

Synthesis of 2-furfurylmaleimide and preliminary study of its Diels-Alder polycondensation

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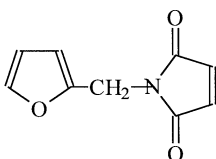
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Summary: 2-furfurylmaleimide (**FM**) was synthesized and characterized unambiguously for the first time by condensing 2-furfurylamine with maleic anhydride to give the corresponding maleamic acid which was in turn cyclized in the presence of acetic anhydride and sodium acetate. A thorough structural assessment was carried out to prove the success of this procedure. **FM** is highly sensitive to ring-opening hydrolysis by atmospheric moisture and must be kept in a dry medium. This investigation was aimed at using **FM** as an AB-type monomer in a polycondensation based on the Diels-Alder reaction. Preliminary experiments are reported on this novel system which provided the first polycondensates of this kind.

INTRODUCTION

Our laboratory has been engaged for many years in a comprehensive study of the behaviour of furanic monomers in polyaddition and polycondensation systems and of the properties of the ensuing materials (1). Recently, an in-depth investigation was initiated on the application of the Diels-Alder reaction to the synthesis (2) and the modification (3,4) of furan-based polymers. In particular, copolymers bearing varying amounts of pendant furan rings were crosslinked with a bismaleimide through intermolecular Diels-Alder coupling and then returned to their initial linear structure thanks to the retro-Diels-Alder reaction, by treating them at 130°C in the presence of an excess of 2-methylfuran (4).

The polycondensation of a difuranic compound with a dienophile has received some attention, as recently reviewed (1,2), but the systems studied yielded mostly low molecular-weight products or conflicting results. We thought that it might be more rewarding to prepare a single furanic-dienophile monomer and study its Diels-Alder AB-type polycondensation. The simplest structure within this context appeared to be 2-furfurylmaleimide (**FM**). Surprisingly, no clear-cut synthesis of this compound was found in the literature and therefore we set out to tackle this task before dealing with the aspects related to its polycondensation.



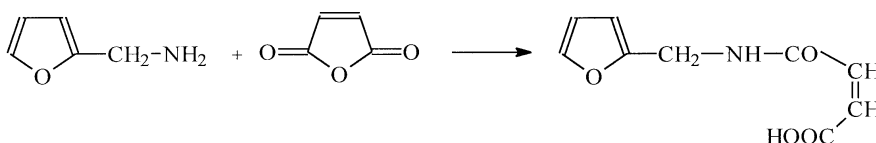
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RESULTS AND DISCUSSION

All reagents, solvents and catalysts used in this work were commercial products of high purity employed as received.

Synthesis of N-2-furfurylmaaleamic acid (FMA)

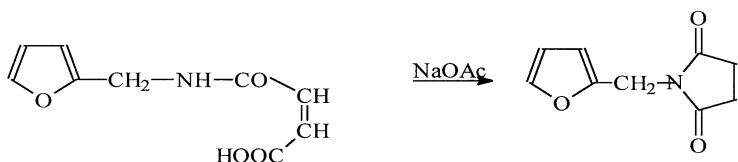
Maleic anhydride was dissolved in acetone to give a 0.8 M solution, which was then cooled with an ice bath before adding dropwise an equivalent amount of 2-furfurylamine under vigorous stirring which was prolonged for a further 12 hours. The ensuing solution was poured into an excess of ice water in which the reaction product precipitated. The final crystalline material was filtered off and vacuum dried to constant weight (65% yield).



Their elemental analysis suggested that indeed the expected maleamic acid had been formed: C 55.50% (calc. 55.38); H 4.75% (calc. 4.61); O 32.67% (calc. 32.82) and N 7.27% (calc. 7.18). The FTIR and ¹H-NMR spectra confirmed this conclusion. The vibrational features included the OH and NH bands around 3300 cm⁻¹, the furanic =CH at 3078 cm⁻¹, the carbonyl absorption at 1704 cm⁻¹, the maleic C=C at 1633 cm⁻¹, the ring breathing at 1016 cm⁻¹ and the typical δCH bands of the heterocycle at 933, 914 and 855 cm⁻¹. The resonance features included the methylene protons at 4.53 ppm, the alkenyl and H3 and H4 protons between 6.2 and 6.4 ppm, the H5 proton at 7.39 ppm, the NH proton at 7.93 ppm and the carboxylic proton at 16.0 ppm, all in the right integration ratios. The melting point of **FMA**, as determined by DSC, was 123°C.

