Polymer Bulletin 21, 555–562 (1989)

Polymer Bulletin

Urethanes and polyurethanes bearing furan moieties

1. Synthesis and characterization of monourethanes

J. Quillerou[1], M.N. Belgacem[1], A. Gandini[1,*], J. Rivero[2], and G. Roux[2]

[1]Ecole Française de Papeterie (INPG), BP65, F-38402 St. Martin d'Hères, France
[2]Centre Scientifique et Technique du Bâtiment, 24, rue Joseph-Fourier,
F-38400 St. Martin d'Hères, France

SUMMARY

In view of a study on the preparation and properties of polyurethanes containing furan rings, it was deemed necessary to carry out a preliminary investigation on the synthesis and characterization of simple furanic urethanes given the paucity of information available on this family of compounds. Three types of combinations were tested, viz; (i) furanic alcohols plus non-furanic isocyanates; (ii) non-furanic alcohols plus furanic isocyanates; (iii) furanic alcohols plus furanic isocyanates. The 21 urethanes thus obtained were fully characterized: they are stable (with one exception) and their synthesis is not marred by secondary reactions, ie the furan ring does not introduce "side effects".

INTRODUCTION

This preliminary study deals with the synthesis of monourethanes of the furan series, the kinetics and mechanisms of their formation, the confirmation of the expected structures (and corresponding search of secondary products) and their stability to long-term storage. Preliminary because our main concern is to investigate the preparation and properties of the corresponding polyurethanes in order to expand further our insight into the field of furan polymers (1).

Little has been published about furanic monourethanes (carbamates) and all available information is rather dated (2) and qualitative with very few elements of characterization. Indeed, even the parent field of furanic monoiosocyanates is scanty and essentially limited to furyl isocyanate (3). It seemed therefore appropriate to conduct a detailed study on these compounds before tackling the problem of polycondensation leading to new polyurethanes bearing furan heterocycles. The results presented in this communication describe the synthesis and characterization of two monofunctional isocyanates and twenty one monourethanes derived from them and/or furanic alcohols.

EXPERIMENTAL

2-Furyl isocyanate (FI) was synthesized from commercial furoyl chloride via the corresponding azide following a classical route already reported (3,4). Its proton NMR spectrum is shown in Fig.1: the chemical shifts agree with published data (3), but here the better resolution provides an access to the coupling constants among the ring protons. The IR spectrum of FI was consistent with the presence of NCO groups (2260cm^{-1}), C=C conjugated with NCO (1640 cm^{-1}) and monosubstituted furan rings (1590, 1520, 930, 800, 725 cm^{-1}). As already pointed out (3,4), this compound readily resinifies in bulk when placed in contact with the atmosphere. It was therefore stored under dry nitrogen at -10°C, but even under these conditions degradation was rather rapid and yielded a polymeric mass. Solutions of FI in chlorinated hydrocarbons were

