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The Anionic Polymerisation of Furfurylidene Acetone: Evidence for Isomerisation Preceding Propagation

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Summary

Furfurylidene acetone and some of its homologues were polymerised by various typical anionic initiators. Low-DP products were obtained and characterised by IR and NMR spectroscopy. The structural analysis and the markedly different behaviour of certain homologues indicate that isomerisation polymerisation involving a proton migration predominates, but that some propagation through C=O opening also occurs under some conditions.

Introduction

Furfurylidene acetone (FA) is readily obtained in high yields from the condensation reaction of 2-furaldehyde and acetone in a basic medium (1). Its cationic polymerisation leading to black cross-linked materials as well as the properties and applications of these thermosetting resins have been the subject of numerous publications (2-5). On the contrary, the possibility of polymerising FA anionically had been substantially ignored and only recently some attention has been paid to it (6,7). This is surprising, because the technical know-how on the preparation of the"monomer"had clearly shown that with aqueous NaOH a mixture of FA, difurfurylideneketone and oligomers therefrom were obtained in variable proportions depending on the experimental conditions (1), i.e. that anionic polymerisation was indeed possible.

Khanmamedov et al. (6) have briefly looked into this issue by polymesing FA with n-BuLi in toluene at room temperature (concentrations not given). The product obtained after four days' reaction (70% yield) was characterised spectroscopically, but its DP was not reported. The authors concluded that the IR, UV and NMR data suggested a stepwise Michael-type mechanism of propagation, but the evidence provided was rather scanty.

More recently, Patel and Patel (7) studied the polymerization of FA in aqueous NaOH solutions at 100°C. Within several hours high yields of water-insoluble polymers were isolated and characterised by UV and IR spectroscopy and by GPC ($\overline{M}_n$ ranged from 800 to 1700 depending on the reaction conditions). Again, the authors opted for a Michael-type isomerisation propagation proceeding stepwise to rationalise their findings, but again no firm proof for such a mechanism was provided.

The present report deals with the anionic polymerisation of FA initiated in non-aqueous media by several classical nucleophiles and with the use of model compounds to unravel the mechanism(s) involved in the propagation.

Experimental

FA was synthesised following the standard technique (1) and purified by vacuum sublimation. The other "monomers" used as model compounds (see text) were prepared by the same synthetic procedure (except for trifluorofurfurylideneacetone for which a large excess of 2-furaldehyde was used with respect to trifluoroacetone) and their purification involved sublimation, distillation or recrystallisation depending on the m.p. and b.p. of the compound. Tetrahydrofuran was purified by distillation and dried on molecular sieves and LiAlH$_4$. The initiators n-BuLi, t-BuOK, MeONa and MeOLi were pure commercial samples, but sodium naphthalene was prepared in THF following the classical procedure.

Reactions were carried out in a dry-nitrogen atmosphere under vigorous stirring. They were quenched with a few drops of acetic acid and the polymers isolated by precipitation in petroleum spirit and dried to constant weight in a vacuum oven.

Molecular weights were determined with a KNAUER vapour-pressure osmometer; IR spectra of films or KBr pellets were recorded on a PERKIN-ELMER instrument and proton NMR spectra run on a BRUCKER FT WP 100 spectrometer.

Results and Discussion

Polymerisation conditions were varied over a wide range in terms of the nature of the initiator, the concentration of both monomer and initiator, the temperature and the reaction time. Tetrahydrofuran proved to be a better solvent than toluene. The details of all these experiments will be submitted shortly. For the present context the relevant points are summarised below. The anionic polymerisation of FA (0.1-1 M) occurs with n-BuLi, t-BuOK and sodium naphthalene (0.001 to 0.1 M) between -60 and 25°C: the yields vary from a few percent to 90% depending on conditions. Reaction times ranged from 5 min. to several days, but typically a few hours represented an adequate duration for reaching a substantial conversion into polymer. The products possessed a wide DP distribution and $\bar{M}_n$ ranging from 500 to 2000. AlEt$_3$ showed a modest initiating capability, compared with the above bases, but gave higher DP. MeONa and MeOLi were found to be inactive.