Synthesis of 2-furfurylmaaleimide (FM)

The cyclisation of N-2-furfurylmaaleamic acid was conducted as follows. A mixture of 2 g of **FMA** and 1.14 g of sodiumacetate was dissolved in 10 ml of acetic anhydride and the resulting solution heated at 60°C under stirring for 15 minutes. The mixture was then rapidly poured into an excess of ice water and the resulting precipitate immediately filtered off and dissolved in methylene chloride. This solution was then shaken with a 5% aqueous solution of sodium bicarbonate. The organic phase was washed with water, rapidly separated and dried over sodium sulfate. After evaporating the solvent under vacuum, the residue was dried under high vacuum at room temperature. This crystalline product (44% yield) sublimed at 55–60°C at 10⁻⁴ torr.



The characterization of the reaction product provided the first unambiguous proof of the successful synthesis of **FM**. Two previous reports are available in the literature concerning the synthesis of this compound. In a French patent (5), a rather complicated route was proposed involving a retro-Diels-Alder reaction, but the characterization of the product was very scanty and therefore no strong evidence was given of the success of this procedure. More recently, Mikroyannidis (6) attempted the cyclization of the same acid we used, but the facts that (i) he could not do a $^1\text{H-NMR}$ spectrum because the product was insoluble in common solvents, coupled with (ii) its brown colour, and (iii) its very poor infrared spectrum (no other analysis reported), suggest that the conditions chosen (90°C for 30 minutes) provoked the resinification of the reaction mixture giving undetermined polymeric materials.

Our crystalline product gave an elemental analysis in tune with the expected structure of **FM**, namely C 60.79% (calc.61.02), H 3.71% (calc.3.95), O 26.88% (calc. 27.12) and N 8.17% (calc. 7.91). The mass spectrum gave the correct molecular peak at $m/u=177$. The melting point of this product (DSC) was 106°C ; upon further heating of the resulting liquid, the thermogram showed a strong exotherm starting at 175°C suggesting its thermal polymerization. Figs 1, 2 and 3 show the FTIR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of **FM**. All these spectroscopic features are fully compatible with the **FM** structure. The proton and carbon resonances are assigned on the corresponding figures. These assignments were confirmed by preparing the FM homologue bearing two methyl groups on the maleic unsaturation. Certain spectroscopic peculiarities suggested that the two cycles of **FM** are not lying either on the same plane or a right angle (2). In fact there are two distinct resonances for the maleic protons (Fig. 2) and two distinct frequencies for the maleic C=O groups at 1700 and 1800 cm^{-1} (Fig. 1) indicating the absence of a plane of symmetry for this molecule.

Note: FM is very sensitive to moisture which causes its ring opening hydrolysis to MFA. It must therefore be stored in a dry atmosphere.

Polycondensation of FM

Small aliquots of **FM** were placed in glass tubes which were sealed off under high vacuum either as such or after adding different dry solvents. The monomer was found to be quite unreactive, as already suggested by the DSC tracing which did not show any appreciable reaction until about 170°C . Of the numerous solvents used to study the solution polymerization of **FM**, the best was 1,1,2,2-tetrachloroethane precisely because it allowed the temperature to be raised to $150\text{--}170^\circ\text{C}$ in the sealed tubes. Thus, typically, a 0.3 M monomer solution left in these conditions for 7 days showed the progressive accumulation of a precipitate. The FTIR spectrum of these insoluble polymers showed the characteristic bands of the corresponding adduct moieties, namely the conversion of the double carbonyl band of **FM** (see Fig. 1) into a

