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The Polymerisation of 2-Furyl Vinyl Ketone

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Summary: 2-Furyl vinyl ketone was polymerised using anionic, cationic and free-radical initiators. Yields and molecular weights varied with the type of activation. Whereas radical polymerisation gave a product possessing a regular vinylic structure, other kinds of units were detected in the polymers prepared with anionic and cationic catalysts.

Introduction

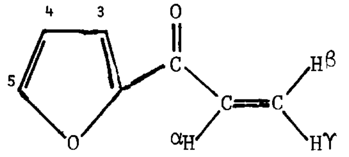
Barnes (1) first synthesised 2-furyl vinyl ketone (FVK) in 1943. Since then, other routes have been proposed (2-4), but no mention has been published about its polymerisation.

Within the context of a general investigation on the behaviour of furan derivatives in polymerisation and copolymerisation reactions and on the properties of the ensuing materials (5), it was decided to fill this gap. Indeed, vinyl ketones are known to respond to various types of initiation (6) and it seemed interesting to assess the role of the furan ring on the mechanistic behaviour of these polymerisations, compared with more traditional monomeric structures.

Experimental

CAUTION!!: FVK is harmful to the respiratory system and to the kidneys (it should therefore be handled with appropriate care).

FVK was synthesised following a technique published by Sam and Mozingo (3) for its homologue 2-furyl isopropenyl ketone. A mixture of 0.21 moles of 2-furyl methyl ketone, 0.30 moles of paraformaldehyde, 0.22 moles of dimethylamine hydrochloride, a drop of conc. HCl and 40 ml of ethanol was stirred under reflux for 4 hours. The solvent was then removed under reduced pressure and the solid residue washed with cold ether to remove the excess of reactants. The remaining salt was recrystallized from acetonitrile to give 85% yield of N,N-dimethyl-2-(2-furoyl)ethylamine hydrochloride, m.p. 173-174°C; ^{1}H-NMR (CD_2Cl_2, TMS, δ/ppm): 7.8 (s,1H), 7.58 (s,1H), 6.7 (q,1H), 4.7 (s,1H), 3.5 (m,4H), 2.9 (s,6H). A concentrated aqueous solution of this compound was steam distilled until the distllate gave a negative carbonyl test. The product extracted with CH_2Cl_2 was purified by distillation under reduced pressure after a thorough drying. FVK was thus obtained in about 30% yield (no attempt was made to optimise this procedure), b.p. 90°C/10 Torr. Its spectroscopic characterisation is given below since it has not been published previously. Fu stands for a 2-substituted furan ring, i.e. $C_4H_3O^\bullet$. ^{1}H-NMR (CD_2Cl_2, TMS, δ/ppm; 100 MHz): 7.66 (m,1H,5-C-$\underline{H}$)



(I)

6.58 (m,1H,4-C-$\underline{H}$); 7.27 (m,1H,3-C-$\underline{H}$); 7.08 (m,1H,$\underline{H}\alpha$),$^3J_{HH}$=17 Hz, $^3J_{HH}$=10.3 Hz; 6.46 (dxd,1H,$\underline{H}\beta$),$^3J_{HH}$=17 Hz, $^2J_{HH}$=1.9 Hz; 5.84 (dxd,1H,$\underline{H}\gamma$), $^3J_{HH}$=10.3 Hz, $^2J_{HH}$=1.9 Hz.

IR (liquid film, ν/cm^{-1}): 3130 (ν C-H of furan ring); 3040 and 3010 (ν C-H of vinyl group); 1670 (ν C=O); 1615 (ν C=C of vinyl group); 1570 (ν C=C of furan ring); 1270 (ν C-O of the furan ring); 1040 (ring breathing); 985 (γ -CH=CH_2); 900, 780 and 740 (γ -CH typical of 2-C-monosubstituted furans).

