Synthesis and Characterization of Furanic Polyamides

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ABSTRACT: Two sets of polyamides bearing furan rings in the main chain were prepared and characterized. The first was based on 2,5- and 3,4-furandicarbonyl and aromatic diamino structures. The second was made exclusively from furanic monomers. After the optimization of the various synthetic routes, the furanic–aromatic polymers had higher molecular weights and better thermal stability than their all-furanic counterparts. Concentrated solutions of high-DP poly(2,5-furandiylcarbonylimino-1,4-phenyleneiminocarbonyl) displayed a lyotropic liquid-crystal behavior.

Introduction

The interest of polymers bearing furan rings stems from (i) the use of monomers derived from the biomass, i.e., renewable and ubiquitous resources, (ii) the novel properties introduced by the presence of the heterocycles within the macromolecular backbone or pendant to it, and (iii) the possibility of specific chemical modifications arising from the peculiar reactivity of the furan moieties.[1] This study on polyamides of the furan series fits within the broader context of a research program on furan polymers, which includes materials obtained from both chain and step polymerization and copolymerization reactions.[2]

The literature on polyamides in which the furan ring appears as one of the groups forming the main chain is not abundant, and most of the work done in this domain is of a qualitative nature. Often the specific polymer containing the furan heterocycle was just one of several new structures within a more general approach and received therefore only scanty attention. Furanic–aliphatic polyamides[3] were first reported 30 years ago, and with some furanic–alicyclic polyamides[3a,3d,4] they represent the only rather well-characterized family of furanic polyamides. Most of these polymers were prepared from 2,5-furandicarboxylic acid (or its dimethyl ester, or its dichloride, according to the synthetic method used) and an aliphatic or alicyclic diamine, but the corresponding 3,4-, 2,4-, and 2,3-furandicarboxylic monomers have also been looked at with the latter diamines.[4c] The melting point, glass transition temperature, decomposition temperature, and inherent viscosity (no molecular weight values of any furanic polyamide has ever been reported) of these polymers, as well as other more specific properties, vary considerably from one study to another for the same expected structure. The experimental conditions used for their synthesis seem to affect these parameters.

Furanic–aromatic polyamides have been the object of only two studies before our investigation. In the first,[5] a short account is given of polymers resulting from the stepwise reaction of 2,5-furandicarboxylic acid dichloride with various aromatic diamines: unfortunately, no structural analysis was conducted on these materials. Inherent viscosities of 0.3–0.5 dL/g were obtained in sulfuric acid at 20 °C with a polymer concentration of 0.5 g/dL. Melting points ranged from 230 to 260 °C with decomposition taking place 5–20 °C above them. No other properties were described. The second publication[3d] only mentions the use of aromatic diacid diamines in the synthesis of 2,5-furanic polyamides containing carboxylic groups and the cyclodehydration products obtained therefrom.

Finally no polyamide resulting solely from furanic monomers has been reported in the literature within the context of conventional polycondensation reactions. Mikhailov and Peeva[6] prepared a furanic polyamide by the acid-catalyzed condensation of –OH groups with C5 hydrogens using a 2-substituted hydroxyamide. The IR spectrum of this polymer (no molecular weight given) was similar to that of the product obtained from the polytransamidation of 2-(aminomethyl)-5-furoic acid methyl ester. This was the only evidence in favor of a polyamide-like structure for both materials. Their thermal behaviors were, however, different. A furanic–thiophenic polyamide has been reported.[5]

The present paper deals with furanic–aromatic and all-furanic polyamides, i.e., the polymers of this series that have received little or no attention. A preliminary report on some of this work has already been published.[7]

Experimental Section

Synthesis and/or Purification of Reagents, Catalysts, and Solvents. 2,5-Furandicarboxylic acid (**1**), its 3,4-homologue (**2**), and their respective dichlorides, **3** and **4**, were prepared as already described.[7] The dimethyl ester **5** of **1** was synthesized by standard acid-catalyzed esterification, which gave 97% yield. These products were purified by repeated recrystallizations from appropriate solvents. All the aromatic diamines were commercial products that were submitted to specific purification procedures (recrystallization, sublimation, distillation). Three furanic diamines were prepared. 2,5-Bis(aminomethyl)furan (**10**) was synthesized from the corresponding diol or from 5-(hydroxymethyl)-2-furancarboxyaldehyde via the dialdehyde as shown in Scheme I (the individual steps have been detailed previously[7,8]). This compound (mp 13 °C; bp[6] 105 °C) showed a marked tendency to resinify on standing and was therefore converted into its stable diammonium dibromide, **11**.