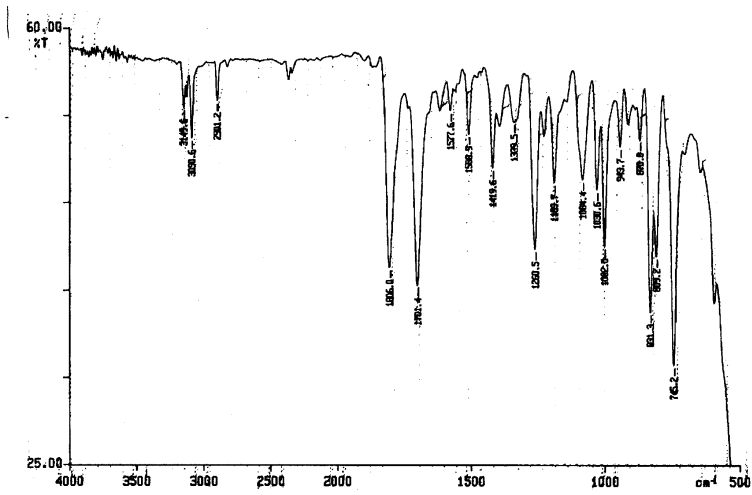
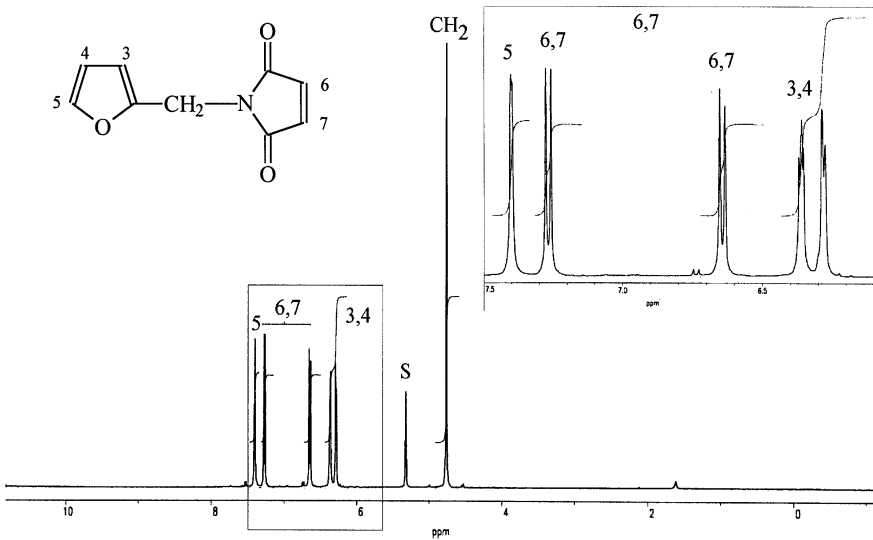
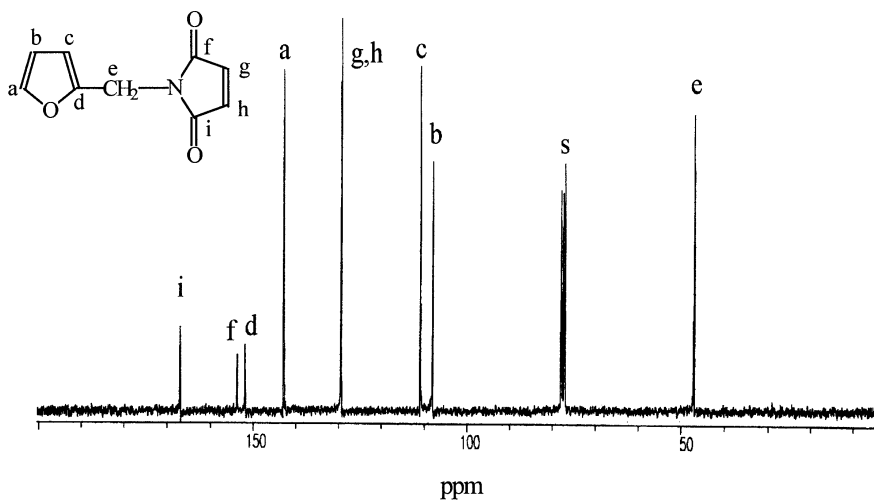
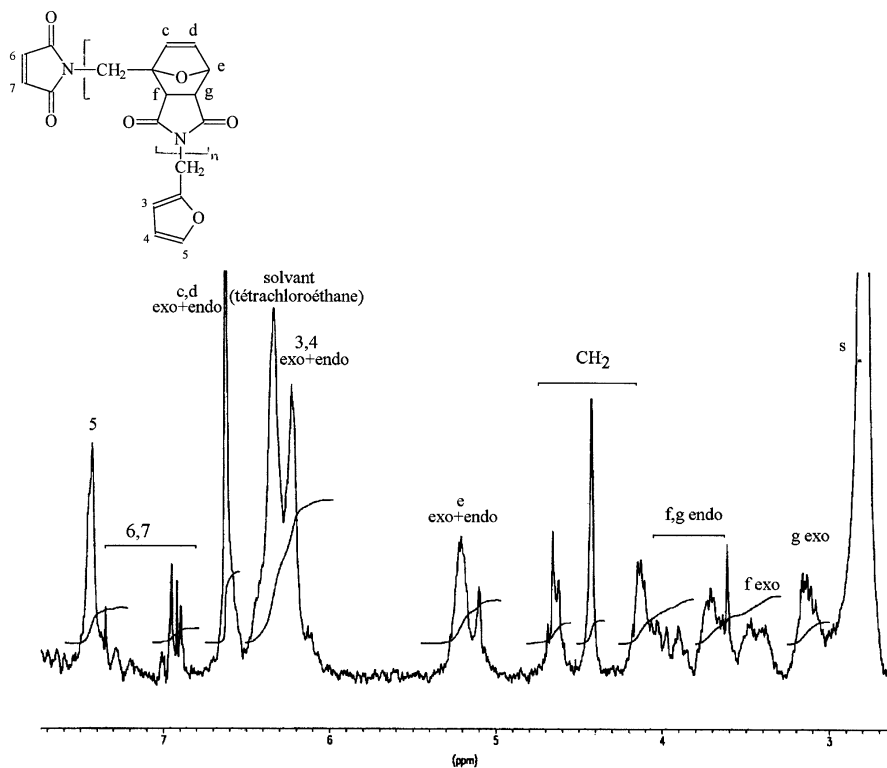
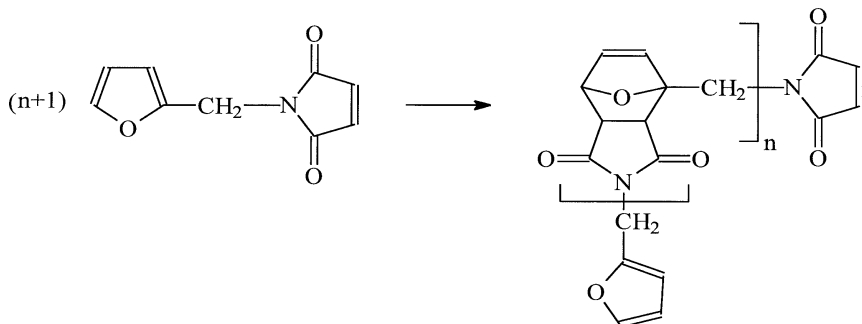


