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On the Polymerisability of 2-Alkenylfurans with Anionic Initiators

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Summary

Various attempts to induce the anionic polymerisation of 2-vinylfuran and some of its homologues were carried out. Negative results were obtained, except with sodium biphenyl in hexamethylphosphotriamide, a system which gave limited yields and not a living polymerisation. The results are interptreted on the basis of side reactions of the furan ring marring the normal vinyl propagation. A critical discussion of previous conflicting reports is also given.

Introduction

Within the general study of the behaviour of furan derivatives in polymerisation reactions, which we have been carrying out for the past several years (GANDINI,1977), we became interested in the possibility of polymerising 2-alkenylfurans with anionic initiators. Previous work on this subject was scanty and contradictory. In fact, while ANDREEVA and KOTON (1956) had reported that 2-vinylfuran (VF) could be polymerised with n-butyl lithium (BuLi) and GOUTIERE *et al.*(1963, 1965) had claimed that the same monomer would give living polymerisations with sodium and sodium naphthalene (NaN) in tetrahydrofuran (THF), KUWATA *et al.* (1960) had failed to obtain poly(2-vinylfuran) (PVF) with sodium in THF and IWAKURA and TODA (1975) had briefly mentioned that 2-alkenylfurans did not give living systems with NaN. Given this dichotomy and the general lack of details in all the papers mentioned, we decided to carry out new experiments using highly purified reagents and high-vacuum techniques to obtain a clear and unequivocal answer.

Experimental

The furan monomers were synthesised, purified, dried and handled *in vacuo* as reported elsewhere (GANDINI and MARTINEZ, 1978). THF and hexamethylphosphotriamide (HMPT) were purified by standard techniques and kept *in vacuo* over a sodium mirror. Solutions of BuLi in hexane and THF (Fluka) were used without further purification. Sodium was prepared by the vacuum thermal decomposition of sodium azide (BDH) and purified by double sublimation in the vacuum line. Solutions of NaN in THF and sodium biphenyl (NaB) in HMPT were prepared follozing strict 'anionic' procedures and placed into breakable phials under vacuum. Their concentration was

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determined spectroscopically. The other monomers used were also purified by standard techniques, then dried, stored and handled in the vacuum line. Reactions were conducted in all-glass devices, provided with 1 mm and 1 cm quartz cells, which were charged with the catalyst phial(s), evacuated, filled with the monomer solution, and sealed off the line. After crushing the catalyst phial at the desired temperature, any change in the uv-visible spectrum was recorded. The search for polymer at the end of each run involved neutralisation with excess methanol containing a little acetic acid, filtration and vacuum distillation of the filtrate. Residues and volatile products were carefully characterised using ir,nmr and uv-visible spectroscopty, glc and elemental analysis. Molecular weights were determined by vapour-pressure osmometry (Knauer).

Results and Discussion

When VF was mixed with BuLi in Hexane or THF at room temperature, no polymerisation was observed even when a) the concentration of catalyst was as high as 2 M, b) repeated additions of the latter were carried out and c) up to 100 hours had elapsed. The solutions slowly turned orange-red without appreaciable change in viscosity. After neutralisation, 95 to 98% of the monomer was recovered and the organic residue consisted of traces of an orange resin of indefinite structure, but certainly not PVF (ir,nmr).

The interaction of sodium mirrors with solutions of VF in THF(-20 to 30°C) also resulted in the development of an orange colour, but in these experiments a reddish deposit was formed on the catalyst's surface. This resinification was the faster, the more concentrated the VF solution. With undiluted monomer the reaction proceeded rapidly with appreciable heating. Once again, analysis of the resin showed complex structural features indicating the presence of conjugation and branching due to the participation and cleavage of the furan ring in the reaction. None of the typical spectroscopic features of PVF (GANDINI and MARTINEZ, 1976) could be discerned.

The reactions of VF (0.2 - 2 M) with NaN (10^{-4} - 10^{-2} M) at temperatures ranging from -78 to 30°C always produced the instantaneous disappearance of the catalyst's green colour, which was slowly replaced by a pink tint characterised by a broad maximum around 500 nm. Successive additions of catalysts reproduced the behaviour of the first mixing. Successive additions of monomer did not produce any noticeable change. The solutions were left for periods ranging from minutes to 50 hours and no increase in viscosity was ever observed. The recovery of uncreacted monomer always amounted to more than 95%, leaving only traces of a resin of complex structure, bearing no resemblance to PVF.

2-isopropenylfuran and 2-vinyl,5-methylfuran was also tried with the same catalytic systems and the results were similar to those obtained with VF, i.e. no polymerisation occurred.

The activity of the catalysts used in this work was tested by carrying out standard polymerisations of isoprene, styrene and methacrylate. All these reactions proceeded normally giving polymers with the expected DP's. Since special care was taken to purify and dry (CaH_2) the alkenylfurans, we can exclude that (acidic)impurities could have been the cause of their failure to polymerise.