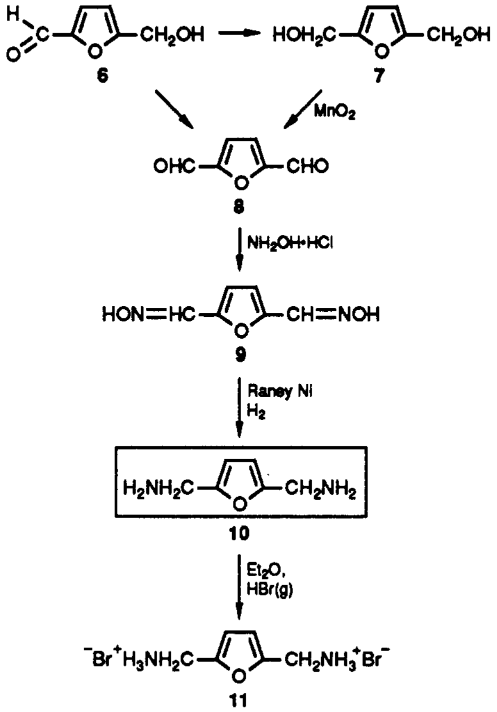
3,4-Bis(aminomethyl)furan (**15**) was synthesized according to Scheme II from the commercial diester through standard procedures, mp 26 °C (lit.[9] mp 29 °C).

Bis[5-(aminomethyl)furfuryl] ether (**18**) has not been reported previously. It was prepared from the corresponding dialdehyde, which can be readily made from 5-(hydroxymethyl)-2-carboxyaldehyde as shown in Scheme III. The yield of the first condensation was 65%, the conversion into the dioxime reached 80% (*EE* isomer, mp 175 °C). Finally, the yield of **18** was about 40% by various reduction routes of the dioxime; mp 15 °C, mass spectrum, $m/e = 236$.

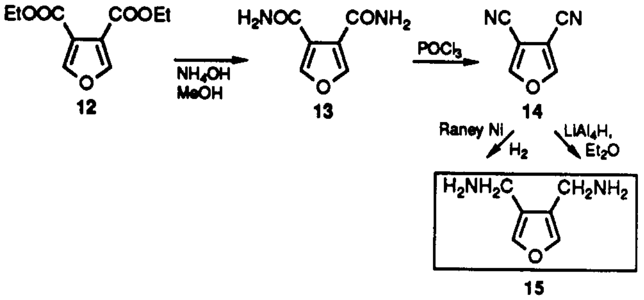
Table I shows the spectroscopic characterization of the noncommercial furanic compounds involved in these syntheses. All other reagents and solvents used in this work were purified and dried following strict procedures.

Polymerization Procedures. Four different techniques were used to arrive at the desired polyamides. (i) One technique is high-temperature bulk polymerization of the acid chloride and the diamine. This procedure was only tried with furanic acid dichlorides and aromatic diamines: the temperature was raised progressively to 250 °C as the viscosity of the medium increased, with a total reaction time of several hours. Since the results were not very encouraging (low molecular weights), the technique was not exploited further. (ii) Solution polymerization involved