---

[*] To whom offprint requests should be sent

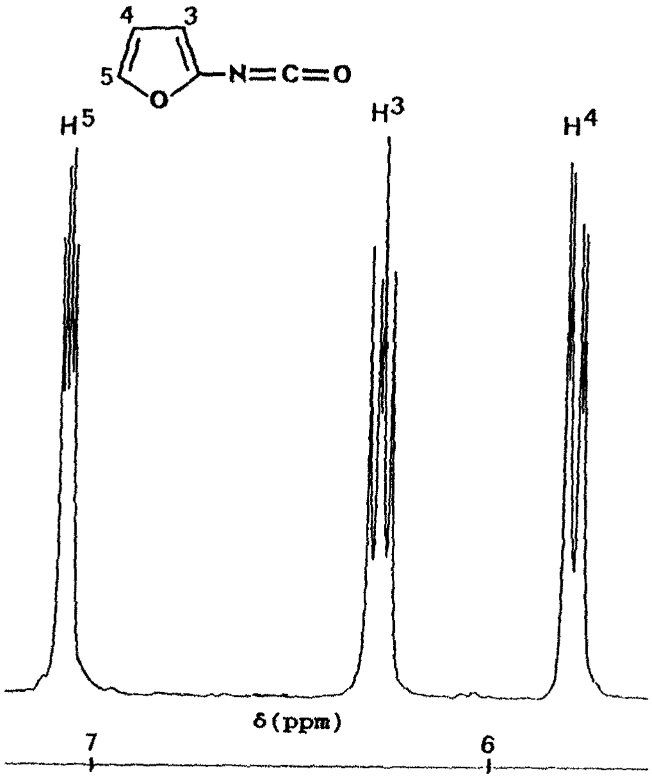


Fig. 1. 100-MHz ^{1}H-NMR spectrum of 2-furyl isocyanate in CD_2Cl_2. The area of the three peaks is the same.

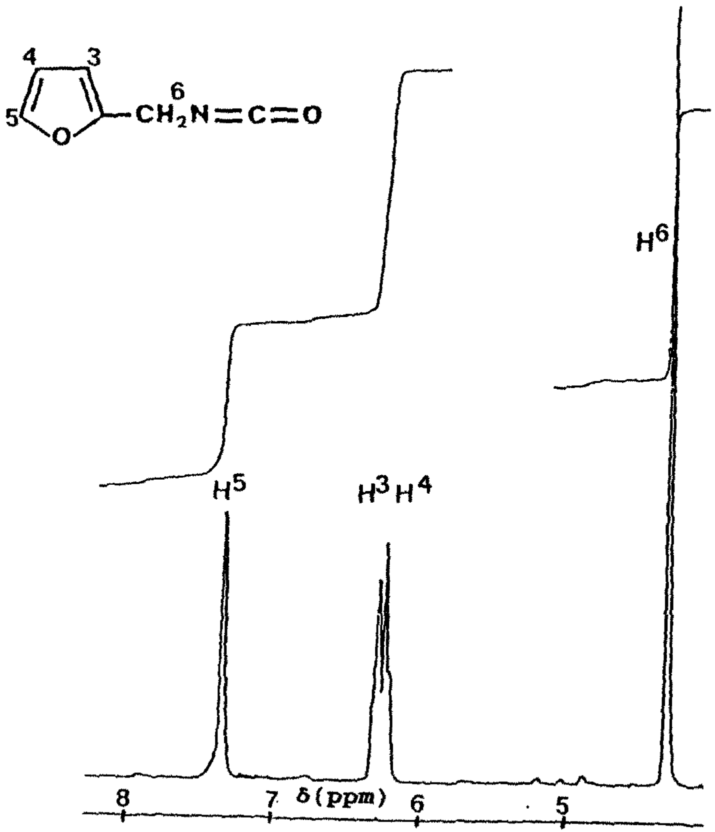


Fig. 2. 100-MHz ^{1}H-NMR spectrum of 2-furfuryl isocyanate in CD_2Cl_2.

stable for weeks as indicated by the fact that the spectrum shown in Fig.1 did not change appreaciably.
The reaction of FI with alcohols were conducted using freshly distilled samples to avoid contamination by the products of its degradation
2-Furfuryl isocyanate (FRI) was prepared from commercial furfuryl amine via its chlorohydrate plus phosgene or directly by its reaction with triphosgene (5). To our knowledge, FRI has not been described before this work. It is a colourless liquid boiling at 158°C at 760 Torr. Its proton NMR spectrum is given in Fig.2 and is consistent with the expected structure. Its IR spectrum showed the characteristic strong band arising from the NCO groups (2260 cm^{-1}), the typical furan vibrations and particularly those belonging to a monosubstituted derivative (1580, 1505, 915, 810, 720 cm^{-1}) and the stretching vibrations due to the methylene group.
FRI slowly resinifies in the presence of acidic impurities, both in bulk and in solution. It was therefore purified by distillation after the synthesis and stored at 3°C under dry nitrogen in neutralized and dried chloroalkanes or chloroarenes.

