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Crystalline furanic polyisocyanates

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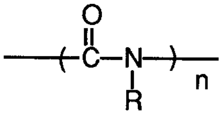
SUMMARY 2-Furfuryl isocyanate and 2-furyl isocyanate were polymerized with several anionic initiators. Cyclic trimers and linear polymers were obtained. These products were characterized by elementary analysis, IR and ^{1}H-NMR spectroscopy, DSC, TGA, polarized-light microscopy, vapour-pressure osmometry and vacuum pyrolysis. The polymers possess a high degree of crystallinity. Their thermal decomposition yields the monomer and the cyclic trimer.

INTRODUCTION

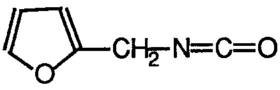
Organic isocyanates are known to give cyclic dimers and trimers in the presence of various basic reagents (1). Shashoua et al. (2) were the first to show that they can be polymerized by an anionic mechanism at low temperature to form linear, high molecular-weight structures which can be classified as "N-Substituted nylons-1".



$$-\!\!\left(\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{N}}\right)_{n}\!\!-$$

Since then, other modes of inducing the polymerization of isocyanates through the N=C double bond have been reported, namely by cationic (3), thermal (4), radiation-induced (4,5) and electrochemical (6) initiation. However, anionic polymerization remains the most versatile technique. Natta and coll. (3,7) obtained crystalline polymers of phenyl and n-butyl isocyanate using anionic initiators such as lithium and sodium alkyls. Many other crystalline polyisocyanates have been prepared and characterized (8) since that pioneering work.

In this paper we report the polymerization of furanic isocyanates as part of our continuing investigation on the polyaddition and polycondensation reactions of furanic monomers and the properties of the resulting polymers and copolymers (9). Two compounds were studied: 2-furfuryl isocyanate **1** and 2-furyl isocyanate **2**.



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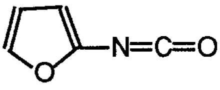

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EXPERIMENTAL

Synthesis and Anionic Polymerization of 2-Furfuryl Isocyanate. Monomer **1** was prepared by the reaction of furfuryl amine with triphosgene, then characterized and purified as previously reported (10). A typical polymerization procedure involved the introduction of 20 ml of solvent and 3 ml of monomer in a three-neck flask equipped with magnetic stirring and dry-nitrogen inlet and outlet. After cooling to the desired temperature, the anionic initiator was added under vigorous stirring. The mixture became rapidly viscous in the runs in which polymer was formed. After 2 hrs, methanol was added in large excess and the precipitated product was filtered, washed with methanol and vacuum dried.

Synthesis and Polymerization of 2-Furyl Isocyanate. Monomer **2** was synthesized from commercial 2-furoyl chloride via the corresponding azide by the Curtius reaction already described (10,11). Because this compound is extremely reactive when exposed to the atmosphere in bulk (10), its polymerization was carried out directly with the toluene solution obtained at the end of the synthesis. Typically, a three-neck flask equipped with magnetic stirring and dry nitrogen inlet and outlet was charged with 20 ml of dry toluene and 5 g of 2-furoyl azide. The resulting solution was heated progressively from room temperature to 90°C in 2.5 hours. When no more nitrogen evolved from the reaction medium, the solution of **2** was cooled to -78°C and the anionic initiator added. After 2 hrs the medium was quenched with excess methanol and the precipitated product filtered, washed and dried as above.

Solvent Extractions and Characterization of Products. The white microcrystalline powders obtained in both polymerizations were extracted with cold acetone to separate the cyclic trimers from the linear polymers. The polymers were then submitted to soxhlet extractions with various solvents in order to separate the low molecular weight polymer of comparatively low degree of crystallinity from its high moleculal weight counterpart which was also highly crystalline. All fractions were analysed by various techniques of structural identification, as discussed below. Some of the products were also submitted to DSC, TGA and vacuum pyrolysis.