Scheme I



Scheme II



Scheme III

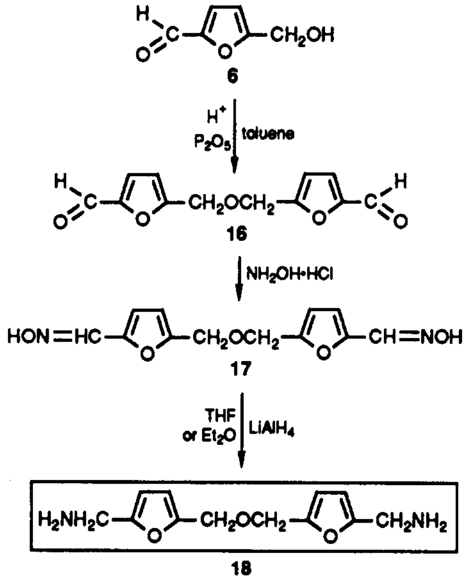


Table I
Characterization of Noncommercial Furan Monomers and Intermediates

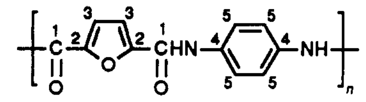
compd	IR, cm^{-1}	^{1}H NMR (in ppm relative to TMS)
8	1700 ($\nu_{C=O}$); 2860 ($\nu_{CH,CHO}$)	acetone-d_6: 7.65 (s, 2 H, H3 and H4); 9.87 (s, 2 H, C*H*O)
9	3020 ($\nu_{=CH}$); 3220 (ν_{OH})	DMSO-d_6: 7.40 (s, 2 H, H3 and H4); 7.8 (s, 2 H, C*H*N); 11.9 (s, 2 H, NO*H*)
10	1640 ($\nu_{C=C,fu}$); 3250 (ν_{NH})	CDCl$_3$: 1.6 (s, 4 H, NH$_2$); 3.8 (s, 4 H CH$_2$); 6.1 (s, 2 H, H3 and H4)
11	–	DMSO-d_6: 4.1 (m, 4 H, CH$_2$); 6.7 (s, 2 H, H3 and H4); 8.5 (m, 6 H, NH$_3^+$)
13	1690 ($\nu_{C=O}$); 3150 and 3300 (ν_{NH})	DMSO-d_6: 8.4 (s, 2 H, H2 and H5); 10.9 (s, 4 H, NH$_2$)
14	2230 ($\nu_{C=N}$)	CDCl$_3$: 8.32 (s, H2 and H5)
15	3150 and 3300 (ν_{NH})	DMSO-d_6: 2.26 (s, 4 H, NH$_2$); 3.56 (s, 4 H, CH$_2$); 7.39 (s, 2 H, H2 and H5)
16	1690 ($\nu_{C=O}$); 2820 ($\nu_{CH,CHO}$)	DMSO-d_6: 4.62 (s, 4 H, CH$_2$); 6.7 (d, 2 H, H3); 7.5 (d, 2 H, H4); 9.58 (s, 2 H, CHO)
17	1640 ($\nu_{C=C,fu}$); 3200 (ν_{OH})	DMSO-d_6: 4.49 (s, 4 H, CH$_2$); 6.59 (d, 2 H, H3); 7.15 (d, 2 H, H4); 7.51 (s, 2 H, CHN); 11.8 (s, 2 H, OH)
18	3140 ($\nu_{=CH}$); 3300 (ν_{NH})	CDCl$_3$: 1.73 (s, 4 H, NH$_2$); 3.77 (s, 4 H, CH$_2$N); 4.43 (s, 4 H, CH$_2$O); 6.1 (d, 2 H, H3); 6.22 (d, 2 H, H4)

the same monomers but lower temperatures and an acid acceptor apart of course from the presence of a solvent. After a good number of preliminary essays with aromatic diamines, the best operating conditions were found to be as follows: a solvent mixture of *N*-methylpyrrolidone (NMP) and hexamethylphosphortriamide (HMPT) (1/1, v/v), total monomer concentrations of 2–3% (w/v), a temperature of about 100 °C, and reaction times of 10–20 h; it was found advisable to use a slight excess of acid dichloride (1–2%) with respect to the stoichiometric amount relative to the diamine. The reaction mixture became very viscous, but the polymer did not precipitate (a serious problem with furanic–aromatic polyamides). The conditions chosen for the synthesis of all furanic polyamides will be given in the specific section below. (iii) "Direct" polycondensation implies that the diamine (aromatic) was used in conjunction with the furanic diacids themselves instead of the dichlorides. This technique, developed for fully aromatic polyamides, gave here the best results with furanic–aromatic combinations: the optimization of experimental conditions was an important part of this work, and therefore it is discussed in the next section. (iv) Interfacial (phase-transfer) polymerization was not applied to aromatic diamines because of their very low solubility in water. Preliminary runs showed very poor results, and the technique was abandoned. With furanic diamines on the contrary this method was satisfactory: the organic phase was either methylene chloride or chloroform; the aqueous phase contained KOH to neutralize the HCl evolved but also to regenerate in situ the furanic diamine when its diammonium salt was used; temperatures ranged from 0 to 10 °C, and the reaction times were between 20 and 40 min.