Before discussing the implications of the present results, it is instructive to review the reactivity of furan and 2-alkylfurans towards strong bases in non-aqueous media. Metallation of furan and 5-methylfuran at C-2 can be accomplished in low yields with Na-K alloy (GILMAN and BREWER, 1934) or much better with BuLi (RAMANATHAN and LEVINE, 1962; HEATHCOCK et al., 1969): 2-furyllithium is stable and has become a common precursor in synthetic work. The reaction of furan with NaN produces some resinification, but no 2-furylsodium (NORMANT and ANGELO, 1961). When 2-ethylfuran is treated with Na-K alloy or with NaN in THF, brown oligomers are slowly formed (DP~10, low yields), the structure of which has not been studied (GOUTIERE, 1963; GOUTIERE et al.,1963; GOUTIERE and GOLE, 1965). The latter authors also examined the effect of sodium, potassium, Na-K alloy and NaN on a THF solution of PVF prepared by radical initiation (DP~1000). In all reactions they observed an increase in viscosity with time and, with Na-K alloy and NaN, the partial precipitation of a brownish crosslinked product. All the reactions studied by GOUTIERE et al. must be regarded as inefficient, given the high catalyst concentrations used and the low yields obtained. Synthetic work carried out in our laboratory (GALEGO and GANDINI, 1975) showed that the metallation of furan and 2-alkylfurans with BuLi proceeded with high yields, but was always accompanied by minor side reactions giving reddish resins which resembled closely those obtained in the attempted polymerisations of 2-alkenylfurans described above. KASAI and McLEOD (1973) found that irradiation with visible light of an argon matrix containing sodium and furan at 4°K induced an electron transfer reaction giving the furan radical anion. Its esr spectrum suggested that the ring had opened at the C - O bond, and the structure proposed placed the negative charge on the oxygen atom and the unpaired electron on the carbon atom at the opposite end. It seems likely that the resinification of furan and 2-alkylfurans, including the branching and crosslinking of PVF, proceeds through such intermediates which of course would be very unstable in solution and prone to attack the parent compound. Ultimately, oligomeric species of complex structure would be formed, i.e. the familiar orange resins, or the brownish gel from PVF. Alternatively, the origin of these products could be attributed to ring-opening reactions similar to those encountered with thiophene and 2-alkylthiophenes in a similar context (GRÄFING and BRANDSHA, 1976), followed by resinification of the acetylides.

Given this basis, we can now analyse the behaviour of 2-alkenylfurans vis-à-vis anionic initiators with more hindsight. We believe that the results we obtained with sodium and BuLi show conclusively that the monomer's vinyl group is not activated for a classical anionic propagation. Instead, the ring is attacked, probably through a mechanism similar to those invoked above, and a little resinification occurs. Therefore, the claim of ANDREEVA and KOTON

(1956) that VF can be polymerised by BuLi (polymer structure not determined), and that of GOUTIERE et al. (1963) that sodium in THF can generate the VF radical anion, which initiates the living polymerisation of its monomer, must be considered erroneous. The latter authors described the radical anion of VF as "a reddish-orange compound little soluble in THF", giving no physico-chemical evidence of its structure. We think that had the radical anion really formed, it would have been quite soluble in THF. Our results with sodium-VF-THF and the report of KUWATA et al. (1960) on the same system (coloration, oligomerisation, but no polymerisation) prove beyond doubt that the reddish insoluble compound was not the radical anion of VF, but the same type of resinous material we obtained.

As for the reaction of VF with NaN in THF, we again reject the conclusion of GOUTIERE and GOLE (1965) claiming the formation of the (little soluble) radical anion and the subsequent living polymerisation. The description of their experiment is somewhat mystifying. We have consulted GOUTIERE's Thesis (1963) for a more detailed account, but found even less convincing evidence than in the subsequent paper (GOUTIERE and GOLE, 1965). No attempt was made to characterise the polymers supposedly formed, no kinetics or yields were determined and no study of the nature of the intermediates was carried out. As for the claim that a block copolymer of VF with methyl methacrylate had also been prepared, it was equally unsubstantiated by any experimental evidence as to its real structure. We think that after the interaction of VF with NaN, leading to complex anionic oligomers (see above), the addition of methyl methacrylate resulted in the latter's normal anionic polymerisation. This is what had been previously reported by KUWATA et al. (1960), viz., that while the adduct of sodium with VF could not produce PVF, it could initiate the anionic polymerisation of other monomers (methyl methacrylate, acrylonitrile, etc.).

Our survey also clearly shows that 2-alkenylfurans are not polymerised through the vinylic double bond by NaN in THF (see also IWAKURA and TODA,1975). These monomers however, interact very rapidly with the catalyst as shown by the disappearance of its green colour upon mixing. This reaction could be an electron transfer process which gives the radical anion of the 2-alkenylfuran, an intermediate which, instead of propagating, undergoes a rapid rearrangement probably involving the participation and rupture of the ring. The ultimate species formed are inactive towards their parent monomer but capable of initiating the anionic polymerisation of other monomers.

We also tried to polymerise VF with NaB in HMPT at room temperature. As with NaN in THF, we observed the immediate discoloration of the solution upon mixing, but this time some 10% of polymer was formed. The conversion did not increase further, indicating that again some side reaction had killed the active species. The ir and nmr spectra (GANDINI and MARTINEZ, 1976) of the white product, DP~100, indicated that linear PVF had indeed been formed. We believe that this is the first authentic report of the anionic polymerisation of an alkenylfuran. The yields, however, could not be improved appreciably by adjusting the various experimental parameters.

It is interesting to note that 2-vinylthiophene polymerises to 100% conversion with NaN in THF through what appears to be a truly living mechanism, but with a k_p two orders of magnitude lower than that of styrene in the same conditions (IWAKURA and TODA, 1975). Thus, the thiophene ring is less reactive than the furan one in that it does not hinder the normal course of the anionic polymerisation of its 2-vinyl derivative.

Conclusions

Although it is possible to induce the anionic polymerisation of 2-alkenylfurans by a suitable choice of catalyst and solvent, the tendency of these monomers, and more specifically of the furan ring, to undergo side reactions after accepting an electron, is detrimental to the propagation through the vinylic double bond. In most cases these side reactions are so fast that no polymer is obtained, but only minor resinification products. Previous reports to the effect that the (living) anionic polymerisation of VF had been achieved are to be regarded as misleading.

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