RESULTS AND DISCUSSION

General Features

The Role of the Initiator. Contrary to the positive effect of sodium cyanide as anionic initiator with aliphatic isocyanates (12), this salt was totally inactive with our monomers: neither polymers nor cyclic trimers were found in reaction mixtures involving polar or non-polar solvents, at various temperatures and monomer (**1** or **2**) concentrations after stirring for several hours. It seems likely that a specific interaction between the cyanide anion and the furan ring, e.g. a complexation making the CN^- moieties unavailable for initiation, could be responsible for these failures. Sodium naphthalene and n-buthyl lithium proved instead quite adequate as initiators. Overall yields were of the order of 80% with the experimental conditions described above. No attempt was made however to optimize these yields.

The Role of Solvent Polarity. A major effect was found when comparing results obtained with different solvents. In toluene the tendency was towards the formation of linear polymers, whereas in demethylformamide (DMF) the dominant product was the cyclic trimer. This is precisely the trend observed previously with other isocyanates (12).

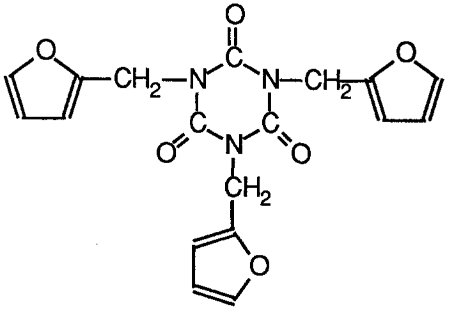
The Role of Temperature. The best results in terms of yield and tendency to give linear polymers were obtained at temperatures between -60 and -80°C.

As a conclusion to this preliminary approach, it can be said that the use of organometallic initiators at low temperatures and non-polar solvents favours the formation of linear polymers.

Characterization of Trimers

The cyclic trimer **3** of 2-furfuryl isocyanate was a white crystalline powder, m.p. 138°C. Anal., calc. for $C_{18}H_{15}O_6N_3$: C 58.54%, H 4.09%, O 25.99%, N 11.38%; found : C 57.92%, H 4.02%, O 26.78%, N 11.28%. Mass spectrum: m/e 369 (M^+). The FTIR and ^{1}H-NMR spectra of **3** are given in Figures 1 and 2. The relevant vibrational bands related to the 2-substituted furan rings are those around 3100 cm^{-1} (w, =CH), 1010 cm^{-1}(m, ring breathing) and 780 cm^{-1} (s, C=C). The strong band at 1690 cm^{-1} reflects the carbonyl stretching and that at 1460 cm^{-1} the -CH_2-deformation (see also the weak band just below 3000 cm^{-1} for the CH stretching of this moiety). The NMR assignments are unambiguous: the singlet at 5.05 ppm (2H) is the resonance of the CH_2 protons, the singlet at 7.36 (1H) is due to the H5 proton, whereas the AB system at 6.37 (2H) arises from the H3 and H4 protons. Structure **3** is therefore unequivocally established

The cyclic trimer **4** of 2-furyl isocyanate was also a white crystalline powder, m.p. 180°C. Anal., calc. for $C_{15}H_9O_6N_3$: C 55.05%, H 2.78%, O 29.33%, N 12.84%; found C 54.54%, H 2.84%, O 29.38%; N 12.43%. Mass spectrum: m/e 327 (M^+). The FTIR and ^{1}H-NMR spectra of **4** are shown in Figures 3 and 4. The IR assignments follow the same criteria as for **3** except for the absence of the strong and weak bands due to the CH_2. On the other hand, the C-N band becomes now clearly displayed at 1410 cm^{-1}. Note also that the C=O band is now at 1740 cm^{-1}. The direct linkage of the furan rings to the nitrogen atom of the isocyanurate heterocycle produces a shift to lower fields for the resonances of the furanic protons, now at 7.71 ppm for H5 and 6.57 ppm for H3 and H4 with the expected integration ratio of 1:2. No other peak is present in the spectrum of Fig.4. All evidence points therefore to the correctness of structure **4**.