Non-commercial alcohols of the furan series, namely 5-methylfurfuryl alcohol (MFA), 1-(2-furyl)-1-ethanol (FE) and 2-(2-furyl)-2-propanol (FP), were synthesized by conventional methods which involved the reduction of 5-methylfurfural with lithium-aluminium hydride for MFA and the preparation of 2-furyllithium and subsequent reaction with acetaldehyde and acetone for FE and FP respectively. The purified products had analytical and spectroscopic characteristics identical to those reported in the literature.

All other isocyanates and alcohols used in this investigation were commercial products of the highest purity available.

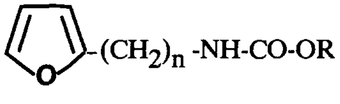
Reactions leading to the urethanes were carried out under nitrogen by mixing with vigorous magnetic stirring equimolar amounts of the specific isocyanate and alcohol as 0.5 M solutions in pure and dry 1,2-dichlorobenzene. The temperature was kept at about 110°C unless otherwise stated. The progress of the reactions was monitored by GLC. Near-quantitative yields were attained for most of the preparations and this required from a few hours to several days, depending on the pair of reagents involved. No catalyst was employed for these syntheses. Products were isolated by evaporation of the solvent under reduced pressure and purified by recrystallization or distillation.

The characterization of these novel monourethanes was conducted by elemental analysis, ^{1}H, ^{13}C NMR and IR spectroscopy, differential scanning calorimetry (DSC) and mass spectrometry.

RESULTS AND DISCUSSION

The urethanes prepared (m.p. in brackets as obtained by repeated DSC scannings) can be classified into three families according to the nature of their precursors, viz :

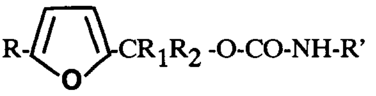
A. Urethanes derived from a furanic isocyanate and a non-furanic alcohol



$-(CH_2)_n$ -NH-CO-OR

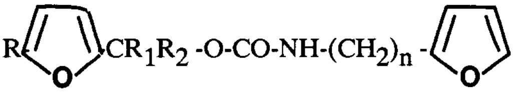
I.*	n = 0,	R = nBu (m.p. 54°C);
II.	n = 1,	R = nBu (m.p. 1°C);
III.	n = 1,	R = Benzyl;
IV.	n = 1,	R = sBu.

B. Urethanes derived from a non-furanic isocyanate and a furanic alcohol



V.	$R = R_1 = R_2 = H$,	R' = nBu (m.p. 26°C);
VI.	$R = R_1 = R_2 = H$,	R' = Ph (m.p. 45°C);
VII.	$R = R_1 = R_2 = H$,	R' = Bz (m.p. 73°C);
VIII.	$R = Me, R_1 = R_2 = H$,	R' = nBu (m.p. 14°C);
IX.	$R = Me, R_1 = R_2 = H$,	R' = Ph (m.p. 39°C);
X.	$R = Me, R_1 = R_2 = H$,	R' = Bz (m.p. 59°C);
XI.	$R = CHO, R_1 = R_2 = H$,	R' = nBu (m.p. 80°C);
XII.	$R = CHO, R_1 = R_2 = H$,	R' = Ph (m.p. 102°C);
XIII.	$R = CHO, R_1 = R_2 = H$,	R' = Bz (m.p. 90°C);
XIV.	$R = H, R_1 = Me, R_2 = H$,	R' = nBu;
XV.	$R = H, R_1 = Me, R_2 = H$,	R' = Ph;
XVI.	$R = H, R_1 = R_2 = Me$,	R' = nBu;
XVII.	$R = H, R_1 = R_2 = Me$,	R' = Ph.

C. Urethanes derived from furanic isocyanates and alcohols



XVIII.*	$R = R_1 = R_2 = H$,	n = 0 (m.p. 65°C);
XIX.	$R = R_1 = R_2 = H$,	n = 1 (m.p. 46°C);
XX.	$R = Me, R_1 = R_2 = H$,	n = 1 (m.p. 30°C);
XXI.	$R = CHO, R_1 = R_2 = H$,	n = 1 (m.p. 70°C).

(* Prepared at room temperature because of the very pronounced reactivity of FI).

