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The effect of temperature and solvent on the polymerization of 2-propenylfuran

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Summary 2-Propenylfuran was polymerized by trifluoroacetic acid in various solvents. The reactions were accomplished over the temperature range of -78 to 70°C depending on the solvent used. The kinetics of the polymerization in CCl_4 at 0°C was second order. It was observed that the 2,5-disubstituted furan moiety in the chain grows as the dielectric constant of the solvents decreases and that the percentage of alkylated furan ring in the polymer increases with temperature independently from the solvent used. Both findings are explained by considering the possibility of 2-propenylfuran to propagate either by the C-5 position of the furan ring or by the vinyl bond.

Introduction

The 2-propenylfuran (PF) can be polymerized by trifluoroacetic acid (TFA) (1) and other cationic initiators (2,3). The most studied system has been the polymerization by TFA in methylene dichloride (1,4). Depending on experimental conditions the furan ring participates preferentially in propagation or transfer reactions. At room temperature the system is best represented as a "pseudo-copolymerization" where instead of two different monomers one had to consider the same monomer with two alternative reactive sites: the C-5 position of the furan ring and the vinyl double bond. About a third of the furan ring is incorporated into the chain in this way and the percentage of disubstituted furan rings remains constant until 85% of conversion is reached. Transfer with polymer, i.e., alkylation of the pendant monosubstituted rings by active centers, prevails at the end of the polymerization. Vinyl propagation is favoured as the temperature decreases and at -78°C polypropenylfuran (polyPF), without alkylated furan rings, is obtained.

With other initiators such as iodine, boron trifluoride ethearate, methane sulfonic acid and triphenyl methane perchlorate, the relationship between the disubstituted rings of the polymer and the temperature is different and even at -78°C the reactions involving alkylation of the furan rings are not eliminated.

In this work the effect of solvents at various temperatures, on the participation of the furan ring in the polymerization of PF by TFA was explored.

Experimental part

The experiments were carried out using high vacuum techniques. All reagents were purified and thoroughly dried.

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Materials

2-propenylfuran (PF) was synthesized, purified, dried and handled on the vacuum line as reported previously (5). Trifluoroacetic acid (TFA, from Carlo Erba) was submitted to the treatments described (5). Methylene chloride (DCM, from Merck) was purified, dried and handled on the vacuum line by a standard procedure (6). Ethylene chloride (DCE, from Merck) was treated in the same way as DCM. Carbon tetrachloride (CCl_4, from Merck) was fractionally distilled. The middle portion was collected over anhydrous magnesium sulfate (b.p. 76,2°C), transferred to the vacuum line and stored over calcium hydride. Nitroethane (NE, from BDH) was purified and dried as CCl_4.

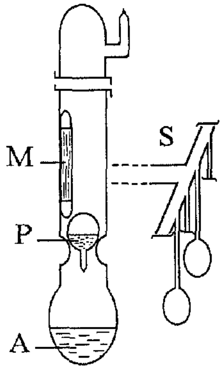


Fig. 1. High-vacuum device used to carry out the experiments.

Techniques

Polymerizations were carried out in a simple device (Fig. 1, without the side arm S). It was charged with a phial, P, containing the TFA solution. PF and DCM were vacuum destilled into the reactor, A, after it was joined to the vacuum line and evacuated for several hours at 10^{-5} Torr. The reactor was sealed off the line and its contents allowed to reach the reaction temperature. The reaction was started by crushing the phial with a magnet covered with glass (M). At the end of the polymerizations the device was opened to the atmosphere, the solution neutralized with aqueous alkali and the polymer isolated by vacuum drying.

The kinetic study was performed in the reactor shown in Fig. 1 but with the side arm S attached to it. The polymerizations were prepared and started as it was explained above. The lateral phials were filled and introduced in a bath at 0°C. They were sealed off periodically. After a phial was opened the polymerizing solution was removed with a pipette. Its content was added into a volumetric flash containing a solution of sodium hydroxide in ethanol. Then it was made level with DCM. The concentration of PF was calculated from the absorption at 264 nm ($\varepsilon = 1{,}40 \times 10^4$), corresponding to the absorption maximum of the π-π^* band of the UV spectrum of PF (7).

Measurements

^{1}H-NMR spectra of polymer solutions were obtained using a Jeol FX-90Q Fourier transform pulse spectrometer at 89,55 MHz.

UV absorptions were determined by a UNICAM SP-1800.

Number-average molecular weights were measured by a Knauer vapor-pressure osmometer.

TABLE 1. *The effect of solvent and temperature on the percentage of alkylated furan rings in polymer chains.*

Solv.	D.C.	°C	% alk.
CCl_4	2,2	- 14	48
		0	50
		45	58
		70	60
DCM	8,9	- 78	0
		23	45
		36	48
DCE	9,1	0	35
		46	45
		58	48
		72	56
NE	28	0	15
		41	38

$[PF]_0 = 0{,}5 - 1$ mol/l
$[TFA]_0 = (1 - 3) \times 10^{-3}$ mol/l.

