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A preliminary study of polyureas and poly(parabanic acid)s incorporating furan rings

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Summary

Novel furanic polyureas were synthesised by solution polycondensation reactions between difuranic diamines and aliphatic diisocyanates and then converted to the corresponding poly(parabanic acid)s by heterocyclisation with oxalyl chloride. These condensation reactions and chemical modifications were first studied with model compounds. The polymers were characterised by FTIR and ^{1}H-NMR spectroscopy and inherent viscosity.

Introduction

The growing interest in thermally stable polymers has stimulated the development of numerous classes of these materials such as polyimides, polyoxadiazoles and polyureas, which are known for their excellent thermal stability and high chemical resistance due to the presence, along their backbone, of aromatic or heterocyclic rings connected by thermally stable bonds [1-3]. However, the major defect of these polymers is their poor solubility in organic solvents and the close proximity of decomposition and melting or softening temperatures [4]. Recent intensive investigations in the field of high-temperature materials have resulted in the development of numerous soluble and processable polymers using novel approaches.

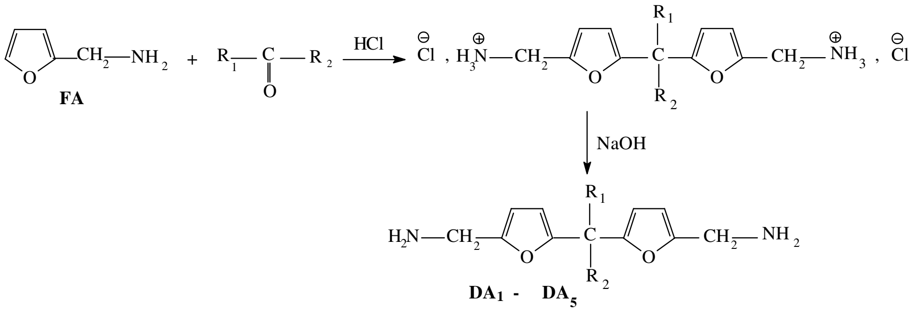
In our recent papers on the synthesis and characterization of some new polyoxadiazoles and polyimides bearing furan moieties [5,6], we showed that the incorporation of this heterocycle along the backbone improved their solubility in organic solvents without sacrificing their heat resistance. It was therefore decided to extend this approach to novel thermally stable polymers bearing furan rings in the main chain, namely polyureas and poly (parabanic acid)s. Typically, polyureas are prepared by solution polycondensation of (i) diamines with diisocyanates, (ii) diamines with carbon dioxide or its derivatives and (iii) diisocyanates with water [7-11], but other synthetic pathways have also been explored [12,13].

The present investigation deals with a preliminary study on the preparation of polyureas based on difuranic diamines and aliphatic diisocyanates in view of both their possible utilisation as elastomers, fibres, adhesives and their role as precursors to the corresponding poly(parabanic acid)s.

Experimental

Monomers and model reagents

The mono- and di-isocyanates used in this work, namely *t*-butyl isocyanate (**BI**), 1,6-hexamethylene diisocyanate (**HMDI**), 1,4-tetramethylene diisocyanate (**TMDI**) and 1,8-octamethylene diisocyanate (**OMDI**), were high purity commercial products employed as received. The difuranic diamines (**DA$_1$-DA$_5$**) were synthesized, as already reported [14], by the condensation of commercial furfurylamine (**FA**) with different ketones or aldehydes in an acidic medium (Scheme 1).



Scheme 1. General pathway for syntheses of the furan diamines.

These diamines (Table 1), purified by vacuum distillation and characterised by FTIR, ^{1}H- and ^{13}C-NMR spectroscopy, displayed the expected structures, without any detectable impurity [14].

Table 1. Yields and boiling points related to the furan amines prepared following the reaction Scheme 1.