In all these reactions the GLC peaks of *both* reagents were found to decrease at the same rate and only one new peak appeared and increased correspondingly. These observations are important because they indicated that the predominant reaction was indeed the -NCO + HO- condensation.

No anomalous structure could be detected from the characterization of these products. In particular, no evidence was found of the participation of the furan ring (eg through the C5 position) in side reactions accompanying the alcohol-isocyanate condensation. Table 1 reports the results of the elemental analyses of a representative selection of the urethanes prepared. The agreement between the calculated and the determined compositions is consistently good except for product I which seems to undergo some atmospheric oxidation (see also comments below).

Table 2 gives the proton NMR features of another typical selection of these products. Fig.3 shows one of these spectra. All the other urethanes gave spectra which were just as consistent with the expected structures as those reported in Table II and no indication of side products when analysing unpurified samples (see however the evolution of product I discussed below).

Several ^{13}C-NMR spectra were also taken to complete the structural assignment. The resonance patterns obtained were always satisfactory as shown in the example of Fig.4.

Composition % / Urethane	C		H		O		N	
	calc.	found	calc.	found	calc.	found	calc.	found
I	59.00	55.97	7.15	7.16	26.20	29.21	7.65	7.31
IV	60.90	60.02	7.67	7.36	24.33	24.80	7.10	7.52
V	60.90	60.34	7.67	7.91	24.33	24.13	7.10	7.32
VI	66.35	66.35	5.10	5.19	22.10	21.22	6.45	6.62
VII	67.52	68.88	5.67	5.65	20.76	20.26	6.06	6.08
VIII	62.54	62.39	8.11	7.99	22.72	21.45	6.63	6.40
XI	58.66	57.90	6.71	6.72	28.41	28.06	6.22	6.07
XII	63.67	63.23	4.52	4.40	26.10	25.77	5.71	5.55
XIII	64.86	64.47	5.05	5.09	24.68	23.91	5.40	5.46
XIX	59.73	59.17	5.01	4.96	28.93	28.69	6.33	6.64
XXI	57.83	57.31	4.45	4.32	32.10	31.19	5.62	5.77

Table 1. Elemental analyses of some of the urethanes prepared in this work (see text).

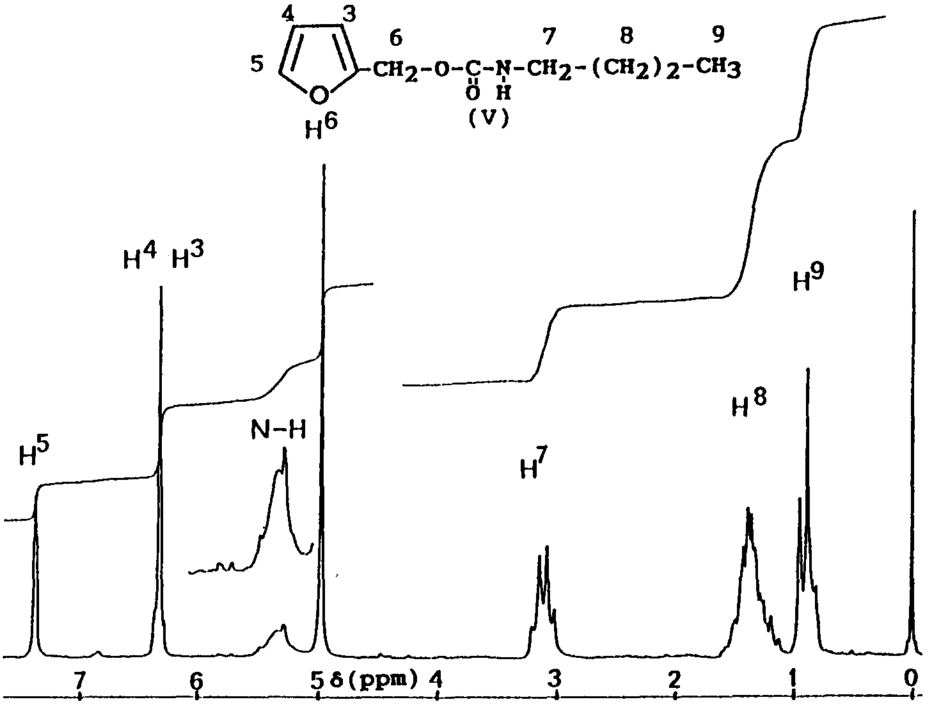


Fig. 3. 100-MHz H-NMR spectrum of urethane V in deuterated acetone.