Polyamide Characterization. Structures were confirmed by IR and ^{1}H and ^{13}C NMR spectroscopy. Absolute molecular weights were only determined for the most interesting polymer obtained, viz., polyamide **19**, resulting from the direct polycondensation of **1** with 1,4-phenylenediamine: light scattering and membrane osmometry were complemented by the analytical determination of the end groups. For all the other polyamides a relative criterion was used, namely, the inherent viscosity in an appropriate solvent, as specified below. The lyotropic liquid-crystal behavior of polymer **19** was studied by optical polarized microscopy, shear viscosity, and differential scanning calorimetry (DSC) of concentrated solutions. Finally, all the polyamides were submitted to DSC and thermogravimetric analyses (TGA).

Results and Discussion

Furanic–Aromatic Polyamides. The structures investigated are shown below and involved the reaction of the furanic diacidic moiety with one of the four aromatic diamines used in this work.



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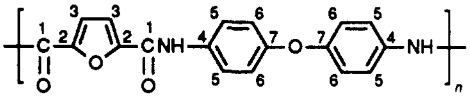

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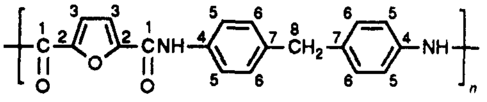

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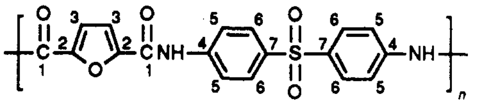

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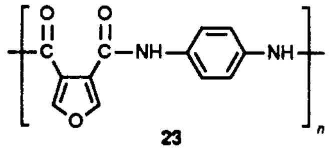

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(The numbers on the structures refer to the ^{13}C NMR assignments given in Table III.)

Most of the work on the optimization of the syntheses in terms of polymer molecular weight and yield was conducted with the combinations giving polymer **19**. Using the inherent viscosity (measured in 98% sulfuric acid at 30 °C with a polymer concentration of 0.5 g/dL) as a test, it was found that technique i gave a value of about 0.2 at best (and 0.25 in the presence of P_2O_5) and yields of 60–70%; technique ii with the optimized condition given in the experimental section gave a value of 0.5 and quantitative yields; technique iv was the most disappointing, definitely not adapted to these systems, whereas technique iii gave consistently complete yields and relatively high inherent viscosities. The latter synthetic route was therefore chosen for a systematic approach, aiming to obtain the highest molecular weights first with polyamide **19** and then with other furanic–aromatic combinations.

The essence of direct polycondensation, as developed by Higashi's group[10] within the context of aromatic polyamides, consists of using triphenyl phosphite as condensation agent for the amidation reactions between –COOH and $-NH_2$ functions in a medium of high ionic strength and in the presence of pyridine. This phosphorylation-based water-elimination reaction mechanism can be represented schematically as in Scheme IV.

The main advantage associated with this procedure is the direct use of the diacid instead of its dichloride as in, e.g., solution polycondensation. Diacids are usually easier to purify thoroughly, less prone to chemical evolution during storage and give fewer problems of side reactions during the polycondensation processes. The disadvantages of direct polycondensation are the low monomer concentrations imposed by the requirements of this technique, a side reaction[11] between the phenol formed and the active pyridinium intermediate, and the fact that if the diamines used are too nucleophilic, they can replace (in part) the pyridine in the formation of an analogous intermediate, thus upsetting the stoichiometric balance between the monomers. Nevertheless this mode of polycondensation has given excellent results with aromatic polyamides following a painstaking investigation of the role of numerous parameters and additives, which resulted in very high molecular weights.[10c] In the present research the optimization of the synthesis of polymer **19** called upon a similar systematic study of parameters such as the reaction time and temperature, the initial monomers concentration and stoichiometry, the solvent composition, the extent and mode of purification of (mostly) the diamine, the relative amount of triphenyl phosphite, the type and quantities of added salts, and the order of addition of reagents at the onset of the polycondensation. The highest inherent viscosities of 2.1–2.3 were obtained in a reproducible manner by using the following conditions: solvent NMP + pyridine in a volume ratio of 5 to 1; added salts $CaCl_2$ + LiCl in a molar ratio of 1.1 (0.4 mol/mol of pyridine); monomer concentration 0.17 mol/L (stoichiometry 1:1); reaction time about 20 h; reaction temperature 90 °C; molar ratio of triphenyl phosphite to diacid (or diamine) 2.2. Of course it is essential to purify and dry all reagents and solvents as thoroughly as required.