1. All the polymers obtained with n-BuLi and those obtained with the other active initiators at temperatures below about -30°C gave IR and NMR spectra as those shown in Figs. 1b and 2b. A comparison of these spectra with those of the monomer (Figs. 1a and 1b) and with literature data concerning furan derivatives (8,9) allows the following conclusions. There is ample evidence that these polymerisations involved the C=C group since: (i) its "opening" becomes evident from the changes in IR spectra (cf. 1a and 1b), viz. the disappearance of the bands at 970 (out-of-plane δCH in R'-CH=CH-R") and 1620 cm^{-1} (νC=C) accompanied by the strong shift of the νC=O band from 1670 to 1710 cm^{-1} reflecting the loss of conjugation between the carbonyl and the alkenyl groups (note that the shift of the fundamental vibration of the ring from 1550 to 1590 cm^{-1} is also an indication of the loss of conjugation between the heterocycle and its substituent at C2, i.e. in this case the transformation of C=C into C-C); (ii) the changes in NMR spectra (cf. 2a and 2b) clearly show the disappearance of the two alkenyl protons which are replaced by the broad triple resonance between ca. 2 and 3.5 ppm; (iii) the inversion of surface areas between Fig. 2a and 2b with respect to the "aromatic" and olefinic region (5-8 ppm) vs. the aliphatic one (1-4 ppm), which is 5:3 for the monomer and 3:5 for the polymer, testify strongly in favour of propagation through the alkenyl unsaturation. The second conclusion is that the furan ring does not participate appreaciably in propagation reactions since its three protons are present with equal intensity in the NMR spectrum of the polymer (their upfield shift compared with the corresponding monomer peaks is further evidence for the removal of conjugation with the C=C substituent). This was confirmed by using 5-methyl-FA in control experiments: this compound polymerised with the same behaviour as FA thus suggesting that no nucleophilic substitution at C5 takes place during the anionic polymerisation of FA, as opposed to facile electrophilic substitution in the cationic polymerisation of many furanic monomers (10).

FA is a 1,2-disubstituted alkene (I) and there seems to exist a strong

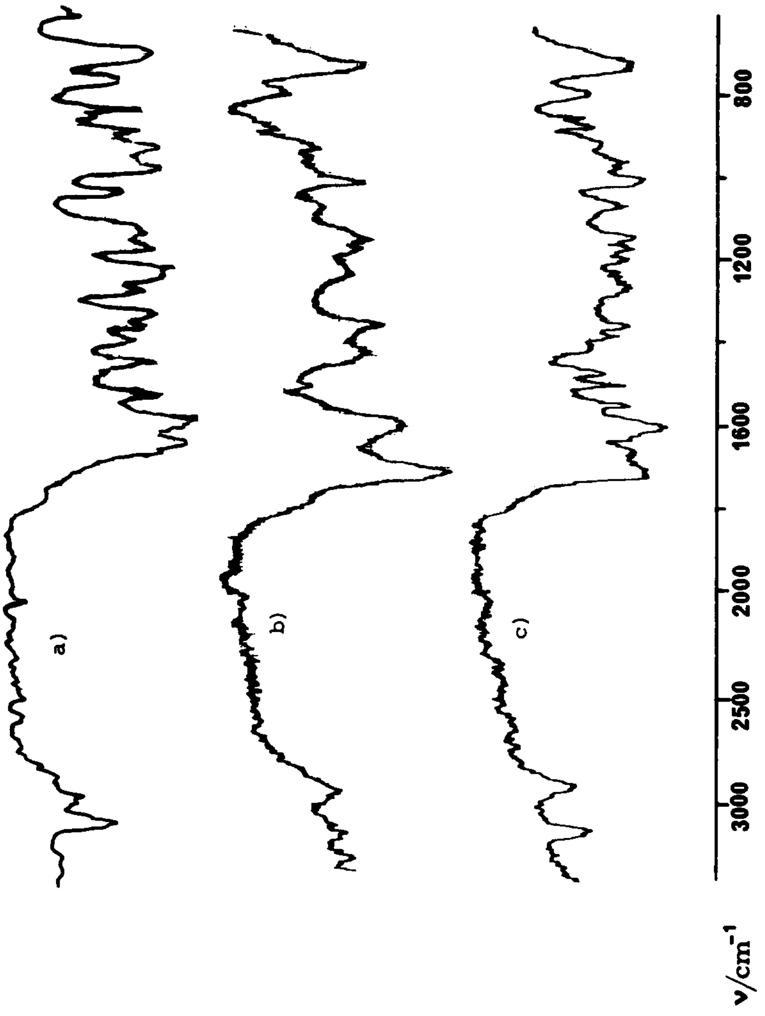


Figure 1. Infrared spectra of: a) Furfurylidene acetone (I), liquid film; b) A typical polymer of FA obtained with BuLi (KBr pellet); c) A polymer of FA obtained with t-BuOK at room temperature (KBr pellet).