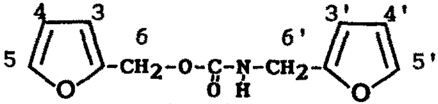
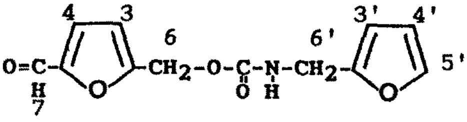
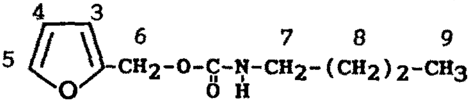
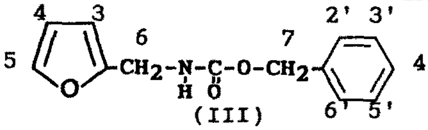
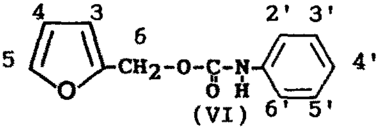
URETHANES	δ,ppm(number of protons, multiplicity)
 (XIX)	H^{3},H^{4},$H^{3'}$,$H^{4'}$:6.19-6.43(4H,m)· H^{5}:7.48(1H,m).H5':7.40(1H,m). H6:5.01(2H,s). $H^{6'}$:4,26-4.32(2H,d). N-H :6.67 (1H,s).
 (XXI)	H^{3}:6.56-6.59(1H,d). H^{4}:7.18-7.21(1H,d). $H^{4'}$:6.23(1H,s).$H^{3'}$ 6.29(1H,s). $H^{6'}$:4.31-4.37(2H,d). H^{6} :5.11(2H,s).H^{7}:9.59(1H,s). $H^{5'}$:7.33(1H,s).N-H:5.52(1H,s).
 (V)	H^{3} ,H^{4}:6.34(2H,s). H^{5}:7.38(1H,s).H^{6}:4.99(2H,s). H^{7}:3.09-3.14(2H,q). H^{8}:1.39(4H,m).H^{9}:0.89(3H,t). N-H:5.29(1H,s).
 (III)	H^{3}:6.16(1H,d).H^{4}:6.23(1H,m). H^{6}:4.23-4.29(2H,d). H^{7}:5.05(2H,s). $H^{2'}$,$H^{3'}$,$H^{4'}$,$H^{5'}$,$H^{6'}$,H^{5}:7.27 (6H,s).N-H:5.47(1H,s).
 (VI)	H^{3}:6.42(1H,s).H^{4}:6.48(1H,s). H^{6}:5.12(2H,s). H^{5},$H^{2'}$,$H^{3'}$,$H^{4'}$,$H^{5'}$,$H^{6'}$:3 res. 7.0(2H,t),7.29(4H,t), 7.55(2H,d).N-H:8.68(1H,s).

Table 2. ^{1}H-NMR data for a selection of urethanes.

