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2-Furyloxirane: 1. Anionic and coordination homo- and copolymerization

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2-Furyloxirane (FO) was polymerized by various anionic and coordination initiators both in bulk and solution. The corresponding polyethers had relatively low DPns (up to about 100) and possessed relatively irregular structures arising from propagation reactions involving both $C\alpha$ and $C\beta$ oxirane ring opening, except when aluminium isopropoxide was used as catalyst. The glass transition temperature (T_g) of these polymers was always lower than room temperature and approached 15°C for the highest molecular weight. Propylene oxide did not copolymerize with FO, whereas butylene oxide gave copolymers, but the reactivity of FO remained much higher and the products were therefore rich in this comonomer unit. Copyright © 1996 Elsevier Science Ltd.

(Keywords: 2-furyloxirane; anionic polymerization; copolymerization)

INTRODUCTION

Our laboratory has a continuous interest in developing new macromolecular materials from natural renewable resources as an alternative to the petrochemical approach. In addition to its renewable character, biomass can give a large variety of furanic monomers by simple acid-catalysed conversion of saccharidic structures[1-3]. These monomers can then be polymerized and copolymerized to give materials with promising chemical and physical properties arising from the presence of the furanic heterocycle in different configurations, viz. within the polymer backbones and/or pendant to them[1-3].

2-Furyloxirane (FO) was synthesized only recently from furfural in high yields and through a relatively simple procedure[4]. This monomer displays an original behaviour compared with its homologues bearing aliphatic (e.g. propylene oxide, PO) and aromatic (e.g. styrene oxide, SO) substituents. The specificities of FO reactivity were encountered when studying its hydrogenation and hydrolysis[5]. In fact, the ring-opening mode of FO was in opposition to the corresponding SN_2 mechanism for aliphatic and aromatic oxiranes. Moreover, the hydrolysis of FO leads to the formation of oligomers suggesting that the diol formed in the first stage reacts with FO to form chain-extended products without the need of a catalyst[5]. It was also found that traces of water induce the homopolymerization of FO yielding the corresponding polyether with a DPn of about 50[5]. These unique features were exploited to synthesize block and graft copolymers from hydroxyl-bearing macromolecular precursors without the use of a catalyst[6], although transfer reactions limited the length of the polyFO branches.

The polymerizability of FO by free radical, cationic and anionic initiation was tested and the results briefly reported previously[7,8]. From that preliminary study it became clear that anionic systems were the most viable way to obtain interesting polymers. This paper describes an investigation of the anionic homo- and copolymerization of FO and of the structural features of the ensuing products.
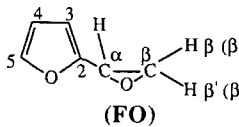
EXPERIMENTAL

Materials

FO was generously provided by our colleagues at the Laboratoire de Chimie des Agroressources of Toulouse National Polytechnic Institute who studied its synthesis[4]. It was purified by a fractional distillation at atmospheric pressure which provided a central fraction displaying a single g.l.c. peak. This pure sample was placed over calcium hydride and thoroughly degassed and stirred on a vacuum line for several days in order to eliminate all traces of moisture and air. It was thereafter stored on the line under its own vapour pressure at room temperature in the dark. Samples were withdrawn by vacuum distillation through a measuring burette into the reaction vessel. The physical properties and spectroscopic characteristics of pure FO are given in *Table 1* and *Figures 1–3*. The other reagents, namely propylene oxide (PO) and butylene oxide (BO) were purified likewise. The catalysts and solvents used in this investigation were commercial dry products of the highest purity available.

Reaction conditions

The homo- and copolymerizations of FO were carried out in sealed tubes after the introduction of a known amount of catalyst and vacuum distillation of the

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Table 1 FO characteristics

(FO)

Physical characteristics			
$M_w = 110.1$	$d = 1.14$	bp = 56°C/18 Torr	mp = −31°C

i.r. characteristic bands (cm^{-1}) (film)

Oxirane ring: 3063 and 2295 (ν_{CH,CH_2}); 1420 (δ_{CH}), 975 (ν_{CO}); 860 and 816 (γ_{CH}); 930 and 890 (γ_{CH}).
Furan ring: 3150 and 3120 (ν_{CH}); 1505 ($\nu_{C=C}$); 1475 and 1373 (δ_{CH}); 1160 (ν_{CO}); 1020 'ring breathing', 780 and 740 monosubstituted ring

^{1}H n.m.r. characteristics (300MHz, CD$_2$Cl$_2$, TMS)