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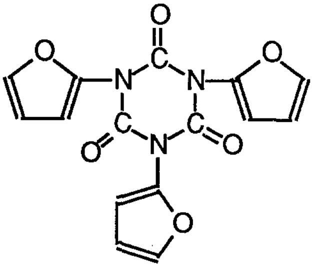

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Characterization of Polymers

Poly(2-furfuryl isocyanate). Samples of crude poly(**1**) gave elementary analyses consistently in agrement with the calculated composition (same as for trimer **3**, i.e. ignoring end groups for the linear polymer). They showed strong birefringence and melted at 180 to 185 °C with decomposition (hot stage polarized optical microscopy). DSC tracings such as that shown in Figure 5 indicated that degradation starts well

Figure 1 : IR Spectrum of trimer **3**

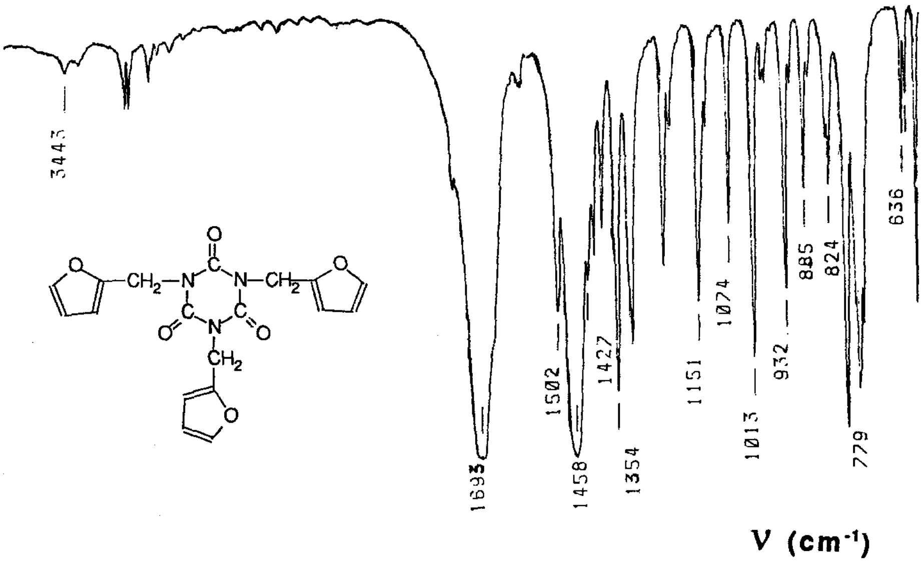


Figure 2 : 'H-NMR Spectrum of trimer **3**

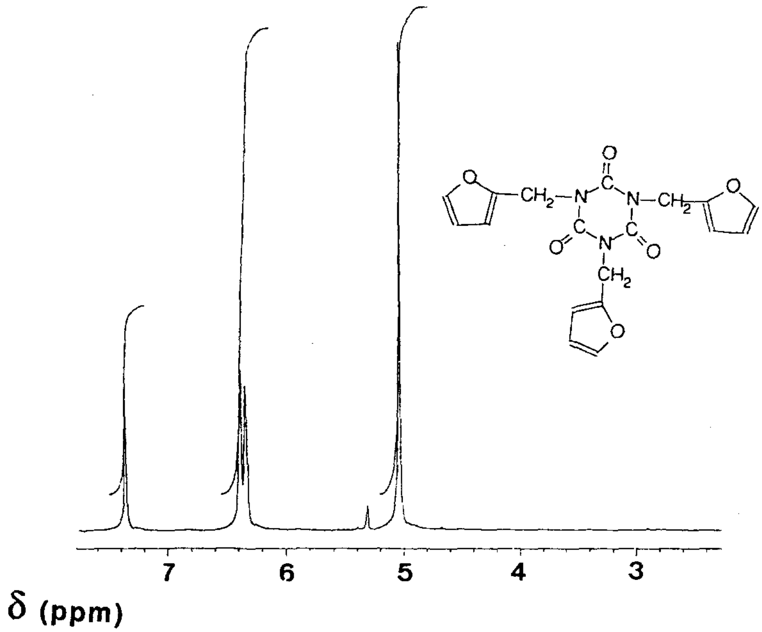


Figure 3 : IR Spectrum of trimer **4**

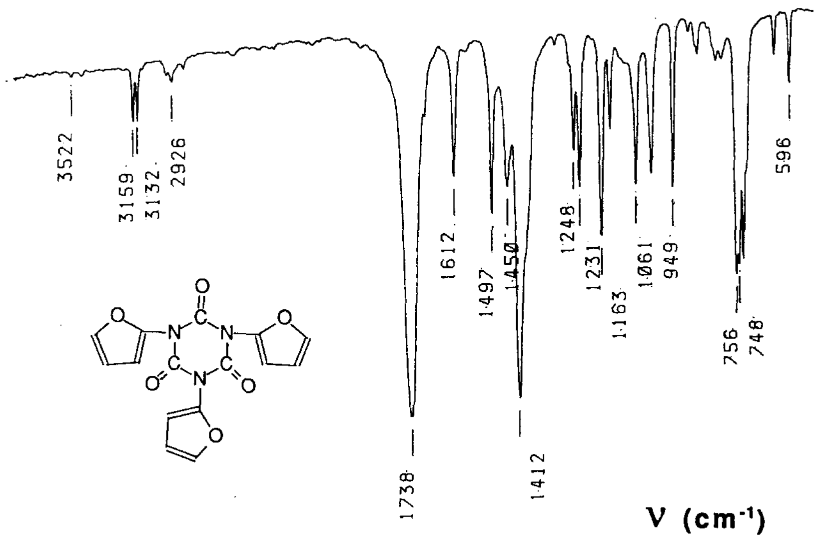
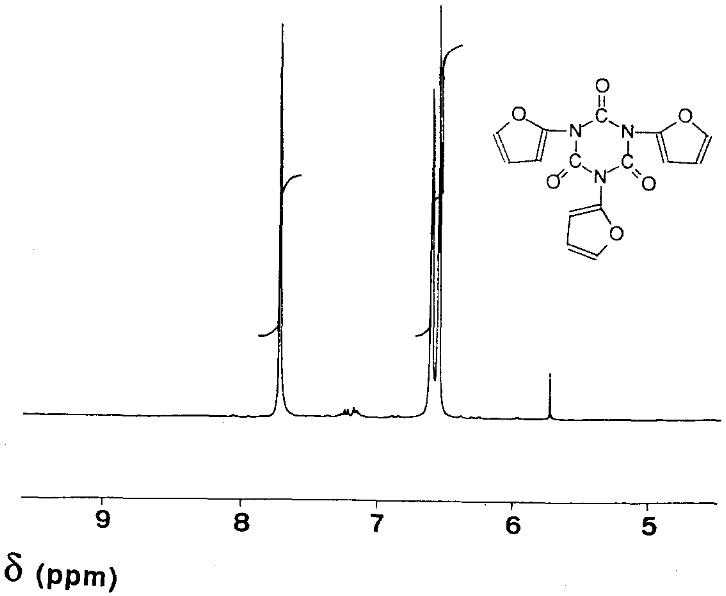


Figure 4 : 'H-NMR Spectrum of trimer **4**



below melting. The FTIR and ^{1}H-NMR (portion soluble in CD_2Cl_2) spectra resembled closely those of the cyclic trimer **3** (see Figs. 1 and 2), but with the less sharp features typical of polymeric structures. There is little doubt that these polymers have a "nylon-1" structure, i.e. arise from the opening of the C=N bond in the polymerization of **1** to give linear chains.

Extraction of these crude polymers with boiling methylene chloride or acetone or benzene gave between 12 and 16% of soluble materials. These had number-average molecular weights of 3000 to 4000 (vapour-pressure osmometry) and the same melting behaviour as the crude polymers. They appeared however less strongly birefringent when observed under polarized light. The residues of these extractions of poly(**1**) were insoluble in all solvent tested probably because of a higher degree of crystallinity and/or a higher molecular weight. The melting features were the same as those of the soluble fractions, but with much stronger birefringence.

Vacuum pyrolysis of these polymers gave a mixture of cyclic trimer **3** (predominant) and monomer **1**, as shown by the FTIR spectra of the collected products. These depolymerizations started at about 160°C. The thermogravimetric analysis of poly(**1**) is shown in Fig. 7 : it confirms the onset of the degradation associated with weight loss at around 150°C.