Diamine	**DA$_1$**	**DA$_2$**	**DA$_3$**	**DA$_4$**	**DA$_5$**
R_1 / R_2	CH_3 / CH_3	C_2H_5 / C_2H_5	CH_3 / H	C_2H_5 / H	C_6H_{13} / H
Yield (%)	90	80	78	70	70
b.p. (°C) /0.07Torr	140	150	155	160	130

Solvents and catalysts

Commercial dimethylacetamide (DMA), dimethylformamide (DMF), N-methylpyrrolidinone (NMP), dichloromethane (DCM), 1,2-dichloroethane (DCE), pyridine (Py) and triethylamine (TEA) were purified by standard techniques prior to their use.

Model compounds

The trimeric model ureas **1**-**2** were prepared by the reaction of **HMDI** with **FA** and of **BI** with **DA$_1$**, respectively, in DMA at 0°C for 12 h using the appropriate stoichiometric between functional groups (Scheme 2). The parabanic model compound **3** was obtained by treating **1** with commercial oxalyl chloride (**OC**) in DCE at room temperature in the presence of Py (Scheme 3).

Polymerisations

The polyureas **4-10** were prepared according to the following procedure: 5 mmol of the diisocyanate, dissolved into 12.5 ml of dry DMA, were added dropwise for 30 min to a stirred solution containing 5 mmol of the diamine in 12.5 ml of DMA, which was kept at 0°C in a nitrogen atmosphere (Scheme 4). The resulting reaction mixture was then stirred for 24 h at room temperature before being poured into 150 ml of water in order to precipitate the ensuing polymer, which was then isolated by filtration, washed with acetone and vacuum dried to constant weight at 80°C. The term “yield” will be used in this work to express the amount of material obtained following these operations.

Cyclocondensation reactions

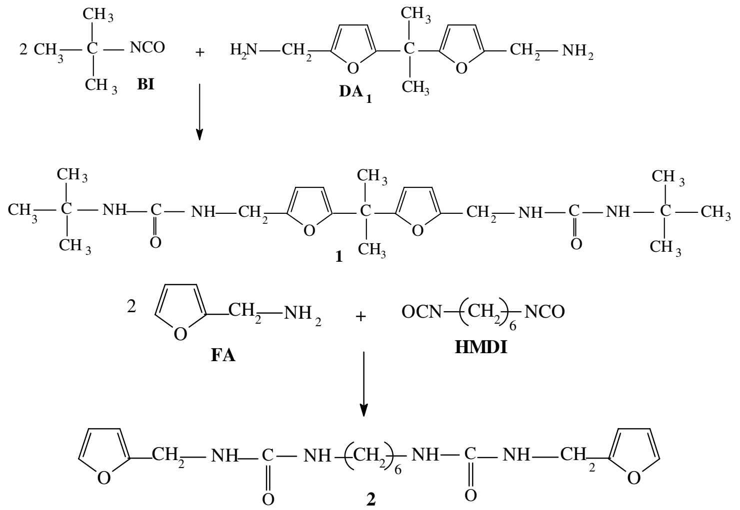
The parabanic polymers **11-17** were prepared by the cyclocondensation reaction of the corresponding polyureas with **OC** (scheme 4). To a suspension of 1 g of the polyurea in 50 ml of dry DCE, containing 1 ml of Py, 4.5 g of **OC** were added dropwise for 30 min at room temperature under stirring. The reaction mixture was then stirred for 12 h at 60°C. The parabanic polymer thus obtained was recovered by precipitation into an excess of water, isolated by filtration, washed with acetone and DCM and finally vacuum dried at 80°C to constant weight.

Characterisation

Structures were examined by FTIR (KBr pellets) and 300 MHz ^{1}H- and ^{13}C-NMR (in DMSO-d6) spectroscopy. Inherent viscosities were measured in m-cresol at 25°C using a 1 g/l polymer concentration.

Results and Discussion

Before tackling the synthesis of the furan polyureas and their chemical modification into polyparabanic polymers, model compounds were first studied, in order to gain an insight into the feasibility and optimisation of the corresponding polymerisation processes. Scheme 2 shows the reactions leading to the urea model derivatives **1**-**2,** prepared by the stoichiometric addition reaction of **DA$_1$** with **BI** and **FA** with **HMDI**, respectively.



Scheme 2. Synthesis of the urea model compounds (**1**: 94% yield, m.p. 265°C; **2**: 92% yield, m.p. 240°C).