δ (ppm)	Attribution	Multiplicity	Intensity	Coupling constant (J, Hz)
7.38	H-5	dd	1	$J_{5-3} = 0.74$
6.42	H-3	dd	1	$J_{5-4} = 1.83$
6.36	H-4	dd	1	$J_{3-4} = 3.29$
3.83	Hα	dd	1	$J_{\alpha-\beta} = 2.70$
3.18	Hβ	dd	1	$J_{\beta'-\alpha} = 1.83$
3.08	Hβ'	dd	1	$J_{\beta-\beta'} = 5.36$

^{13}C n.m.r. characteristics (300MHz, CD$_2$Cl$_2$, TMS)

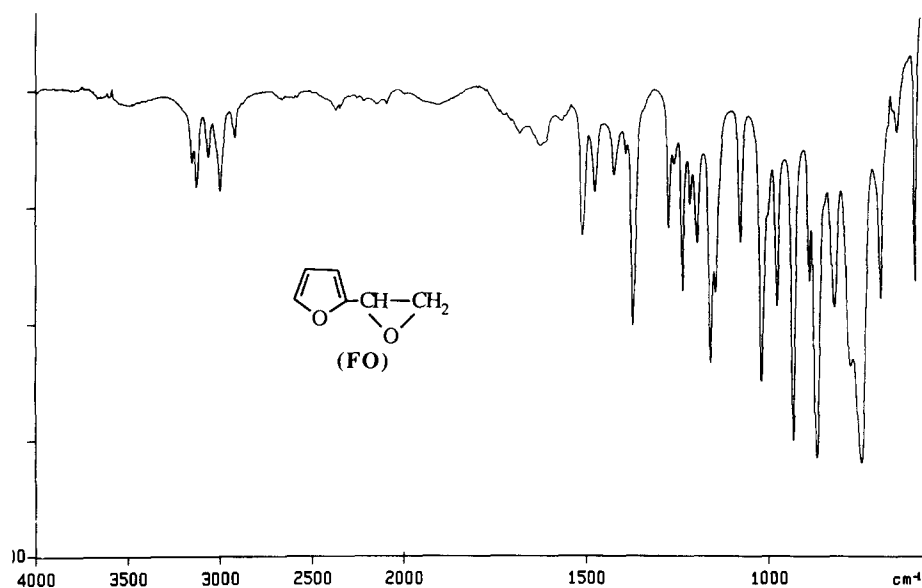| δ (ppm)	Attribution	δ (ppm)	Attribution	δ (ppm)	Attribution
151.2	C-2	109.9	C-4	47.8	Cα
111.1	C-3	143.2	C-5	46.3	Cβ

Figure 1 *FT* i.r. spectrum of FO

monomer(s), solvent (if any) and additives (if any). Reactions were stopped by neutralizing with an aqueous solution of acetic acid. The ensuing products were recovered by precipitation in an excess of hexane or by vacuum removal of the solvent and unreacted monomer(s), depending on their molecular weight.

Characterization

The various oligomers, polymers and copolymers obtained were characterized by ^{1}H, ^{13}C n.m.r. and

FT i.r. spectroscopy, size exclusion chromatography (s.e.c.), vapour pressure osmometry and differential scanning calorimetry (d.s.c.).

RESULTS AND DISCUSSION

Homopolymerization of FO

Bulk anionic polymerization. *Table 2* shows the conditions and the results related to bulk reactions with various

nucleophiles. Sodium carbonate failed to activate FO. With KOH and NaOH at room temperature, polymerizations were slow and gave DPns of about one half the expected value for a living system. Raising the temperature to 100°C produced a considerable acceleration, but
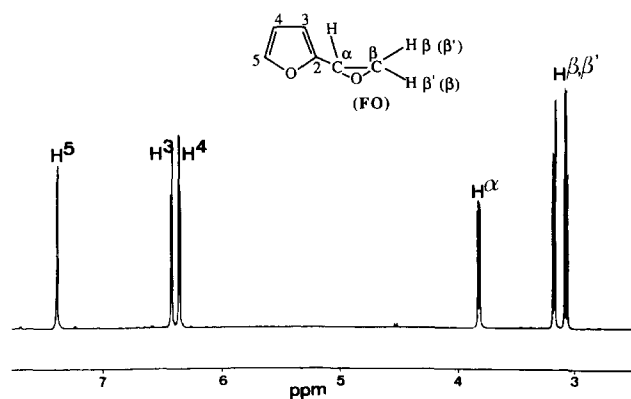