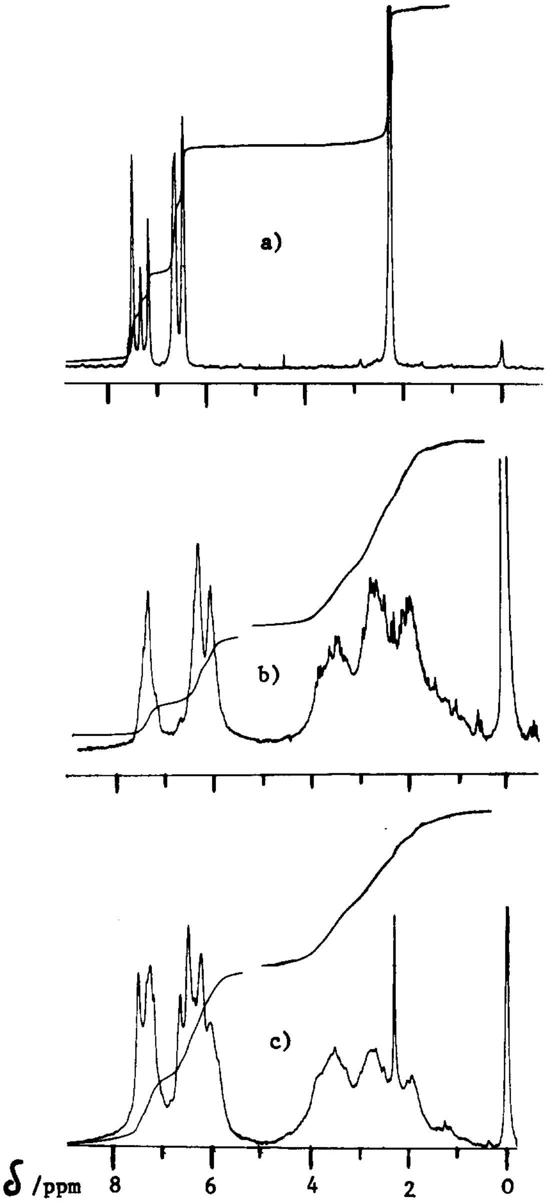
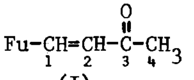


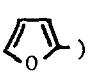
Figure 2. Proton magnetic-resonance spectra of FA and the two polymers as in Fig.1. Solvent CD_2Cl_2 ; reference standard TMS.

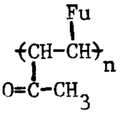
contradiction between the evidence in favour of propagation through the C=C and the fact that 1,2-disubstituted alkenes are reluctant to polymerise because of steric hindrance. Moreover, structure II, arising from such a polymerisation, is at odds with some of the features of NMR spectrum 2b, namely the three bands between 2 and 3.5, which should instead have been a strong singlet (3H) at ca. 2.2 ppm for the methyl group and a broader but weaker resonance around 3 ppm due to the two methyne protons.



$\mathrm{Fu{-}\underset{1}{CH}{=}\underset{2}{CH}{-}\underset{3}{\overset{O}{\overset{\|}{C}}}{-}\underset{4}{CH_3}}$

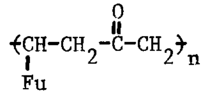
(I)

(Fu= )



$\left(\mathrm{\underset{\underset{O{=}C{-}CH_3}{|}}{CH}{-}\overset{Fu}{\overset{|}{CH}}}\right)_n$

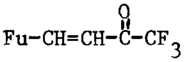
(II)



$\left(\mathrm{\underset{\underset{Fu}{|}}{CH}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_2}\right)_n$

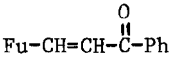
(III)

In view of the possibility that the propagation through the C=C unsaturation might be accompanied by an isomerisation of the active species, particularly involving the methyl group, several FA homologues were synthesised and tested in typical polymerisation conditions. Furfurylidene trifluoroacetone gave no polymer, even under the most drastic situations, i.e. high catalyst concentration and long reaction times (IV). The same results were obtained with furfurylidene acetophenone (V) and furfurylidene t-butyl ketone (VI).