The optimized syntheses (see experimental section) gave good yields and it was observed that the use of Py or TEA as catalyst was without effect on the progress of the reaction. The expected structures of **1** and **2** were clearly confirmed by the spectroscopic analyses which showed the presence of urea functions (ν C= O at 1632 cm^{-1}; δ N<u>H</u> at 5.75 and 6.02 ppm; δ <u>C</u>O at 158.75 ppm) and the absence of peaks related to the isocyanate and primary amino groups. As an example of this structural assessment, Figures 1 and 2 show the FTIR and ^{1}H-NMR spectra of model **1**.

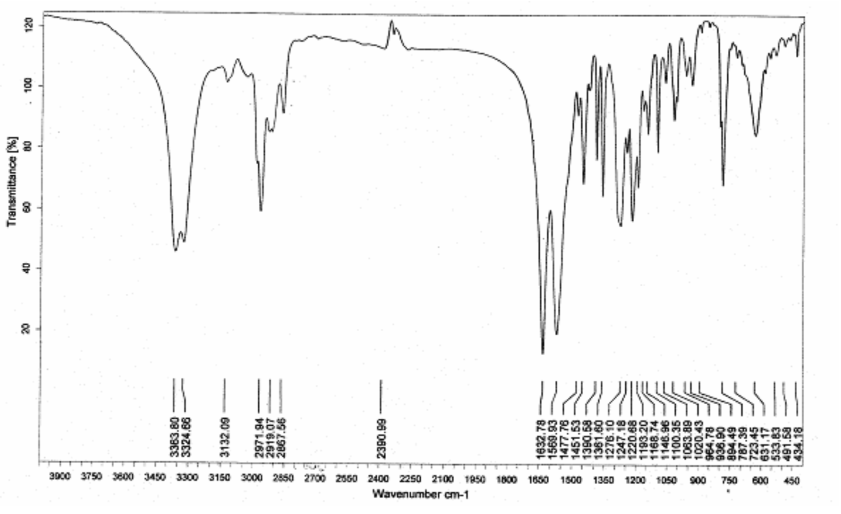


Figure 1. FTIR spectrum of **1** (KBr pellet).

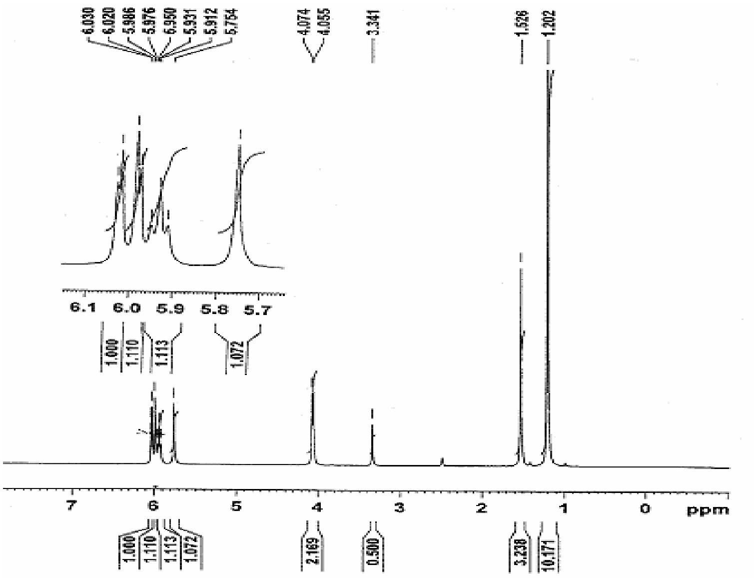
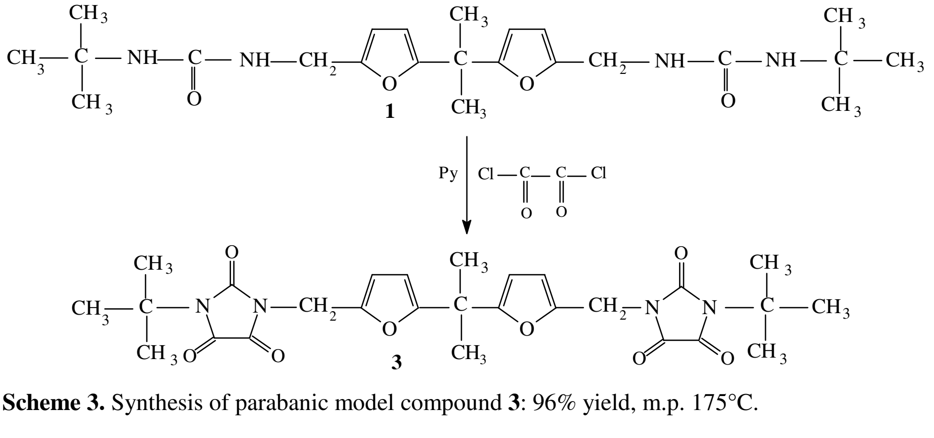