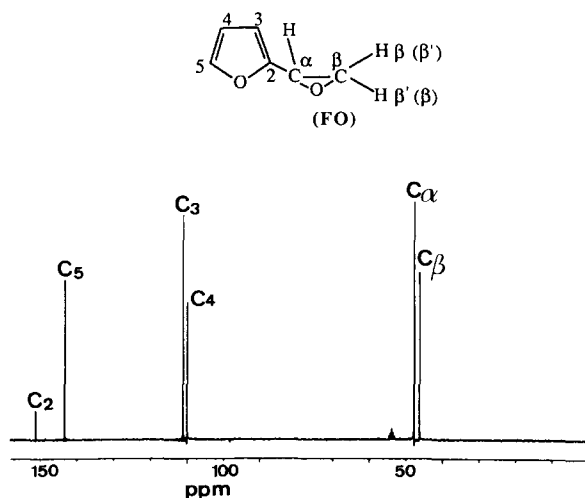**Figure 2** 300 MHz ^{1}H n.m.r. spectrum of FO

Figure 3 75 MHz ^{13}C n.m.r. spectrum of FO

to the detriment of the average chain length. The use of a saturated solution of KOH in MeOH as homogeneous initiator resulted in a drastic decrease in DPn, probably because of transfer reactions induced by the alcohol.

A more systematic study was conducted with tBuOK as initiator, as shown in *Table 2*. The DPn was sensitive to the monomer/initiator ratio, although again, transfer reactions obviously played a detrimental role because the increase in DPn with decreasing [FO]/[I] ratio was not linear and seemed to level off to a value of about 100, an obvious sign of a non-living character. An increase in temperature again produced an acceleration of the monomer consumption, but negatively affected the molecular weight, probably by a stronger acceleration of transfer reactions. This is a quite common phenomenon since in most polyadditions the activation energy related to the propagation rate constant is lower than that pertaining to transfer events.

The different polymers obtained from the bulk reactions exhibited similar *FT*i.r. and n.m.r. spectra. *Figures 4–6* give typical illustrations of these structural features. A detailed analysis of the ^{13}C n.m.r. spectra showed that

Table 2 Reaction conditions, yields and $\overline{M}_n$ of bulk polymerizations of FO

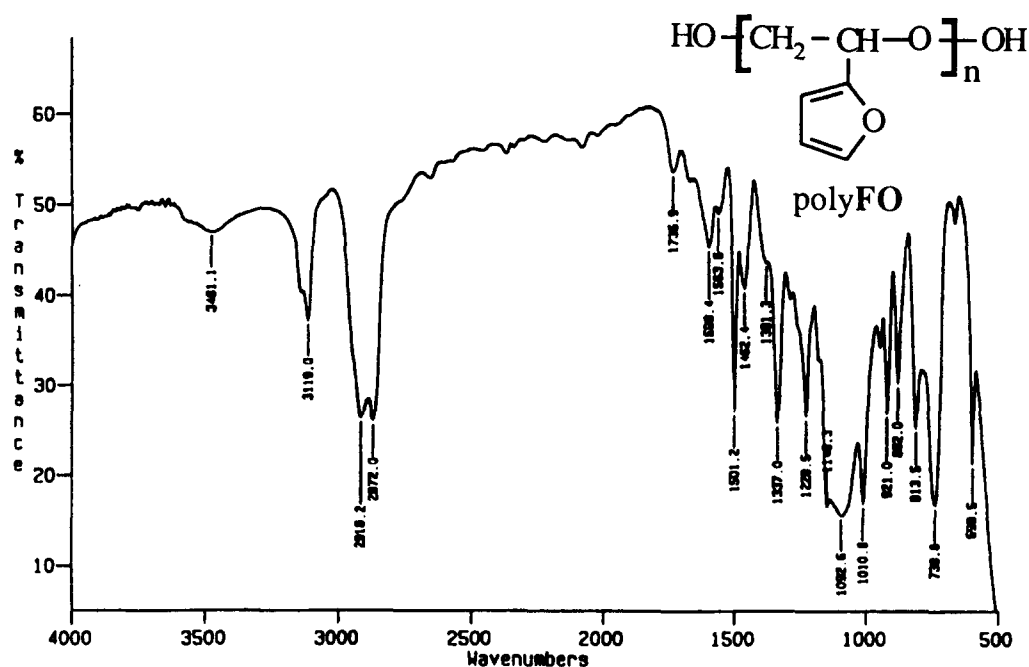| Initiator (*I*)	[FO]/[I]	*T* (°C)	Reaction time	Yield (%)	$\overline{M}_n$
KOH	100	25	1 week	80	5000
KOH	100	100	1 day	85	2000
NaOH	100	25	1 week	80	4200
Na$_2$CO$_3$	100	25	1 week	0	—
tBuOK	20	25	3 days	98	2000
tBuOK	50	25	3 days	95	4100
tBuOK	100	25	3 days	90	5500
tBuOK	200	25	3 days	85	8200
tBuOK	1000	25	3 days	82	10 100
tBuOK	20	60	1 day	97	1500
tBuOK	100	60	1 day	94	2000
KOH/MeOH	50	25	3 weeks	95	700