The initiators were all commercial samples of high purity and solvents were purified and dried following standard procedures. Reactions were carried out in a dry nitrogen atmosphere under vigorous stirring. They were quenched with acetic acid (anionic polymerisation), methanolic ammonia (cationic polymerisation) or hydroquinone (radical polymerisation). Polymers were precipitated in light petroleum spirit and dried to constant weight in a vacuum oven.

Number-average molecular weights were determined with a KNAUER vapour pressure osmometer. Infrared spectra of films or KBr pellets were taken on a PERKIN-ELMER instrument and proton NMR spectra were run on a BRUCKER FT WP 100 spectrometer.

Results and Discussion

1. Anionic Polymerisation

Conditions were varied over a wide range in terms of the nature of the initiator, its concentration, the solvent, the temperature and the duration of the reaction. Only the most relevant features are summarized here.

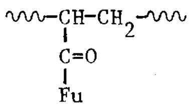
With Et_3Al and Et_2Zn in THF low yields of polymer were obtained even after 24 hours and an increase in initiator concentration produced the crosslinking of the material (white insoluble powders). Aliphatic vinyl ketones polymerise well with these catalysts and the mechanism proposed for the active species (7,8) involves the formation of a complex between the metal (Al or Zn) and the carbonyl group. In the present situation, the carbonyl function in FVK is conjugated with the furan ring and might therefore be less active towards complexation with the metal. Conversely, the heterocycle might be an important alternative for complex formation and consequent "diversion" of the initiator from the proper activation for the polymerisation. Once again, the furan ring in a monomer structure brings about a radical change in the behaviour towards polymerisability (9).

With alkali metal alkoxides and n-butyllithium reasonably high yields were obtained, but again concentrations of initiators had to be kept low to avoid crosslinking. Some typical results are shown in Table 1. It is important to underline that in this study the main aim was to explore the response of FVK under a wide variety of conditions and no attempt was therefore made to optimise the parameters in order to increase yields and/or molecular weights. Since non-linear chains were obtained in these polymerisations,as suggested by the network formation at high catalyst concentrations, it is essential to find what mechanism(s) accompanied the normal vinylic propagation and introduced first branching then crosslinking.

TABLE 1. Anionic polymerisation of FVK (1 M) in THF at 0°C.

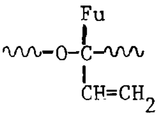
N°	Initiator (I)	[I] / [FVK]	Time	Yield (%)	$\bar{M}_n$	Remarks
1	MeONa	3.6×10^{-2}	4 h	70	-	Insoluble
2	t-BuOK	10^{-2}	30 min	55	860	
3	n-BuLi	5×10^{-2}	4 h	75	-	Insoluble
4.	n-BuLi	10^{-2}	30 min	42	940	

Investigations on the structure of polymers obtained from aliphatic vinyl ketones and anionic initiators (10-11), would suggest that with FVK three structures could be expected, viz. the normal vinylic unit (II), the structure arising from the opening of the carbonyl group (III) and possible units arising from nucleophilic substitution followed by H^- migration (IV), i.e. isomerisation propagation somewhat similar to that encountered with furfurylidene acetone (12).



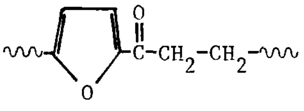
$$\sim\!\!\sim \underset{\substack{|\\ C=O\\ |\\ Fu}}{CH}-CH_2\sim\!\!\sim$$

(II)



$$\sim\!\!\sim O-\underset{\substack{|\\ CH=CH_2}}{\overset{\substack{Fu\\ |}}{C}}-\sim\!\!\sim$$

(III)



(IV)

Of course structure (IV) could also arise from substitution on a furan ring of a preformed polymer chain, thus giving rise to branching and ultimately to crosslinking.