Results and discussion.

The reactions were carried out over a temperature range of -78 to 70°C, depending of the solvent. The dielectric constants (D.C.) of the solvents ranged between 2.2 and 28.

TABLE 2. *Kinetic results of the polymerization of 2-propenyl furan in Cl_4C a 0°C*

Polim	$[PF]_0$	$[TFA]_0 \cdot 10^2$	$\{[TFA]_0^2/[PF]_0\} \cdot 10^3$	k'
I	0,22	5,3	12,77	0,730
II	0,17	4,2	10,38	0,598
II	0,26	4,2	6,78	0,360
IV	0,35	2,7	2,08	0,117
V	0,70	3,4	1,65	0,106
VI	0,62	4,0	2,58	0,139
VII	0,33	7,5	17,05	0,993

Concentration: mol/l   k' : $l \cdot mol^{-1} \cdot min^{-1}$

Polymerizations in DCM at -78 °C yielded polymers with number-average molecular weights from 3000 to 6000; lower values (800 to 2000) were obtained with increasing temperature.

The structure of the polymers was examined by ^{1}H-NMR spectroscopy. The spectra are identical to those reported previously (1). The content of disubstituted (alkylated) furan rings was calculated from the intensities of proton signals. The results are shown in Table 1.

The kinetics of the polymerization in CCl_4 at 0°C was studied to support the hypothesis that the polarity of the solvents does not change the mechanism relative to that reported for the PF-TFA-DCM system at 36°C (4).

The PF polymerizations shown in Table 2 are kinetically second order.

A plot of the pseudo-constant of reaction, k', vs. the ratio $[TFA]_0^2/[PF]_0$, displayed in Fig. 2, shows a straight line, therefore

$$k' = k\frac{[TFA]_0^2}{[PF]_0}$$

The constant of the reaction, calculated from the slope is $k = 58{,}8\ l^2\ mol^{-2}\ min^{-1}$.

Thus, it can be concluded that the rate of polymerization is given by

$$-\frac{d[PF]}{dt} = k\frac{[TFA]_0^2}{[PF]_0}[PF]^2$$

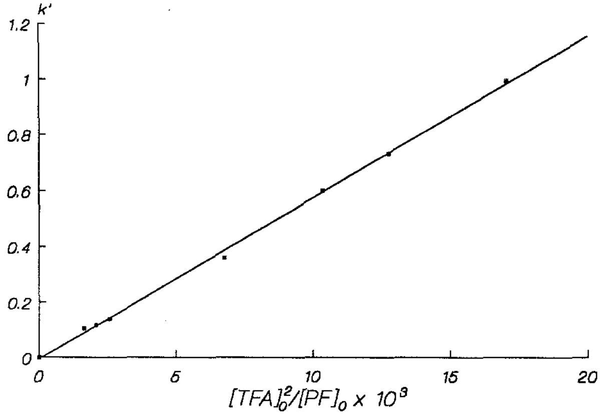
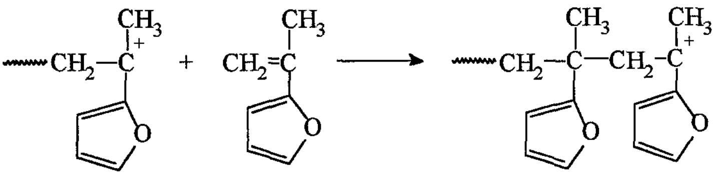
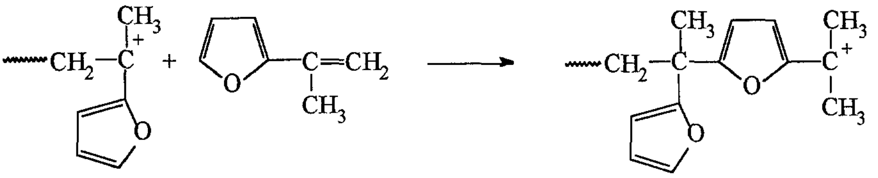


Fig. 2. Dependence of the second order pseudoconstant on the initial concentration of acid and monomer.