Figure 2. ^{1}H-NMR spectra of **1** in DMSO-*d6*.

The cyclocondensation of **1** with **OC** (Scheme 3) started as a heterogeneous system because of the insolubility of the model urea in DCE. The mixture became homogeneous as the reaction proceeded, because of the solubility associated with the ensuing parabanic ring.

In this case, the presence of Py was essential because it acted both as a catalyst, by activating the chloroformyl functions, and as an acid acceptor. The optimised cyclisation took place quantitatively as confirmed by the fact the ^{1}H-NMR spectrum of **3** (Figure 3) showed the presence of a peak at 4.57 ppm, assigned to the C$\underline{H}_2$ linking the furan and the parabanic rings, and no residual resonances at 4.05 ppm (δ C$\underline{H}_2$NH) nor at 5.75 and 6.02 ppm (N$\underline{H}$CONH$\underline{}$CH$_2$Fu).



Scheme 3. Synthesis of parabanic model compound **3**: 96% yield, m.p. 175°C.

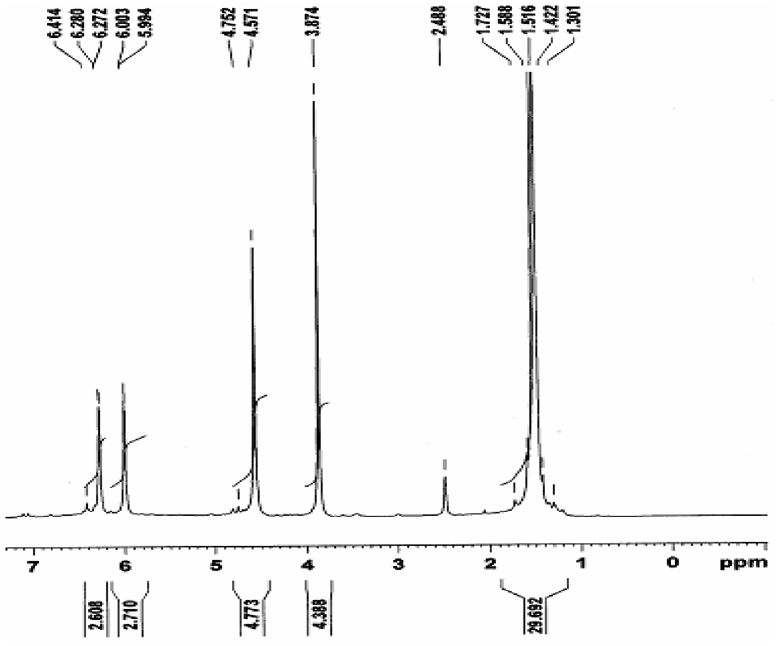
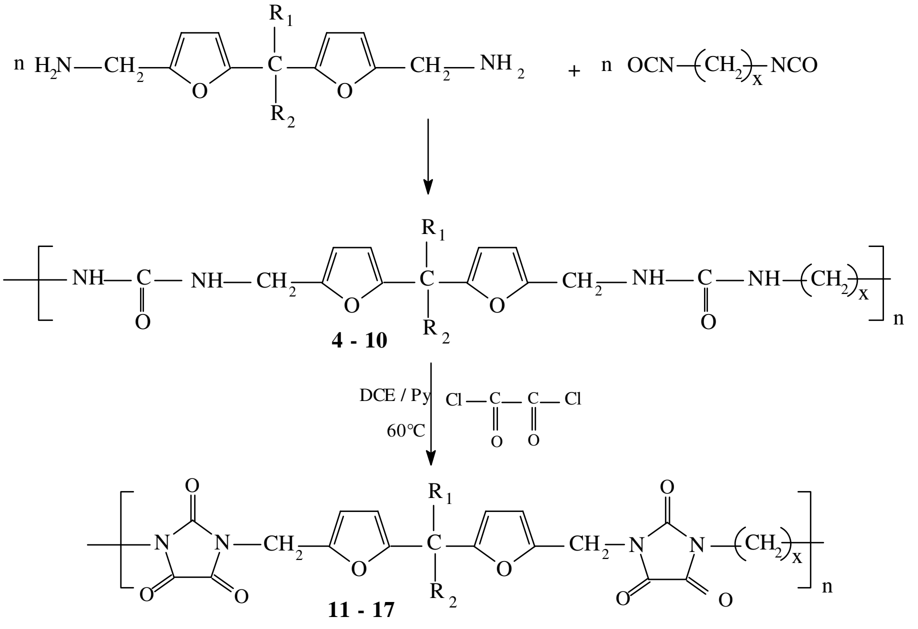