Figure 4 *FT*i.r. spectrum of polyFO obtained in THF at room temperature using tBuOK as initiator
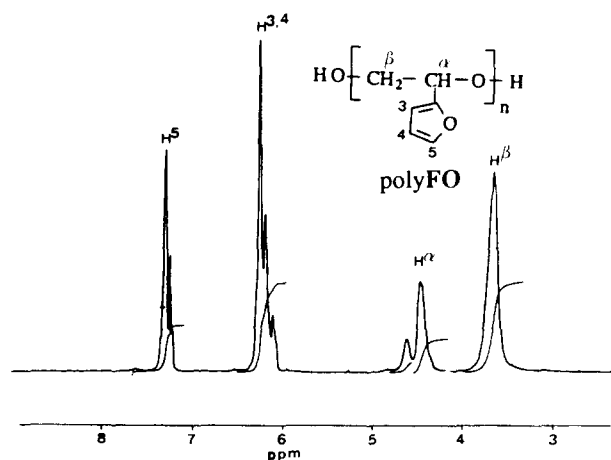
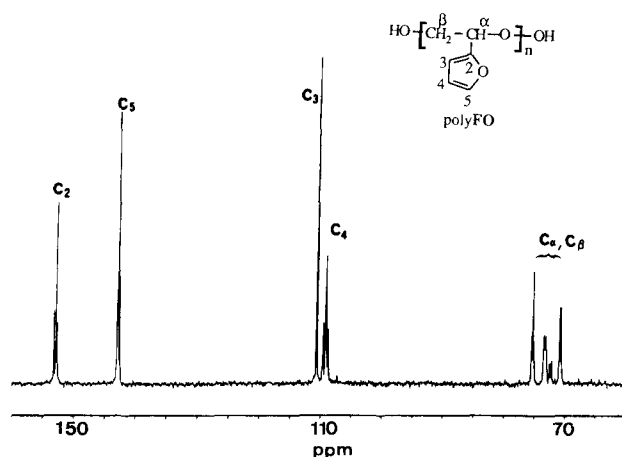**Figure 5** 300 MHz ^{1}H n.m.r. spectrum of polyFO of *Figure 4*

Figure 6 75 MHz ^{13}C n.m.r. spectrum of polyFO of *Figure 4*

Figure 7 75 MHz ^{13}C n.m.r. spectra of $C\alpha$ and $C\beta$ carbons of polyFO, of *Figure 4*: (a) as such and (b) in DEPT mode

Table 3 Reaction conditions, yields and $\overline{M}_n$ of polymerization of FO by tBuOK in THF

[FO]	[FO]/[I]	T ($^{\circ}$C)	Reaction time	Yield (%)	$\overline{M}_n$
1	50	25	6 weeks	30	700
1	200	25	6 weeks	10	1000
1	50	25	1 day	50	300
1	200	25	1 day	30	650
5	50	25	3 weeks	40	1000
5	200	60	3 weeks	60	1300
10	200	60	6 weeks	80	2500

in all instances the monomer units were not inserted regularly into the polymer backbone, suggesting that both $C\alpha$ and $C\beta$ cleavage accompanied the FO addition to the active species. This is clearly shown in *Figure 7* which represents the resonances of aliphatic carbons taken as such and with the DEPT procedure which wipes out secondary nuclei. The fact that one obtains four distinct groups of resonances in the DEPT spectrum suggests that the CH moieties can exist in four different environments, as is indeed the case if the monomer can enter in the polymer structure according to either $C\alpha$ or $C\beta$ oxirane ring opening giving rise to two sets of four triads. The various peaks in each group of resonances stem from this double set, but also from the existence of R and S configurations for each chiral carbon atom. In the same way, an analysis of the resonances arising from the CH$_2$ moieties revealed two sets of peaks attributed respectively to regular (head-to-tail) and irregular (head-to-head or tail-to-tail) diads which are also sensitive to the chirality of the adjacent tertiary carbon atom.