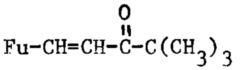
$\mathrm{Fu{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}CF_3}$

(IV)



$\mathrm{Fu{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}Ph}$

(V)



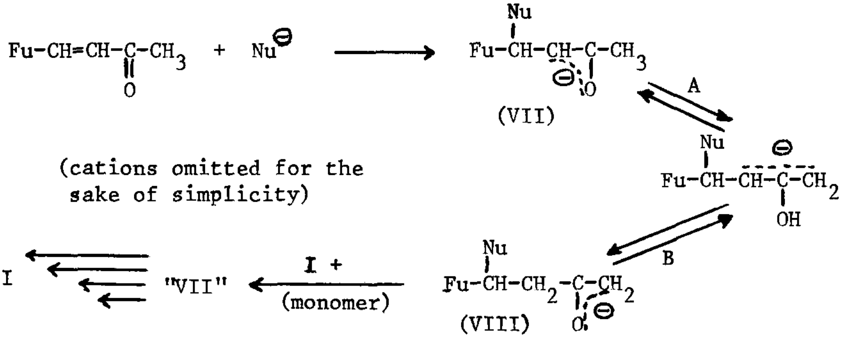
$\mathrm{Fu{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}C(CH_3)_3}$

(VI)

Clearly, the anionic polymerisation of furfurylidene ketones takes place *via* the alkene group, but is accompanied by a rearrangement of the chain carrier (which would be otherwise inactive because of steric hindrance) which is only possible if the carbon atom *next* to the carbonyl group bears (at least) a hydrogen atom.

Both the mechanism proposed by Khanmamedov et al. (6) for non-aqueous systems and that put forward by Patel and Patel (7) for aqueous alkali initiation are stepwise reactions resembling typical polycondensations. Their occurrence would thus imply a progressive increase in DP with reaction time or yield. This point was carefully checked and it was found that the molecular weight of the polymers did not depend upon such variables (typically, for a given reaction the DP was practically the same for polymers isolated at 2% or 80% yield), but was instead sensitive to such parameters as the nature and the concentration of the initiator and the temperature, i.e. factors which usually influence the DP in polyaddion reactions.

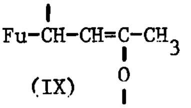
In order to rationalise all the evidence gathered in this context, the following mechanism of isomerisation polymerisation is proposed:



(cations omitted for the sake of simplicity)

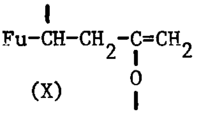
Initiation is classical, but the anion VII cannot propagate (steric hindrance) as confirmed by the lack of polymerisation with IV, V and VI. Equilibria A and B show its isomerisation by proton migration to give the anion VIII which can add onto the monomer in a typical nucleophilic addition which regenerates structure VII (but in a dimer form). A succession of isomerisation and addition reactions is thus responsible for the growth of the polymer III whose structure seems adequately confirmed by the IR and NMR spectra 1b and 2b.

2. Polymers prepared with t-BuOK or sodium naphthalene at temperatures above about -30°C gave more complex IR and NMR spectra which suggested the occurrence of a second propagation step whose incidence relative to that giving "pure" III increased as the temperature was increased or when going from sodium naphthalene to t-BuOK under the same conditions. Figs 1c and 2c show the IR and NMR spectra of a polymer for which this second mode of propagation reached its strongest contribution (room temperature, t-BuOK). A comparison of these spectra with the corresponding ones of the monomer (1a and 2a) and of polymer III (1b and 2b), leads to the conclusion that furfurylidene units, viz. Fu-CH=CH-, must be present in the "hybrid" polymer. In fact, both the vibration frequencies and the resonance peaks proper to this group (as seen in the monomer spectra) are clearly visible in Figs. 1c and 2c respectively, mixed with the typical features of polymer III. Propagation through the carbonyl group will give structures IX, X or XI depending on whether the active species is VII, VIII or one resulting from initiation by nucleophilic addition on the C=O, respectively. Structure XI will also result from propagation of VII and VIII onto the carbonyl group of FA.



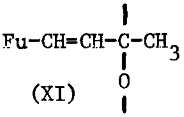
$$\overset{|}{\mathrm{Fu{-}CH}}\mathrm{{-}CH{=}}\underset{\underset{|}{O}}{\underset{|}{\mathrm{C}}}\mathrm{{-}CH_3}$$

(IX)



$$\overset{|}{\mathrm{Fu{-}CH}}\mathrm{{-}CH_2{-}}\underset{\underset{|}{O}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CH_2}$$

(X)



$$\mathrm{Fu{-}CH{=}CH{-}}\overset{|}{\underset{\underset{|}{O}}{\underset{|}{\mathrm{C}}}}\mathrm{{-}CH_3}$$

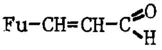
(XI)

Of these three possible monomer sequences arising from C=O rather than C=C opening, XI must be the most frequently present in the "complex" polymer. Indeed, it is the only one bearing the conjugated Fu-CH=CH- function detected in the spectra. Although the other two structures cannot be totally excluded, their role is certainly minor or negligible.