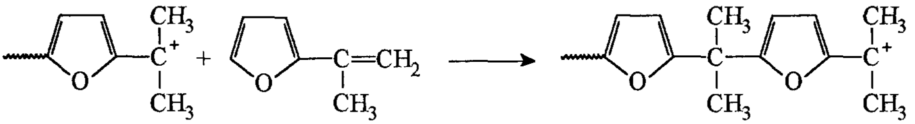
These results agree with those obtained for the PF-TFA-DCM system at 36°C and suggest that the mechanism of the reaction is not altered considerably by a change in the D.C. from 8.9 (for DCM) to 2.2 (for CCl_4) or by a decrease in the temperature. Differences should not be expected in DCE and DCM, and we assume an analogous trend in NE. The mechanism of polymerization of PF may be visualized as a pseudo-copolymerization:



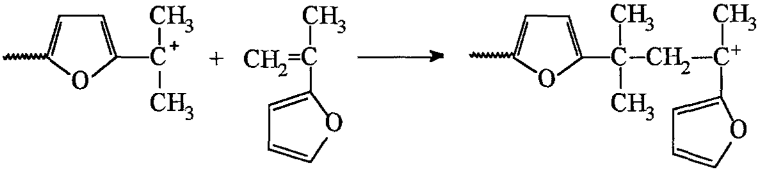
$$M_1^* + M_1 \longrightarrow M_1^* \qquad (1)$$



$$M_1^* + M_2 \longrightarrow M_2^* \qquad (2)$$



$$M_2^* + M_2 \longrightarrow M_2^* \qquad (3)$$



$$M_2^* + M_1 \longrightarrow M_1^* \qquad (4)$$

The relative rate of these reactions determines the structure of polyPF. Thus, the polymerization carried out in DCM at -78°C yields a vinyl polymer because only reaction 1 takes place. At a higher temperature reactions 2 and 3 gain importance and are responsible for the presence of disubstituted furan rings in the polymer.

Concerning the nature of the active centers it was previously reported (8) that the rate decreases in the presence of traces of water and upon the addition of common-anion salts. These observations point out that ionic chain carriers must be present. Moreover, polyPF was obtained from dimethyl furyl carbinol and TFA or trifluoroacetic anhydride. This result was similar to those obtained in an earlier study with aromatic carbinols (9) and indicates that one of the active species must be the ester derived by the initial reaction of the vinyl bond with the acid.

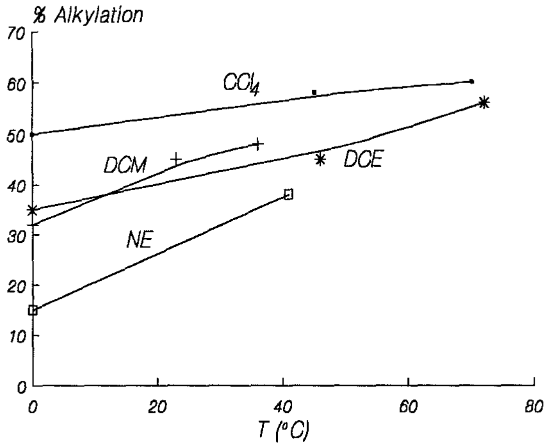


Fig. 3. The content of disubstituted furan rings in polypropenylfuran obtained in various solvents at different temperatures.

According to the data in Fig. 3 above 0°C the percentage of alkylation at a fixed temperature increased in low D.C. solvents, i.e. reactions 2 and 3 are favoured. This trend is typical of ion-dipole reactions. If it is accepted that both ionic and covalent active centers are present in the polymerization, it should be concluded that alkylation is mainly due to ionic centers.

The pseudo-copolymerization scheme allows to rationalize the effect of temperature on the structure of polyPF. Hence, two factors should be considered: First, the activation energies of propagation through the vinyl double bond (eqs. 1 and 4) and the furan ring (eqs. 2 and 3) are quite different since the proportion of alkylated rings in the polymer decreased steadily as temperature was lowered. Thus, the higher activation energy of the alkylation reaction 2 allows the preparation of polyPF of regular structure by working at -78°C (Table 1). This expedient is well known in cationic polymerization in the context of the reduction of transfer reactions, which also display higher activation energies than propagation.

Second, the ceiling temperature (Tc) of vinyl polymerization of PF could be close to the higher temperature used, maybe similar to α-methyl styrene, its phenyl homologue, with a Tc of 61°C (10). To support this possibility some radical polymerizations were tried but all failed in agreement with the report that PF resists radical polymerization (11) while vinyl furan does not (12) (although the furan ring retards (13) or inhibits free radical polymerization (14)). Moreover, 5-methyl-2-propenylfuran polymerizes faster than PF but only through the vinyl bond but at 36 °C; the reaction initiated by TFA in DCM yields only oligomers with a fair amount of unsaturated dimers (1).

The conversion of M_1* to M_2*, by alkylation reaction 2, avoids that reaction 1 comes to equilibrium. With increasing temperature the tendency toward equlibrium should be enhanced and the chain growth will proceed by propagation through the ring. Therefore the percentage of disubstituted furan rings in the polymer should increase at higher temperatures and a limiting value should be reached irrespective of the nature of the solvent.

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