.1
3	69.5	70.6
4	27.3	26.6
5	59.6	60.3
6	33.3	32.6
7	62.1	- ^a
8	29.8	- ^a

^a Not observed

the $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$ and $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$ groups, respectively, in good agreement with the calculated values (Table 2) and literature values⁶. In addition to the main peaks, the spectra also show a number of smaller peaks, at the level of about 7% of the main ones, which are assigned to end groups and 1,4-butanediol fragments. From the additive scheme, it is clear that the terminal CH_2OH resonances will occur to high field of the main resonances, at about 60 ppm. The spectra show only one peak in this region, at 60.3 ppm. This is close to the calculated value for the terminal CH_2OH group of an oxetane end group (structure III, Table 1). The calculations suggest that a tetramethylene oxide end group (structure IV) should have an appreciably different chemical shift (62.2 ppm), and we have observed this resonance at about 62.5 ppm in a number of polymers. We therefore conclude that the polymer contains only one type of end group, derived from oxetane (structure III), and that it does not contain end groups derived from 1,4-butanediol (structure IV). This assignment is confirmed by the resonance at the observation of a peak at 32.6 ppm, which is assigned, on the basis of the additive shift calculations, to the penultimate carbon atom in an oxetane end group, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}$. The fact that this is of equal intensity to the peak at 60.3 ppm is further evidence that there is only one type of CH_2OH end group. The carbon spectra do indicate the presence of fragments

derived from the 1,4-butanediol initiator, however, by the presence of peaks, of similar intensity to those associated with the end groups, at 26.6 ppm and 70.6 ppm. These are assigned to tetramethylene oxide units in a symmetrical in-chain environment, as in structure II.

There are, in principle, six types of polymer structure.

- Type 1: $\text{HO}-(\text{CH}_2)_3-\text{O}-[(\text{CH}_2)_3\text{O}]_m$
 $-(\text{CH}_2)_4-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_3-\text{OH}$
 Type 2: $\text{HO}-(\text{CH}_2)_3-\text{O}-[(\text{CH}_2)_3\text{O}]_m$
 $-(\text{CH}_2)_4-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_4-\text{OH}$
 Type 3: $\text{HO}-(\text{CH}_2)_4-\text{O}-[(\text{CH}_2)_3\text{O}]_m$
 $-(\text{CH}_2)_4-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_4-\text{OH}$
 Type 4: $\text{HO}-(\text{CH}_2)_3-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_3-\text{OH}$
 Type 5: $\text{HO}-(\text{CH}_2)_3-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_4-\text{OH}$
 Type 6: $\text{HO}-(\text{CH}_2)_4-\text{O}-[(\text{CH}_2)_3\text{O}]_n-(\text{CH}_2)_4-\text{OH}$

Type 4, which does not contain fragments derived from the 1,4-butanediol cointiator, could arise from the presence of small quantities of water in the system or competing ACE propagation, and is probably present in small proportions. Of the other structures, only type 1 is consistent with the observed ^{13}C n.m.r. spectra, since all the other structures contain tetramethylene oxide end groups. The results presented so far do not conclusively prove that the polymerization is proceeding via AMM because the activated monomer oxonium ion species has not been directly observed; the clear difference in end groups and cointiator incorporation between this polymerization and ones thought to proceed by the ACE mechanism are consistent with an activated monomer polymerization mechanism. Certainly, the s.e.c. and n.m.r. results show that the polymerization method employed in this work produces a polymer which is significantly different from one produced by a more conventional ACE polymerization.

From the relative areas of the end group and in-chain resonances, it is possible to estimate M_n for the polymer. While accurate quantitative ^{13}C measurements require careful consideration of relaxation times and experimental conditions, semiquantitative measurements were readily made using a gated decoupling pulse sequence to eliminate nuclear Overhauser enhancements, and a pulse delay of 5.0 s. From the relative areas of the CH_2OH carbons at 60.3 ppm and the in-chain OCH_2 carbons at

67.7 ppm, a value of M_n 1050 was estimated, in reasonable agreement with the value from s.e.c.

Conclusion

The s.e.c. and n.m.r. results seem to confirm that the oxetane is polymerized via AMM, very similar to the mechanism for oxiranes, rather than the ACE mechanism. This involves the steps shown in *Scheme 1*. The slow addition rate of the monomer minimizes the competing ACE mechanism and this in turn reduces the formation of cyclic oligomer because of the absence of charged cyclic oxonium ion species on growing chains.

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