All polymers obtained with anionic initiators gave IR spectra like the one shown in Fig. 1b, and all soluble polymers gave NMR spectra like the one shown in Fig. 2b. A comparison of these spectra with those of the monomer (Figs. 1a and 2a) suggests that: (i)the vinyl group is responsible for most of the propagation as indicated by the disappearence of the characteristic vibrations at 1615 and 985 cm^{-1} and of the resonances of the three vinylic protons between 5.8 and 7.1 ppm, these features being replaced by the corresponding ones for "saturated" groups around 2900 cm^{-1} and around 1 and 3 ppm respectively; (ii)the carbonyl group does not seem to be involved in these polymerisations as shown by the strong IR peak at 1680 cm^{-1} for the polymer and the absence of any significant absorption due to ether or acetal bonds; (iii)the relative areas corresponding to the furanic and the aliphatic protons (Fig. 2b) is not in the right proportion of 1/1 as expected from structure (II), the latter protons being in excess; this observation coupled with the fact that four peaks appear in the region of the furanic protons, can be interpreted as evidence of nucleophilic substitution at C-5 on furan rings belonging to the monomer or to the polymer possessing a sequence of structures (II). More specifically, the peaks at 7.54, 7.13 and 6.51 ppm correspond to monosubstituted furan rings: these chemical shifts are very close to those for furyl methyl ketone, thus corroborating the opening of the vinyl group; the peaks at 7.13 and 6.17 ppm are attributed to 2,5-disubstituted rings and this interpretation is supported by the identity of the resonances for the C-3 and C-4 protons in 5-methylfuryl methyl ketone.

The structural evidence gathered through these spectroscopic analyses points to a polymer possessing units (II) and (IV) in a ratio of about 2.5. Given the ease with which these materials form networks, it seems plausible to postulate that most of the units (IV) are in fact present as branches, i.e. they were formed by reaction of an active species onto the C-5 position of a furan ring belonging to a preformed polymer. In other words, it is likely that propagation only occurs through the vinyl group and the anomalous structures observed (and the related crosslinking) are due to interactions not involving the monomer, but only polymeric species. This situation is therefore very different from the isomerisation process (12) with furfurylidene acetone and is instead the counterpart in anionic polymerisation of the branching by alkylation observed in the cationic polymerisation of alkenyl furans (13).

2. Radical Polymerisation

Table 2 gives a summary of the experiments conducted with two typical free radical initiators. The products were white powders soluble in benzene methylene chloride and other common solvents.

TABLE 2. Radical polymerisation of FVK (1 M) in benzene.

N°	Initiator (I)	[I]/[FVK]	T/°C	Time/h	Yield/%	$\bar{M}_n$
5	AIBN	10^{-2}	60	4	4	2500
6	AIBN	10^{-1}	60	4	10	1200
7	Benzoyl peroxide	10^{-2}	80	3	10	750
8	Benzoyl peroxide	10^{-1}	80	3	17	920

The IR spectra of these polymers were very similar to that shown in Fig. 1b. The NMR spectra were all the same and are typified by the one given in Fig. 2c. The furan protons resonated at 7.6, 7.2 and 6.5 ppm and the aliphatic ones between 1 and 3 ppm. The ratio of the areas corresponding to these functions was 1/1. All spectroscopic evidence points therefore to a regular enchainment of units (II), i.e. to a predominant propagation through the vinyl moiety. Aliphatic vinyl ketones have been reported to polymerise likewise (6,14). Thus the introduction of the furan ring does not alter the mode of chain growth with radical initiation.