In conclusion, the bulk anionic polymerization of FO leads to regioirregular enchainments of monomer units because ring opening upon propagation can occur both ways. Moreover, the stereoregularity was very poor since a detailed analysis of the resonances of the furan carbon nuclei showed that these polyadditions were not
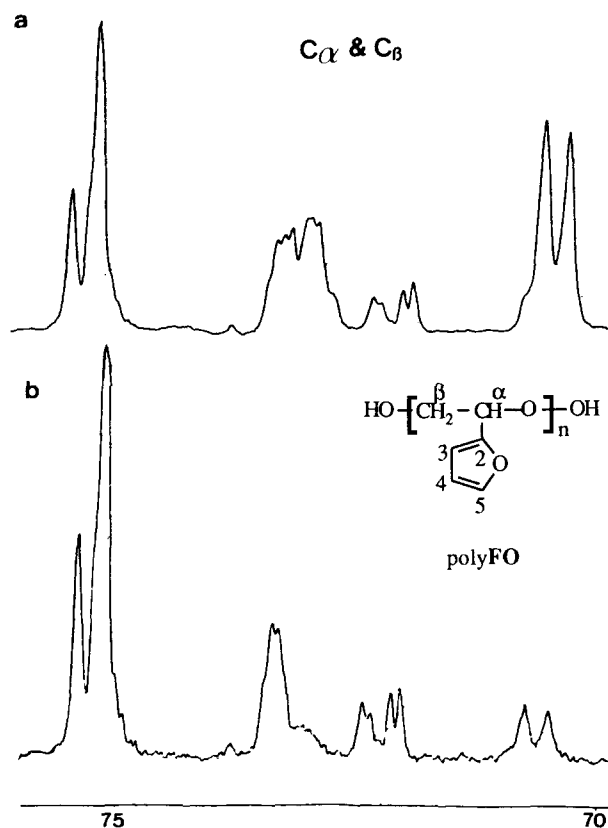
Bernoullian and favoured alternating configurations. It is, therefore, not surprising that these materials were entirely amorphous, as suggested by their d.s.c. tracings (see below).

Solution anionic polymerization. The first experiments on the anionic polymerization of FO in solution involved the use of potassium carbazyl (as a sealed sample kindly provided by Dr Boileau of the Collège de France) in THF. This system was totally inactive even after months at room temperature. Given the fact that potassium carbazyl is usually a powerful initiator of the polymerization of aliphatic oxiranes, it seems likely that with FO, an important side reaction probably induced by the furan heterocycle, destroyed the initiator.

Table 3 shows the results obtained from a set of runs carried out using tBuOK with THF as solvent. Reactions were very slow at room temperature and gave oligomeric products with structural features resembling those discussed above for the bulk systems. Again, an increase
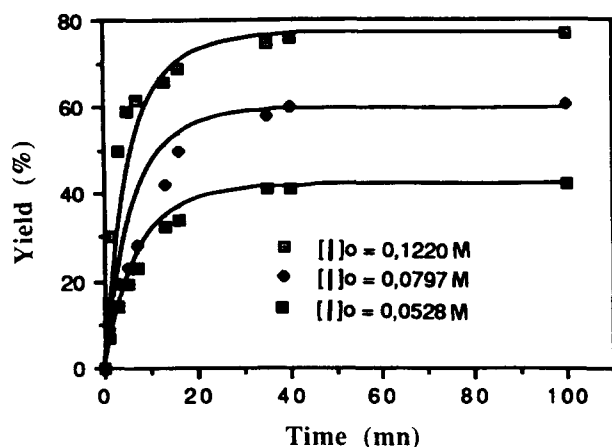
Figure 8 Kinetics of FO polymerization in DMSO (1.65 M) using tBuOK as initiator at room temperature

in temperature accelerated the polymerization, but reduced the DP to very low levels. The sluggishness of these reactions must be related to the low polarity of THF ($\varepsilon \approx 7$), as confirmed by the fact that when this solvent was replaced by the very polar DMSO ($\varepsilon \approx 50$), polymerizations became much faster.

A kinetic study was conducted with the system FO/ tBuOK/DMSO/20°C. The variation of monomer concentration with time was monitored by g.l.c. *Figure 8* shows the typical trends observed and in particular the fact that a limiting yield was attained indicating the occurrence of termination reactions. The most likely mechanisms leading to deactivation are proton abstraction reactions[9] which can occur either from the monomer, viz.:
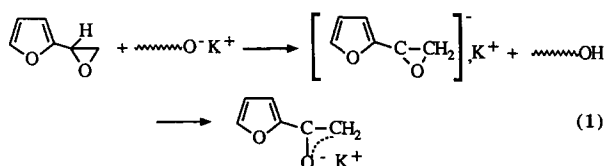