Figure 3. ^{1}H-NMR spectrum of **3** in DMSO-*d6*.

The polyureas **4-10** (from diamines $\mathbf{DA_1}$-$\mathbf{DA_6}$ and the aliphatic diisocyanates, see Table 2) were synthesised by the classical polycondensation reaction applied here to furan diamines and diisocyanates (Scheme 4), following the experimental procedure optimised for the synthesis of model compounds **1** and **2**. The evolution of the reaction medium was monitored by visual observation and frequent samplings. Thus, the progressive increase in polymer molecular weight was clearly shown by both the evolution of the medium viscosity and the changes in both the FTIR and ^{1}H-NMR spectra which revealed the progressive decrease in the NCO peak around 2200 cm^{-1} and the concomitant increase in the relative intensity of the $N\underline{H}$ peaks of urea units at 5.90 and 6.10 ppm.

The treatment of polyureas **4-10** with **OC**, following the optimised conditions found for the synthesis of model compound **3**, gave the corresponding polyparabanic polymers **11-17** (Scheme 4). The progress of these cyclisations was followed by the changes in the FTIR spectra of samples withdrawn at regular intervals from the reaction media, which showed a progressive decrease in the intensity of the absorption bands characteristic of the urea group and the corresponding growth of a peak at 1730 cm^{-1}, assigned to the parabanic ring. Moreover, all parabanic polymers exhibited ^{1}H-NMR spectra in good agreement with their expected structures. In particular, (i) the presence of correctly integrated resonances at 4.5 and 3.4 ppm, assigned to the two methylene groups attached to the 1 and 3 positions of the parabanic heterocycle, and (ii) the absence of peaks arising from the starting $C\underline{H}_2N\underline{H}CON\underline{H}C\underline{H}_2$ units, gave a clear indication that the cyclocondensation reactions had gone to completion.



Scheme 4. Synthesis of polyureas **4-10** and polyparabanic homologues **11-17.**

Table 2. Yields and inherent viscosities of the furan polyureas and corresponding polyparabanic materials.

Polyurea/polyparabanic acid	Comonomers	Poyurea Yield (%)/ η_{inh} (l/g)	Polyparabanic acid Yield (%)/ η_{inh} (l/g)
4 / 11	**DA_1 / HMDI**	90 / 0.095	92 / 0.067
5 / 12	**DA_2 / HMDI**	80 / 0.075	75 / 0.048
6 / 13	**DA_3/ HMDI**	88 / 0.117	90 / 0.085
7 / 14	**DA_4 / HMDI**	75 / 0.086	77 / 0.065
8 / 15	**DA_5 / HMDI**	65 / 0.080	70 / 0.054
9 / 16	**DA_1 / TMDI**	70 / 0.095	85 / 0.068
10 / 17	**DA_1 / OMDI**	90 / 0.070	95 / 0.055

Figure 4 shows, as an example, the ^{1}H-NMR spectra of polyurea **9** and corresponding parabanic polymer **16** and Table 2 gives the two basic sets of results related to the syntheses of both types of polymers, i.e. the yields of the isolated materials and their inherent viscosities.