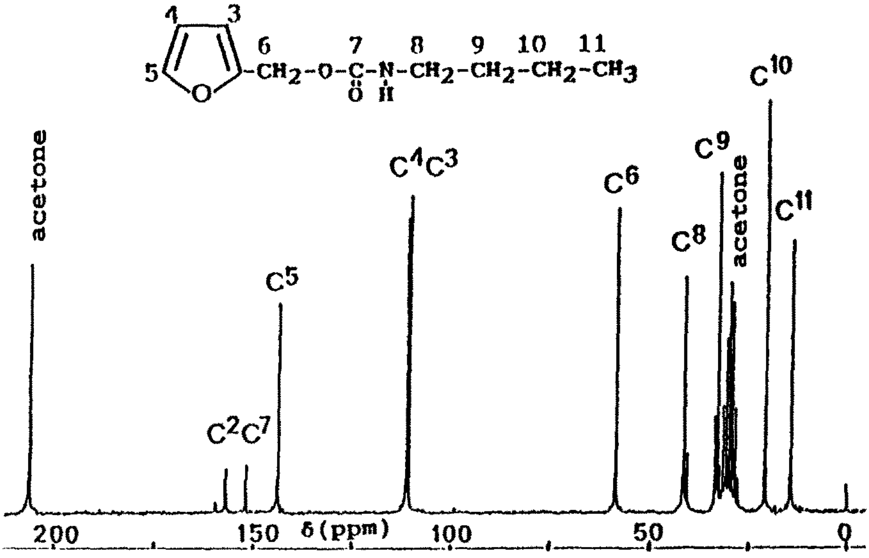


Fig. 4. 25-MHz ^{13}C-NMR spectrum of urethane V in deuterated acetone.

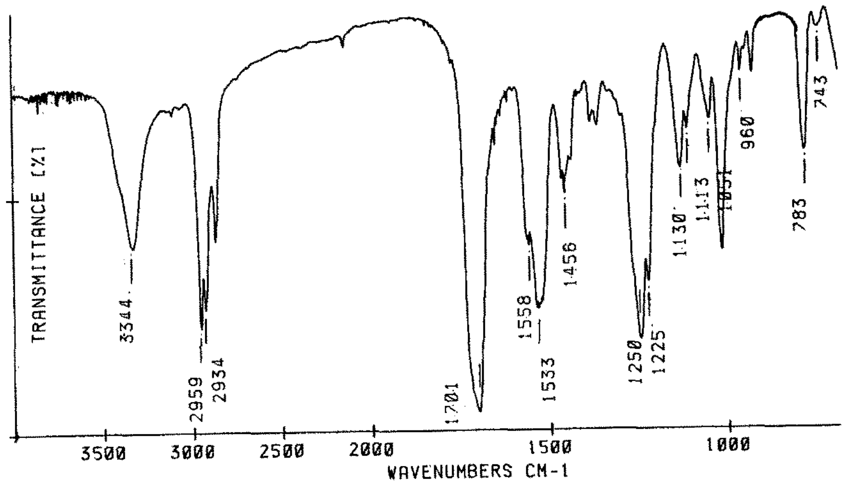


Fig. 5. FTIR spectrum of urethane VIII (liquide film).