Scheme IV

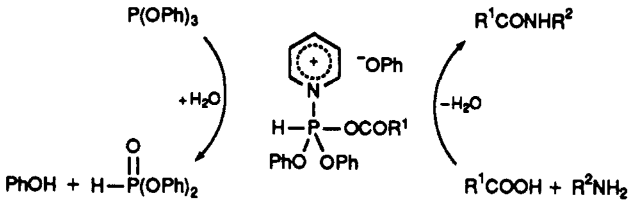


Table II
Optimized Values of Inherent Viscosities for Furanic–Aromatic Polyamides (See Text)

	η_{inh},[a] dL/g	
polyamide	"direct" polycondensn	solution polycondensn
19	2.12 (1.33)[b]	0.50
20	1.03 (0.95)[b]	0.43
21	0.33 (0.28)[b]	0.20
22	0.26 (0.20)[b]	0.17
23	0.61 (0.55)[b]	0.23

[a] Measured in 98% H_2SO_4 at 30 °C with c = 0.5 g/dL. [b] Values in parentheses refer to polyamides prepared at 100 °C.

These conditions were then applied to the synthesis of the other four furanic–aromatic polyamides **20–23**. Table II gives the results expressed in terms of inherent viscosity for the optimized conditions with both solution and direct polycondensation. The differences within each set of results, relating to monomer structure and reactivity and to chain flexibility, have already been discussed.[7] The most relevant aspect in terms of novelty, which is worth restating, is the important drop in viscosity between **19** and **23**, which arises at least in part from the different modes of inclusion of the furan ring in the polyamide backbone, the 3,4-incorporation giving a more flexible chain than the 2,5-situation. This is confirmed by the difference in T_g (325 °C for **19**, 205 °C for **23**[7]), which cannot be due only to differences in the molecular weights of the polymers, as indeed was confirmed, after our preliminary paper,[7] by DSC analyses of samples of each polymer structure with varying inherent viscosity for which T_g only changed by a few degrees.

The ^{1}H NMR and IR spectra of these polyamides have already been discussed.[7] Since then, the 350-MHz version of the ^{1}H NMR spectra confirmed the assignments and the regularity of the structures. Figure 1 shows one such spectrum. The ^{13}C NMR spectra were also taken; after an analysis based on the corresponding spectra of the monomers, the assignments given in Table III were derived. Again, no structural anomaly (unexplained peaks) could be detected, as in the typical spectrum given in Figure 2.

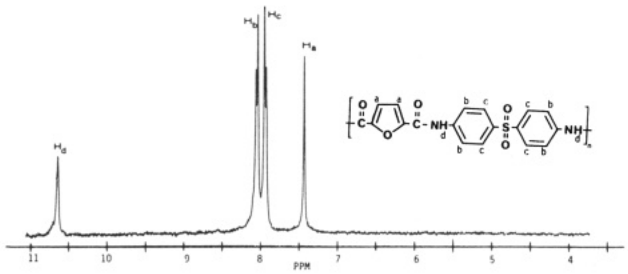


Figure 1. 350-MHz ^{1}H NMR spectrum of polymer **22** in DMSO-d_6 at 120 °C.

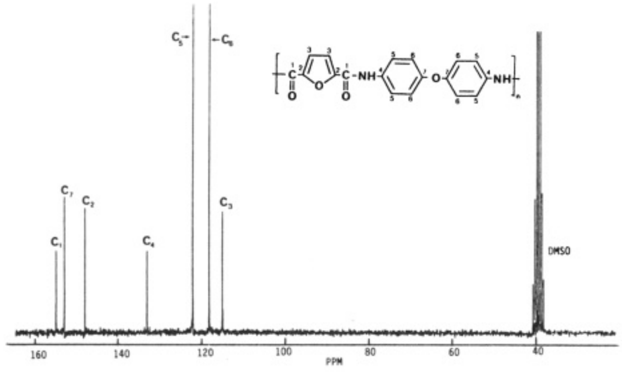


Figure 2. 50-MHz ^{13}C NMR spectrum of polymer **20** in DMSO-d_6 at 120 °C.