Figure 1 : FTIR spectrum of FM

Figure 2 : ¹H-NMR spectrum of MF (CD₂Cl₂, S)

Figure 3 : ¹³C-NMR spectrum of MF (CDCl₃, S)Figure 4 : ¹H-NMR spectrum of polyAB soluble part (acetone, S)

broad peak centered around 1705 cm^{-1} . The soluble products gave essentially the same FTIR spectrum and a $^1\text{H-NMR}$ spectrum (Fig. 4) which indicated an oligomeric structure derived from the polycondensation reaction:



Reactions carried out in bulk at different temperatures ranging from 90 to 180°C during various times ranging from 15 minutes to several hours gave systematically a brown solid insoluble in most solvents. The FTIR spectra of these products were all similar to that of the polymer precipitated from solution, suggesting a similar polycondensation mechanism.

The TGA thermograms of the polycondensate, taken under nitrogen, showed a progressive weight loss of about 40% between 230 and 400°C and thereafter a remarkably stable thermolysis product which did not degrade up to 850°C . This behaviour suggests that irreversible chemical changes, such as the aromatization of the adduct moieties, occurred within the polymer structure giving rise to thermally stable materials.

Two homologous monomers were also tested in this context, viz. the product arising from the reaction of 5-methylfurfurylamine with maleic anhydride and that already mentioned, obtained from furfurylamine and dimethylmaleic anhydride. The former was too reactive even to allow its isolation. Indeed, the inductive effect of the methyl group at C5 enhanced its tendency to selfcondense. Conversely, the latter could be isolated, but the two bulky substituents on the unsaturation reduced its reactivity in the Diels-Alder polycondensation.

This investigation is being pursued since much remains to be done in order to gain a deeper understanding of the reactions involved and to characterize the ensuing novel polymers.

REFERENCES

1. Gandini A, Belgacem MN (1997) *Prog. Polym. Sci.* 22: 1203
2. Goussé C (1997) Doctorate Thesis, Grenoble Polytechnic Institute
3. Goussé C, Gandini A (1997) *Eur. Polym. J.* 33 : 667
4. Goussé C, Gandini A, Hodge P (1997) *Macromolecules* (in press)
5. Delaire M (1969) French Patent 2.031.538
6. Mikroyannidis JA (1992) *J.Polym.Sci. : Part A: Polym.Chem.* 30 : 125