The regularity of the macromolecular structure is however accompanied by a serious drawback in terms of yields. Even with very high initiator concentrations, the formation of polymer stopped short of 20% conversion. This feature is not new with furanic monomers (9) particularly with vinylfuran and even worse with vinyl furoate (15), and is due to the retarding effect produced by the attack of primary radicals onto the furan ring rather than onto the vinylic function. The behaviour of FVK is similar to that of 2-vinylfuran in that the monomer is activated in the "normal" fashion by the primary radical (addition onto the vinylic bond), but the formed polymer

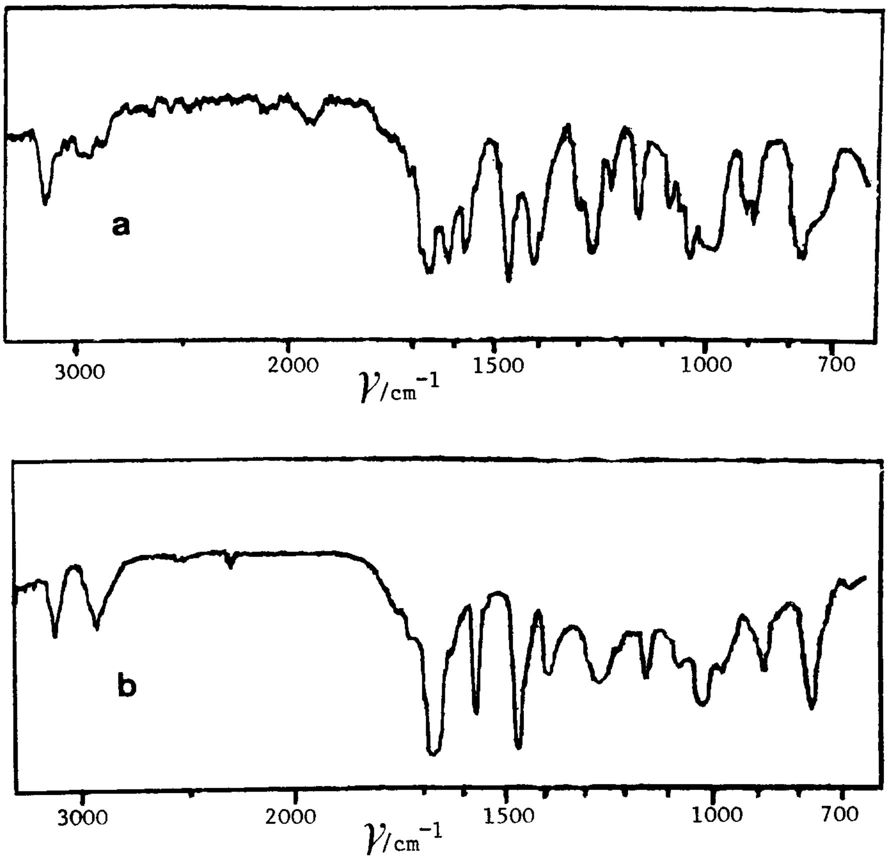


FIGURE 1. Infrared spectra of a. FVK (liquid) and b. poly-FVK obtained with anionic, radical and cationic initiators (KBr pellet).

chains act as radical traps through their pendant furan rings. Thus, at a critical polymer concentration (limiting yield) practically all primary radicals are quenched to form stable furyl radicals and normal initiation cannot take place. This phenomenon of self-retardation is also responsible for the low molecular weights through degenerative transfer reactions (9).

3. Cationic Polymerisation

Fairly low yields were obtained even when a high concentration of initiator was used, as shown in Table 3 which gives the "best" results with this type of initiation.

The IR spectra of these polymers closely resembled those taken with poly-FVK prepared by anionic and radical activation (cf. Fig. 1b). The NMR spectra of products 9 and 10 (cf. Table 3) are shown in Figs. 2d and 2e. Holleck and Mahapatra (16) studied the cationic polymerisation of methyl vinyl ketone and proposed a polymer structure involving alternation of nor-