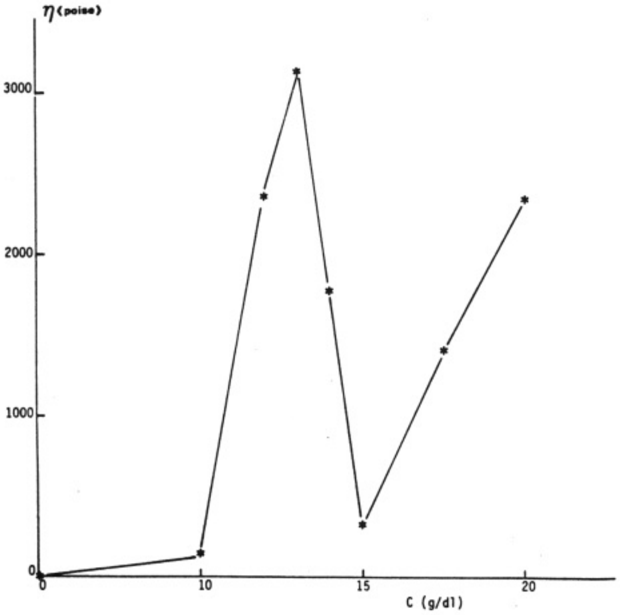


Figure 3. Plot of the shear viscosity (measured at a shear rate of 2.84 s^{-1}) as a function of polymer concentration for solutions of polyamide **19** in NMP containing 4% LiCl, at 40 °C. The sample used had an inherent viscosity of 2.1 dL/g (measured in 98% sulfuric acid at 30 °C with a concentration of 0.5 g/dL).

The DSC and TGA analyses of these polymers have already been reported and discussed.[7] Melting was never observed, but a few glass transition temperatures could be determined together with the thermal degradation features. They all showed a good stability at least up to 350 °C.

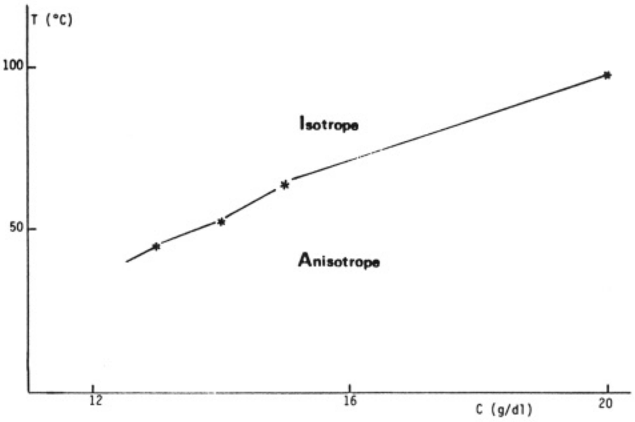


Figure 4. Phase diagram of the system described in Figure 3, obtained from DSC measurements and confirmed by polarizing light microscopy.

Table III
^{13}C NMR Data for Furanic–Aromatic Polyamides (DMSO-d_6 at 120 °C)

polyamide	δ (ppm with respect to TMS)
19	154.9 (C1); 148.0 (C2); 135.8 (C4); 120.6 (C5); 114.6 (C3)
20	155.0 (C1); 153.0 (C7); 148.0 (C2); 133.1 (C4); 122.4 (C5); 116.2 (C6); 115.0 (C3)
21	155.2 (C1); 148.0 (C2); 136.6 (C4); 135.5 (C7); 128.3 (C6); 120.5 (C5); 115.0 (C3); 39.6 (C8)
22	155.2 (C1); 147.8 (C2); 142.0 (C7); 136.0 (C4); 127.5 (C6); 120.1 (C5); 115.7 (C3)

Table IV
Molecular Weights of Furanic–Aromatic Polyamides

polyamide	η_{inh},[a] dL/g	M_w	M_n[b]	M_n[c]
19	2.10		16500	15500–16800
19	1.70	89 000	8700	9100 ± 500
19	1.30	49 000	7050	7300 ± 300
19	1.24	41 200	6700	6800 ± 200
19	0.55	29 500		
20	0.95	37 000		
21	0.28	12 300		

[a] Measured in 98% H_2SO_4 at 30 °C with c = 0.5 g/dL. [b] Obtained by membrane osmometry. [c] Obtained by analytical determination of end groups.