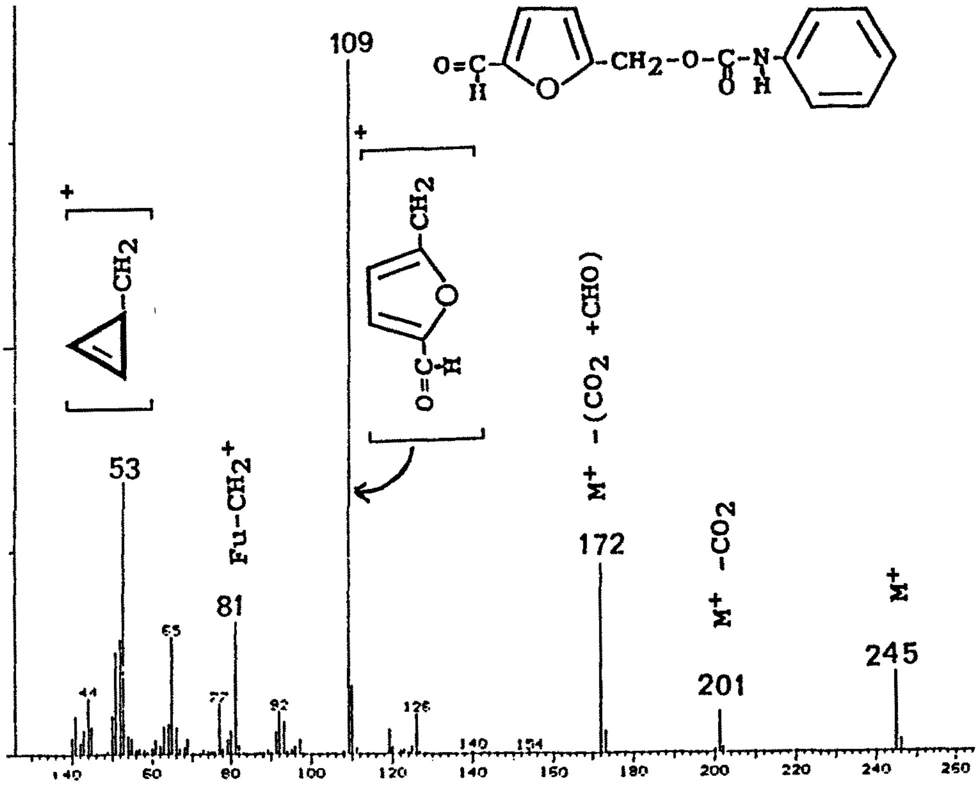


Fig. 6. Mass spectrum of urethane XII. Ionisation potential: 70 eV.

The IR spectra were all characterized by the absence of peaks arising from OH and NCO groups. Conversely, they all exhibited the typical urethane NH band around 3340 and C=O band around 1700 cm^{-1} and the specific patterns of either 2-monosubstituted and/or 2,5-disubstituted furan rings depending on the precursors. Obviously each IR spectrum also bore the features arising from the aliphatic and/or aromatic rest of the its proper structure. A typical example of IR spectrum is given in Fig.5.
Mass spectra representative of the three families of monourethanes were also taken. All molecular ions M^+ appeared at M/e values coinciding with the expected molecular weight of the corresponding compounds. The fragmentation patterns were consistently in line with the structure under scrutiny. Fig.6 displays one such spectrum.
The melting point of those urethanes which crystallized are given above: the values reported were reproducible within experimental error (± 1°C) for each compound from several samples and over several thermal cycles. The latter observation corroborates the conclusion concerning the stability of these products.
One exception must however be reported. In fact, urethane I showed appreaciable degradation with storage time or with respect to heating (melting). Just after its synthesis and isolation it gave spectra entirely in tune with the predicted structure, but after about one week at room temperature the white crystals started deliquescing to give an orange vitreous mass. The proton-NMR and IR spectra of the degraded samples showed the partial disappearence of the furanic "fingerprints" and, as shown in Table 1, the elemental analysis deviated from the calculated composition. The reasons for this lack of stability are most probably to be attributed to the fact that the urethane group is directly linked to the furan ring, and more specifically to the 2-Fu-NH (Fu = furyl) function which is prone to tautomerization, at least in the case of furanic amines. It is nevertheless surprising that whereas urethane I undergoes this slow evolution, its homologue XVIII retained its structure over several months under the same storing conditions.

From the results obtained in this investigation a major conclusion can be drawn, viz that there is no problem or anomaly associated with the use of furanic alcohols and/or isocyanates for the preparation of the corresponding urethanes of the type A, B and C described above. In other words, the presence of furan moieties does not perturb the normal course of these condensation reactions nor does it induce spurious interactions.

The kinetics and mechanism of these processes relative to the well-known behaviour of more common reagents are presented in the following paper of this series (6).

The financial assistance of the 'Agence Française pour la Maîtrise de l'Energie' is gratefully aknowledged.

References

1. Gandini A. (1986), in "Encyclopedia of Polymer Science and Engineering", John Wiley and Sons, New York, Vol.7, p. 454
2. Dunlop A.P., Peters F.N. (1953) "The Furans" Reinhold Publ. Corp., New York.
3. Garcia T., Macias A. (1981) Rev. Sci. Quim. (Cuba) **12** : 239. Chem. Abs. (1982) **98** : 34981.
4. Masson M.A., Bouchy A., Dormoy J.R., Roussy G. (1981) J. Mol. Str. **74** : 11
5. Eckert H., Foster B. (1987) Ang. Chem. Int. Ed. **26** : 894
6. Quillerou J., Belgacem M.N., Gandini A., Rivero J., Roux G., submitted.

Accepted March 21, 1989 C