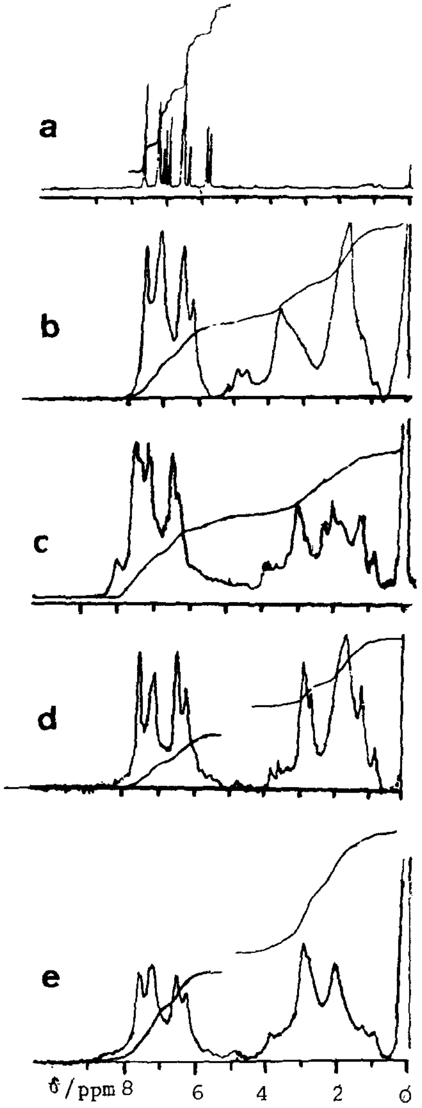


FIGURE 2. ^{1}H-NMR spectra of:

a. FVK

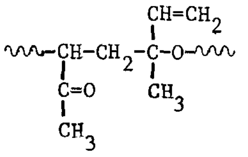
b. Poly-FVK prepared with anionic initiators

c. Poly-FVK prepared with radical initiators

d. Poly-FVK prepared with cationic initiation, viz. $BF_3.Et_2O$ at -60°C (cf. expt.10,Table 3)

e. Poly-FVK prepared as in d., but at 0°C (cf. exp. 9, Table 3)

mal vinylic units and units arising from propagation through the carbonyl group, as shown in structure (V).



$$\sim\sim\underset{\begin{array}{c}|\\C=O\\|\\CH_3\end{array}}{CH}-CH_2-\overset{\begin{array}{c}CH=CH_2\\|\end{array}}{\underset{\begin{array}{c}|\\CH_3\end{array}}{C}}-O\sim\sim$$

(V)

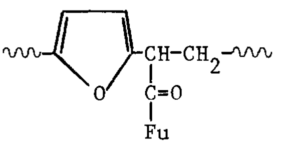
TABLE 3. Cationic polymerisation of FVK (1 M) in CH_2Cl_2.

N°	Initiator (I)	I / FVK	T/°C	Time/h	Yield/%	$\bar{M}_n$	Remarks
9	$BF_3.Et_2O$	0.1	0	2	16	880	yellow pwdr.
10	$BF_3.Et_2O$	0.1	-60	3	13	1750	white pwdr.

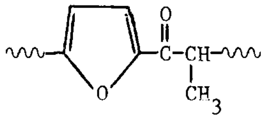
A structure like (V) for the poly-FVK prepared in this context is incompatible with the spectroscopic features of the products, because one would have noticed a significant decrease of the carbonyl peak, a strong ether band and the persistence of the characteristic vibrations of the vinyl group in the IR spectra and the persistence of vinylic protons in NMR as well as a ratio of intensities of 3/1 between vinylic plus furanic protons and aliphatic protons. Instead (cf. Figs. 1b and 2d-e) the vinylic bands have practically disappeared whilst the carbonyl vibration remains strong. Also, the ratio of furanic to aliphatic protons is 0.8 for the polymer prepared at 0°C and 0.85 for that synthesised at -60°C. These observations and the remaining features of the spectra point to a sequence of vinylic units with occasional irregularities which must arise from electrophilic substitution reactions at C-5 as suggested by the four peaks in the 6 to 8 ppm region (see discussion of anionic polymerisation) and by the lack of furanic protons with respect to structure poly-(II). 2-alkenylfurans have been found to undergo facile alkylation at C-5 (13) and the present findings extend this propensity to FVK although the extent of this side reaction is substantially lower with the latter monomer due to the unfavorable effect of the carbonyl substitution at C-2.