The question then arises concerning the non-polymerisability of compounds IV, V and VI, if polymerisation through the carbonyl group is possible for these ketones. The probable answer is that polyketals (i.e. sequences of C=O openings) are thermodynamically impossible because of the excessively low ceiling temperature associated with the polymerisation of ketones and since IV, V and VI cannot polymerise through the C=C group either (because of steric hindrance and lack of isomerisation of the anion), no propagation will occur. With FA, however, an occasional step involving C=O opening can be thermodinamically allowed if followed by a C=C opening, as shown previously in a similar context (11). In principle, the maximum content of ether units XI in such a mixed polymer is 50%, i.e. a perfectly alternating sequence of structures III and XI, although exceptions have been found due to penultimate effects (11). An inspection of the relative areas corresponding to furanic and vinylic protons (5.5 to 8 ppm) and to aliphatic protons (1.5 to 4.5 ppm) in the NMR spectrum of the complex polymer shown in Fig. 2c, gives a ratio of approximately 1:1. This is compatible with such an alternating polymer structure because unit III gives a ratio of 3:5 (as for the regular polymer, Fig. 2b) and unit XI the reciprocal value of 5:3.

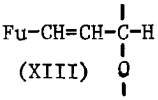
It can therefore be concluded that the second mode of propagation, which accompanies the C=O opening and isomerisation mechanism discussed in section 1. in some anionic polymerisations of FA, takes place through the carbonyl bond. The products of these reactions are thus random sequences of the two alternative structures III and XI, although the latter is probably not found in repeated units for thermodynamic reasons. The occasional presence of structures IX and/or X cannot be excluded or confirmed at present.

In order to corroborate the mechanistic interpretation given above, 2-furylacrolein (XII) was tested as a monomer for anionic polymerisation in the conditions used for FA. It is well known that acrolein can polymerise through the C=C and the C=O bonds and specific conditions have been found to favour either opening so as to obtain polyvinyl aldehyde or polyacetal with pendant vinyl groups(12).Thermodynamic restrictions concerning the opening of the carbonyl bond do not play an inhibiting role with this monomer: indeed, aldehydes polymerise more readily than the corresponding ketones because their ceiling temperature is somewhat higher. 2-Furylacrolein has only been polymerised cationically and by γ-radiation (13). The present experiments showed that the anionic initiation with BuLi and t-BuOK produces low molecular-weight polymers containing predominantly the unit XIII arising from C=O propagation. Under similar experimental conditions, t-BuOK gave much higher polymerisation rates than n-BuLi.



$$\text{Fu-CH=CH-C}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow H}$$

(XII)



$$\text{Fu-CH=CH-}\overset{|}{\underset{\underset{|}{\overset{|}{O}}}{C}}\text{-H}$$

(XIII)

These results confirm the tendency of furfurylidene carbonyl compounds to propagate anionically through the opening of the C=O group, particularly with t-BuOK. This tendency is restricted to a single step with ketones because of thermodynamic limitations, and no polymerisation occurs with IV, V and VI since the alkenyl group is sterically hindered and no proton transfer is possible. With FA, the isomerisation polymerisation through the C=C bond is instead possible and prevails under most conditions or is concomitant to single C=O opening events. Note that with 2-furylacrolein polymerisation through the alkenyl group is also sterically prohibited and isomerisation of the active species by proton transfer obviously impossible.

The low molecular weights obtained with FA must be due to chain-breaking reactions. The nature of these processes is still obscure and work is in progress to characterise possible transfer and termination reactions and the structure of the polymer end-groups.

Conclusions

The anionic polymerisation of furfurylideneacetone does not proceed by a simple 1,2-opening of the carbon-to-carbon unsaturation because that moiety is too crowded by the substituents at each side. Under suitably selected conditions, the activation of the C=C bond is followed by rearrangement of the anion to give a sterically-free active species through a 4-2 proton transfer, and the repetition of the sequence of events produces low molecular-weight polymers possessing the 1,4 structure III. Another type of propagation is also possible, viz. one involving the opening of the carbonyl bond, but this step cannot repeat itself due to thermodynamic restrictions and units with structure XI are found in the polymers prepared with certain initiators at the higher temperatures. Their maximum concentration is 50%, in which case an alternating "copolymer" of units III and XI is obtained. Previous mechanistic interpretations based on a Michael-type stepwise propagation (6,7) seem unlikely in the light of the present results.

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