or from the polymer, i.e.
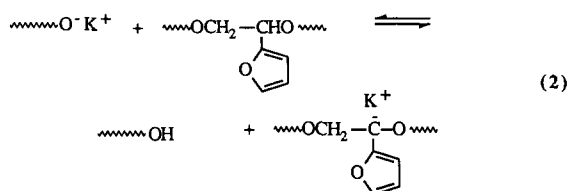
both leaving a resonance-stabilized carbanion incapable of propagating any further. Evidence for reaction (1) was obtained by analysing the volatile products at the end of these polymerizations: traces of 2-acetylfuran were detected suggesting that, indeed upon neutralization with acetic acid, the momomeric carbanion was converted into that product, viz.:
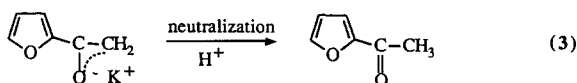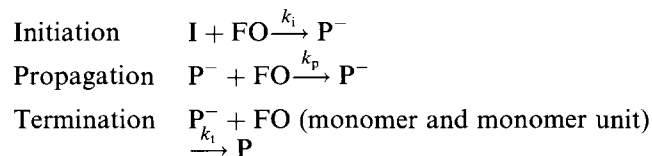

Evidence for proton abstraction from the polymer

was suggested by the fact that the products were yellow-brown, indicating the presence of conjugations along their chains, which would arise upon neutralization, as confirmed by a specific structural study which is reported in another context[6], viz.:
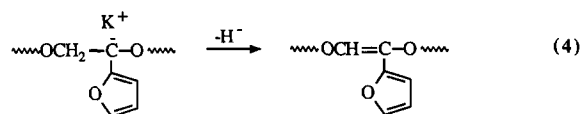
Moreover, this type of reaction is well documented in the anionic polymerization of styrene[10] and should be considerably enhanced by furan ring substitution which is well known to favour hydrogen (proton, hydride ion, hydrogen atom) mobility in the $C\alpha$ position[1-3].

The curves in *Figure 8* resemble strikingly those obtained by Hayes and Pepper[11] with the cationic system styrene/H_2SO_4/CH_2ClCH_2Cl/20°C. We, therefore, treated our results according to their kinetic scheme, namely a fast initiation accompanied by propagation, but in our case we considered a bimolecular termination reaction involving an active species and either the monomer or a monomer unit in the formed polymer as per *Schemes 1* and *2*. We assumed that the rate constants of these two events were similar, which allowed us to write a single expression for the rate of termination. The overall kinetic scheme used was therefore:

Initiation $\quad$ $I + FO \xrightarrow{k_i} P^-$

Propagation $\quad$ $P^- + FO \xrightarrow{k_p} P^-$

Termination $\quad$ $P^- + FO$ (monomer and monomer unit) $\xrightarrow{k_t} P$

Treatment of this simple situation, assuming $k_i \gg k_p$, leads to the integrated expression:

$$Ln\frac{[FO]_o}{[FO]_t} = \frac{k_p[I]_o}{k_t[FO]_o}(1 - e^{k_p[FO]_o t}) \quad (5)$$

As the limiting yield is reached, the exponential term becomes much smaller than unity and equation (5) reduces to:

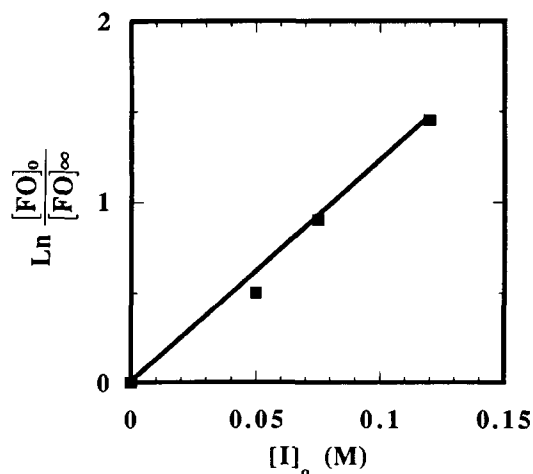$$Ln\frac{[FO]_o}{[FO]_t} = \frac{k_p[I]_o}{k_t[FO]_o} \quad (6)$$