It seems clear that these chains are readily activated by heat to give species capable of depropagating. Most probably the end groups are responsible for this fragility. No attempt was made to end-cap the polymers in this preliminary study because of the lack of knowledge about the chemical nature of the end groups.

Poly(furyl isocyanate). All samples of poly(**2**) gave very satisfactory elementary analyses, but had molecular weights lower than those of the corresponding poly(**1**). Indeed, extractions with boiling benzene afforded up to 90% of soluble fractions with Mn of only 800 to 1000. Again, the residue was totally insoluble in organic solvents and again both the soluble and the insoluble fractions had the same melting point of 370 to 375°C as observed at the microscope and confirmed by DSC. This transition of crystalline poly(**2**) takes place without apparent decomposition before the melting, as shown by the DCS tracing of Figure 6.

The FTIR and 1H-NMR spectra of these polymers were practically identical to those of the cyclic trimer **4** (see Figs.3 and 4). Therefore, here too one is dealing with linear chains with a "nylon-1" structure resulting from polymerization of **2** through the C=N double bond.

The fact that the percentages of soluble fractions were high and their molecular weight low suggests that chain transfer might have been very important in the polymerizations of **2**. Since the monomer was not purified after its synthesis, it seems likely that traces of furoyl azide remaining in solution and/or side products formed in these syntheses could have been responsible for such transfer reactions.

Vacuum pyrolysis of poly(**2**) confirmed the remarkable thermal stability of these products: monomer and cyclic trimer were formed, but only above about 385°C.

The large difference in the thermal stability of the two polymers is not easy to rationalize. The behaviour of poly(**1**) is close to that of poly(alkyl isocyanate)s (13) which start decomposing just below 200°C. The absence of the methylene group in the poly(**2**) structure makes it stiffer with respect to chain bending. This would account for the much higher melting point, but not necessarily for such a major stabilization towards depolymerization, unless the latter process required considerable chain bending to release the cyclic trimer through a concerted intramolecular rearrangement, as suggested for poly(alkyl isocyanate)s (13).

This investigation is being pursued further in order to (i) disentangle some of the persistent problems, (ii) optimize the polymer syntheses and molecular weights and (iii) try and stabilize the product from 2-furfuryl isocyanate.

Figure 5 : DSC tracing of poly(1)