All these polymers were only soluble in highly polar media like DMA, NMP, DMSO and DMF, and their solubility was the higher, the longer the aliphatic moieties R_1 and R_2. Preliminary results on their thermal properties indicate Tg values around 100°C and a good thermal stability up to at least 350°C.

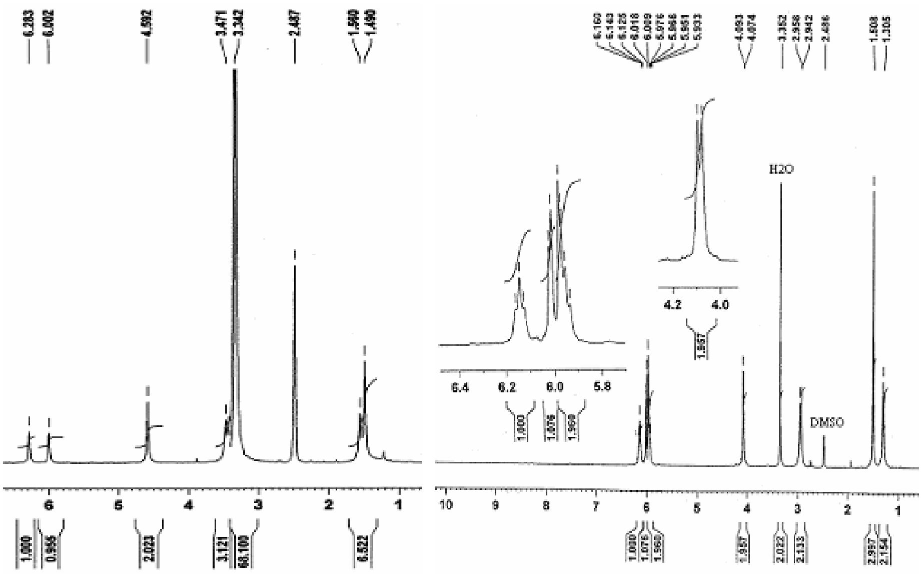


Figure 4. ^{1}H-NMR spectra of **5** (left) and **11** (right) in DMSO-*d6*.

Conclusion

To the best of our knowledge, this is the first report on the synthesis and characterisation of furan-based polyureas and the parabanic structures derived from them. Given the encouraging results related to the ease of obtaining good yields of regular polymers with relatively high molecular weights, work is in progress to assess the properties and possible applications of these materials.

References

1. Yang CP, Chen RS, Hung KS (2001) Polymer 42:4569
2. Mayti S, Ray A (1983) J Polym Sci Polym Chem Ed 21:999
3. Koros WJ, Fleming CK (1993) J Membr Sci 83:1
4. Rami Reddy AV, Sreenivasulu Reddy P, Anand PS (1998) Eur Polym J 34:1441
5. Afli A, Gharbi S, El Gharbi R, Le Bigot Y, Gandini A (2002) Eur Polym J 38:667
6. Abid S, El Gharbi R, Gandini A (2004) Polymer 45:6469
7. Sörensen WR, Campbell TM (1961) Preparative Methods of Polymer Chemistry. Interscience Publishers, New York
8. Kumar GS (1984) Macromolecules 17:2463
9. Lukaszczyk J, Urbas P (1997) React Funct Polym 33:233
10. Oishi Y, Kakimoto M, Imai Y (1987) J Polym Sci. Polym Chem Ed 25:2185
11. Yang Y, Zhi Z, Yang X, Lu L, Wang X (1998) Eur Polym J 34:1893
12. Ogata N, Watanabe M, Kosako Y (1986) J Polym Sci Polym Lett 24:66
13. Chiriac CI (1986) Polym Bull 15:65
14. Gharbi S, Gandini A (2004) J Soc Chim Tunisie 6:17