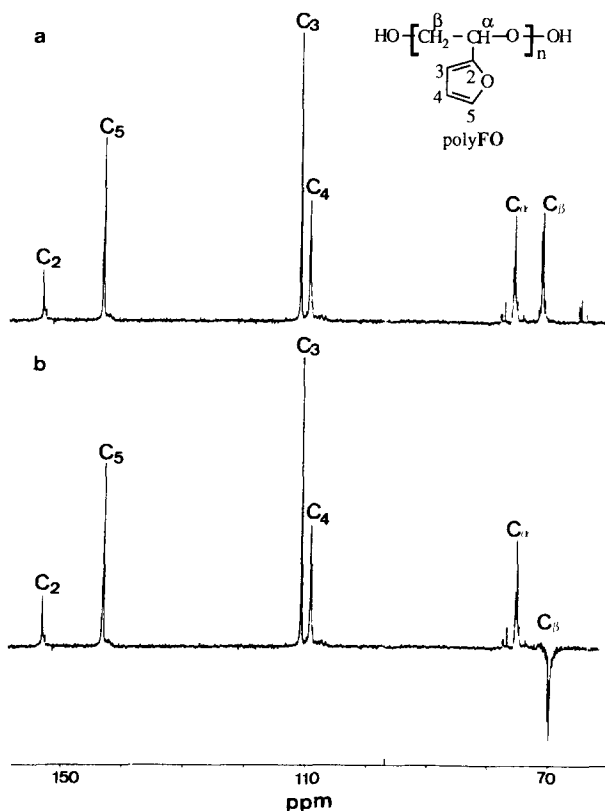

Figure 9 Plot according to equation (6)

Figure 10 75 MHz ^{13}C n.m.r. spectra of polyFO, obtained by bulk polymerization at room temperature using $(iPrO)_3Al$ as initiator: (a) as such and (b) in INEPT mode
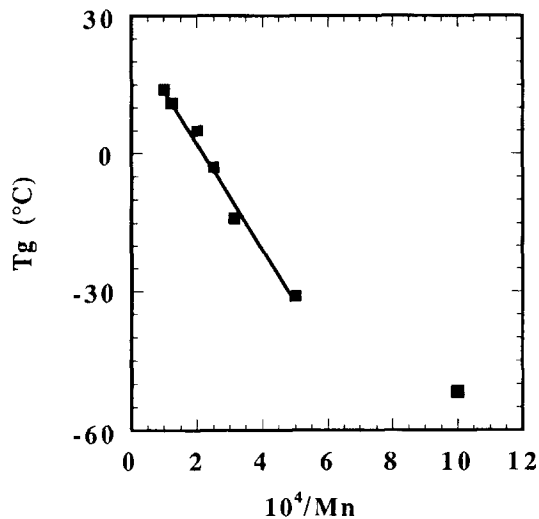

Figure 11 Glass transition temperature of polyFO as a function of $1/\overline{M}_n$

Figure 9 shows the good linearity of the plot of our data according to equation (6) which suggests that the scheme adopted is plausible. From this plot a value of k_p/k_t of about 20 was obtained. We then proceeded to fit the experimental data given in *Figure 8* with an exponential expression using equation (5) and varying k_t until *the three* curves covered the data points most adequately, as previously done by Hayes and Pepper[11]. The best fitting is shown in *Figure 8* and was obtained with $k_t = 1.2 \times 10^{-3}$ l

Table 4 Glass transition temperature of polyFO as a function of $\overline{M}_n$

$\overline{M}_n$	T_g (°C)
1000	−52
2000	−31
3200	−14
4000	−3
5000	5
8200	11
10 100	14

$mol^{-1} s^{-1}$, which therefore produced a k_p value of 24×10^{-3} l $mol^{-1} s^{-1}$.

Coordination polymerization. In a preliminary study on the role of aluminium isopropoxide (AIP) in promoting the polymerization of FO, we made two major observations, namely (i) that this initiator is particularly active and (ii) that the polymers obtained possess a more regular structure both in terms of the predominance of $C\alpha$ oxirane opening in the propagation step and with respect to tacticity. As an example, the polymer obtained from a bulk reaction at room temperature had a DP of about 100 and gave the ^{13}C n.m.r. spectra (normal and in the INEPT mode) shown in *Figure 10*. A close inspection of the various resonances revealed a much simpler pattern than that obtained with the various polymers prepared with classical anionic initiators, with homogeneous m and r diad sequences longer than 5, instead of about 1.5. Work is in progress to gain a better knowledge of these systems.

Structural and thermal analysis of polyFO. All the polymers obtained in this study showed two major structural features, apart from the sequential and configurational aspects discussed above: (i) they were in fact telechelic macrodiols since the acidic neutralization step introduced a terminal hydroxyl group in the place of the active end and also produced the hydrolysis of the tBu-O function in the case of systems initiated by tBuOK; (ii) the furan ring was not involved in any side reaction since we systematically found not only its quantitative presence, but also the correct integration of each of its protons in the n.m.r. spectra.