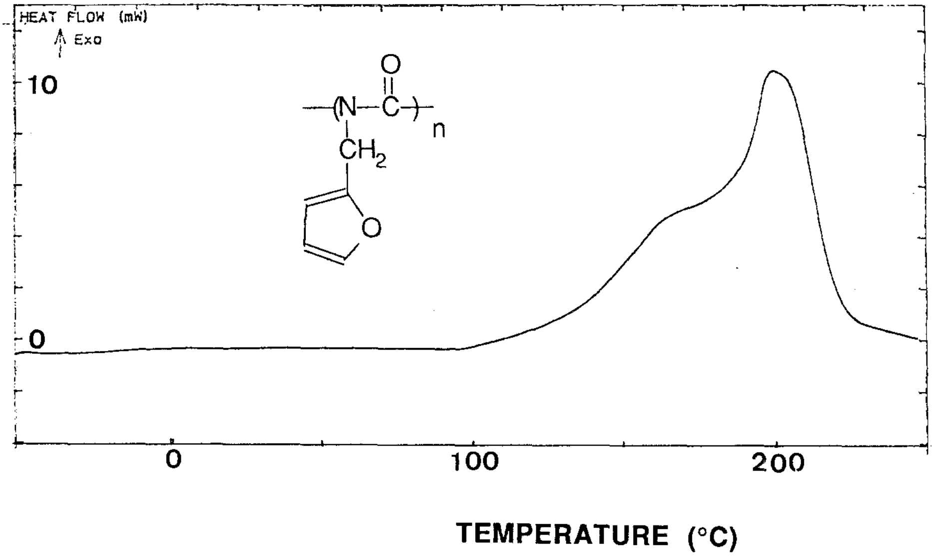
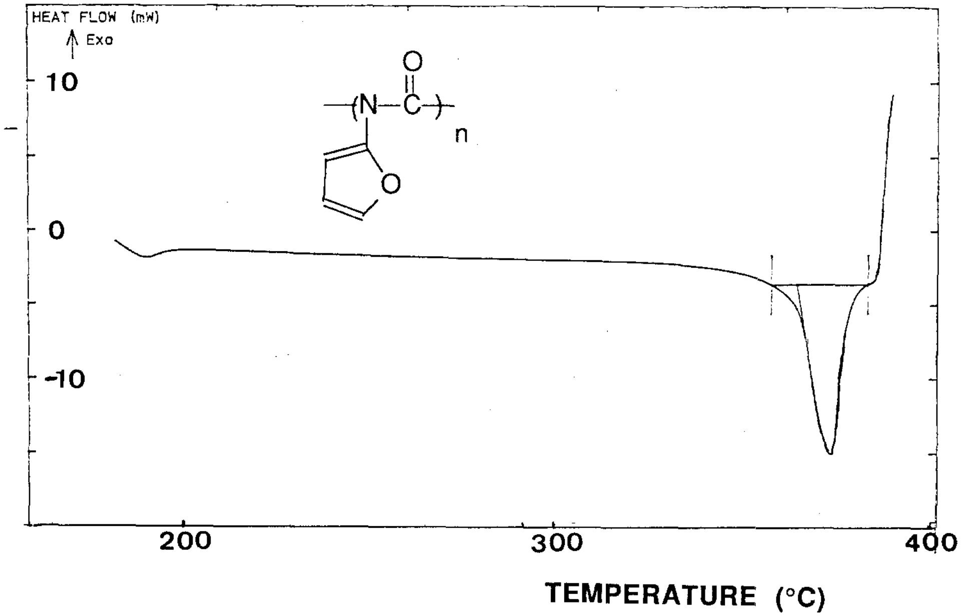


Figure 6 : DSC tracing of poly(2)



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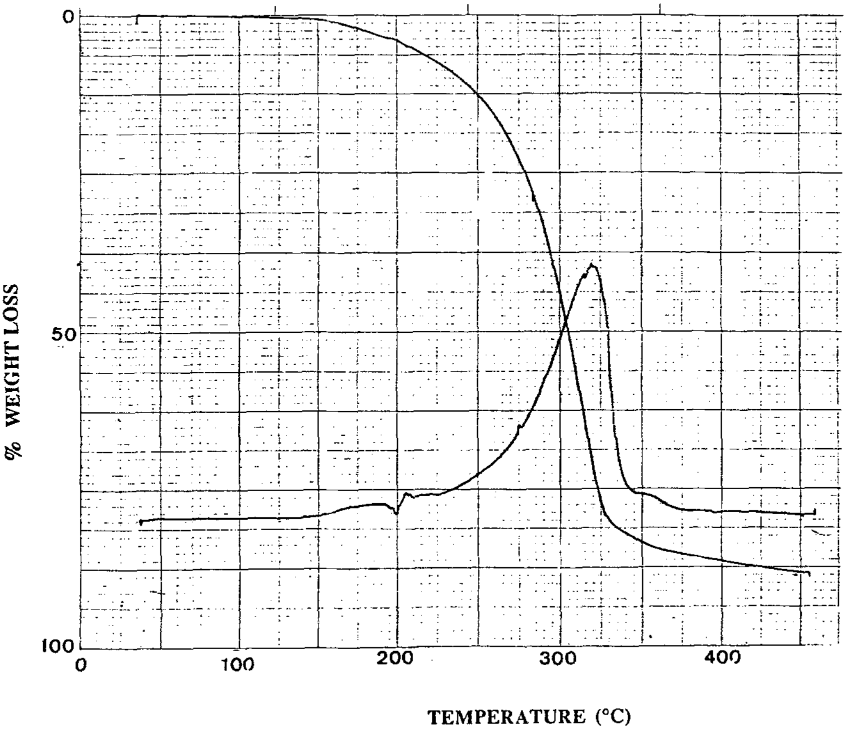

Figure 7 : TGA of poly(**1**)

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