Whether the electrophilic substitution occurs on the monomer as an alternative to normal vinylic propagation or on furan rings pendant to the polymer, it is impossible to say from the amount of data available. No crosslinking was observed in the polymerisation, but the low yields obtained can readily account for that. Confirming previous results on 2-alkenylfurans (13), the extent of alkylation decreased with decreasing temperature. This behaviour is related to a higher activation energy for alkylation compared to propagation.

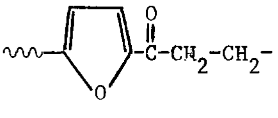
In conclusion, the possible anomalous structures accompanying the predominant units (II) are (13):



(VI)



(VII)



(VIII)

The low yields of polymer are probably due to the fact that the initiator can either complex with the carbonyl group or react (through cocatalytic protonation) with the vinyl moiety to give an active species. The competition between these two steps is obviously a function of the relative basicity of the two sites and in FVK the C=O is certainly quite nucleophilic (17) and diverts therefore the potential propagating activity away from the carbenium ion chain carrier. The fact that a normal active species can revert to an inactive protonated or complexed carbonyl form is detrimental to the rate of polymerisation and a self-retarding process takes place because the polymer acts here as a quencher by sequestering the initiator through its many C=O groups. Thus autoinhibition occurs at a critical polymer yield in a similar fashion, but for different mechanistic reasons, to that discussed for the radical polymerisation.

The low molecular weights arise probably from very important transfer reactions which were however not studied.

Conclusion

2-furyl vinyl ketone can be polymerised by a variety of initiators, but anionic activation gives the best results in terms of yields. In all instances the specific peculiarities of the chemistry of the furan ring manifested themselves through interference with the kinetics of chain growth or with the mechanism of regular propagation by C=C opening.

This investigation was not pursued further because of the toxicity of the monomer and will be resumed if this aspect becomes better understood and specific measures can be taken to avoid any health hazard.

References

1. C.E. Barnes, U.S. Patent 2,309,727 (1943).
2. M.I. Shevchuk and A.V. Dombrowskii, Zh. Obshch. Khim. 34, 916 (1964); Chem. Abs. 15810 (1964).
3. J. Sam and J.R. Mozingo, J. Pharm. Sci. 58, 1030 (1969).
4. S. Watanabe et al., Yukagaku 25, 110 (1976); Chem. Abs. 84, 120611 (1976).
5. A. Gandini et al., in "Topics in Furan Chemistry", J. Kovac, Ed.,Bratislava University Press, Bratislava, 1983, p.33.
6. A.R. Lyons, Macromol. Rev. 6, 251 (1972).
7. A.R. Lyons and E. Catterall, Europ. Polym. J. 7, 849 (1971).
8. T. Tsuruta and R. Tsushima, Makromol. Chem. 177, 337 (1976).
9. A. Gandini, Adv. Polym. Sci. 25, 47 (1977).
10. S. Iwatsuki, Y. Yamashita and Y. Ishii, J. Polym. Sci. B1, 545 (1963).
11. A.R. Lyons and E. Catterall, Europ. Polym. J. 7, 839 (1971).
12. M.C. Salon, A. Gandini and H. Cheradame, Polym. Bull. 12, 441 (1984).
13. A. Gandini and R. Martinez, Makromol. Chem. 184, 1189 (1983).
14. C.S. Marvel, E.H. Riddle and J.O. Corner, J. Amer. Chem. Soc. 64, 92 (1942).
15. A. Gandini and J. Rieumont, Tetrahedron Lett. 1976, 2101.
16. L. Holleck and S. Mahapatra, Monatsch. Chem. 100, 1928 (1969).
17. A. Gandini and J. Rieumont, British Polym. J., 1977 (3), 28.

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