As already mentioned, the polyFOs prepared in this investigation were totally amorphous and therefore only displayed a glass transition when analysed by d.s.c. *Table 4* gives the T_g values as a function of M_n and *Figure 11* shows the corresponding plot which provides a limiting value for the T_g of polyFO of 'infinite' chain length of 26°C.

The thermogravimetric scan of these polymers showed that the onset of weight loss occurred around 320°C, compared with somewhat lower temperatures for aliphatic polyethers and that, in a nitrogen atmosphere, about 70% of the material was vaporized leaving 30% of carbonaceous residue.

Anionic copolymerization of FO with PO and BO. Several attempts to copolymerize FO with PO under different experimental conditions with respect to the type and concentration of initiator, the presence or absence of solvent, the relative amount of comonomers and the temperature, showed that FO was much more reactive than PO as measured by the relative rate of
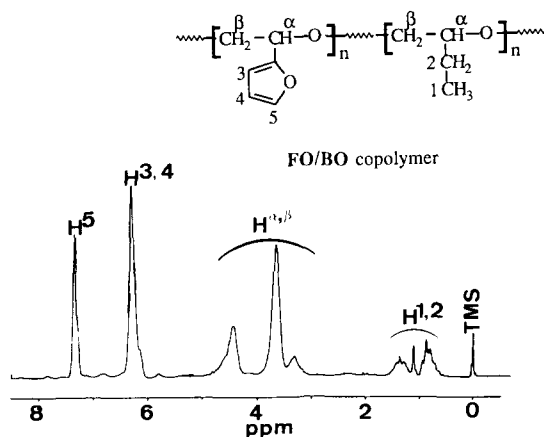
FO/BO copolymer

Figure 12 300 MHz ^{1}H n.m.r. spectrum of copolymer FO/BO (feed ratio 10/90), obtained by bulk copolymerization at 30°C using tBuOK as initiator
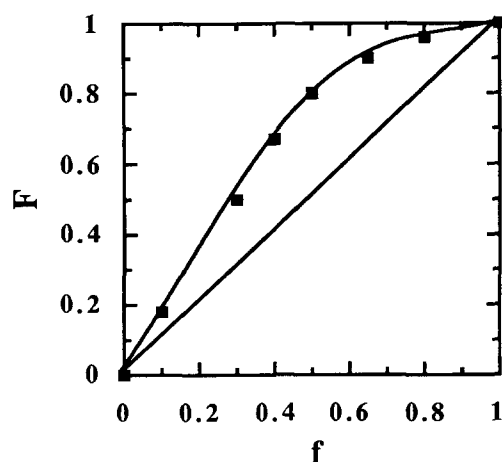
Figure 13 FO/BO copolymer composition as a function of the initial feed ratios

comonomer feed. The products isolated at low conversion were analysed by ^{1}H n.m.r. spectroscopy to determine the copolymer composition. *Figure 12* shows a typical spectrum in which the lateral aliphatic CH_3–CH_2 of the BO units resonate between 0.7 and 1.5 ppm, the furanic protons of the FO units appear between 6.3 and 7.5 ppm and the main chain protons, due to both units show up between 3 and 5 ppm. The copolymerization diagram obtained from this study is given in *Figure 13* which clearly shows that FO is more reactive than BO. The data were processed according to the Finemann–Ross standard procedure and gave $r_1 \approx 5$ ($M_1 = $ FO) and $r_2 \approx 0.8$.

CONCLUSION

The behaviour of 2-furyloxirane in anionic polymerization is that of a reactive monomer, more so than aliphatic oxiranes, and the polyethers prepared from it are telechelic macrodiols with T_g values spanning a range from about −50°C to room temperature depending on their DP. These materials could play an interesting role as macromonomers in the synthesis of polyurethanes. As for the copolymers of FO with BO, although the incorporation of the latter is modest, its role should be examined in terms of a possible modifier of properties. The use of aluminium propoxide, or of other coordination catalysts as initiators, seems promising in view of insuring a good regularity in the mode of FO insertion and in the configuration of the chiral sites along the chain.

monomer consumption by g.l.c. The product was essentially homopolyFO for short reaction times and a mixture of the two homopolymers (as suggested by the presence of two peaks in the g.p.c. traces) when the systems were left for much longer times.

A different behaviour was observed when the comonomer was BO, since the rates of monomer consumption were similar, albeit higher for FO. The product gave a single g.p.c. peak, but the DPns were low. A systematic study of this copolymerization was therefore carried out in bulk at 30°C using tBuOK as initiator, by varying the

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