The properties of dilute solutions of polyamide **19** were studied in some detail. This polymer is soluble in concentrated sulfuric acid and in NMP and dimethylacetamide (DMA), both containing 3–5% LiCl. A sample with an inherent viscosity of 1.30 dL/g in 98% sulfuric acid at 30 °C gave an intrinsic viscosity of 1.53 dL/g in the same solvent at the same temperature with good linear extrapolation of the reduced viscosity at infinite dilution. In DMA with 5% LiCl the intrinsic viscosity was 1.49 at 25 °C again with a normal dilution behavior. With LiCl concentrations below 4%, a progressively stronger polyelectrolyte effect provoked a substantial increase in the intrinsic viscosity (5 dL/g with 2% LiCl, 2.04 with 3%, 1.52 with 4%) and a corresponding deviation from linearity in the reduced viscosity vs concentration plots.

It is again with polymer **19** that molecular weights were determined. Values of $\bar{M}_w$ were obtained from light scattering measurements at 546 nm from solutions in DMA containing 4% LiCl. $\bar{M}_n$ values were obtained from osmometry with a regenerated cellulose membrane and by chemical analysis of the end groups: –COOH concentrations were determined potentiometrically following the method reported by Garmon for aromatic polyamides,[12] whereas $-NH_2$ concentrations were determined by using the technique described by Kreshkov et al.[13] again for aromatic polyamides. Good agreement was found between the two sets of analyses. Table IV gives the results of these various determinations. The good agreement between the $\bar{M}_n$ values obtained by osmometry and end-group titrations is encouraging. On the other hand, the high values of $\bar{M}_w$ and the increasing value of $I_p = \bar{M}_w/\bar{M}_n$

Table V
Synthesis of All-Furanic Polyamides

polyamide	method	monomer concn, M	temp, °C	time, h	yield, %	η_{inh},[a] dL/g
24 (**3** + **10**)	interfacial	0.1	0	0.5	50	0.1
24 (**3** + **10**)	solution	0.1	5 → 25	6	5	0.08
25 (**3** + **15**)	interfacial	0.1	0	0.5	10	
25 (**3** + **15**)	solution	0.1	80	15	20	
26 (**3** + **18**)	interfacial	0.1	0	0.5	22	0.15
26 (**3** + **18**)	interfacial	0.06	0	0.5	8	0.04
26 (**3** + **18**)	solution	0.25	20	48	40	0.06
26 (**3** + **18**)	solution	0.015	30	15	60	0.12

[a] Measured in DMSO at 30 °C with $c = 0.5$ g/dL.

with increasing molecular weight are suspicious. Various elements suggest that intermolecular association phenomena are at the origin of these features, e.g., the nonlinearity of the components of the Zimm plots and the high values of the dissymetry ratio, Z. Moreover, given the apparently well-behaved character of the polycondensation reaction, it is surprising that I_p should be so much higher than the expected value of about 2. Finally, it is unlikely that weight-average molecular weights as high as 10^5 should be attained in these syntheses. In conclusion, the $\bar{M}_w$ values are probably incorrect (too high) whereas $\bar{M}_n$ values are most likely to be right.

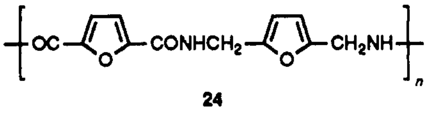
The properties of concentrated solutions of **19** were also investigated. The samples studied had high molecular weights (inherent viscosity higher than 2 dL/g) and were dissolved in NMP containing 4% LiCl. Up to about 12% (w/v) these solutions were clear and did not show any birefringence when observed through an optically polarized microscope. The appearance of a lyotropic mesophase at room temperature (20 ± 2 °C) began at that critical concentration: solutions became cloudy and spherulites were clearly visible at magnification 100× within an isotropic background. At a concentration of about 15% the ratio of anisotropic-to-isotropic phases had increased very considerably with the same type of spherulites as mesophase. With solutions containing around 20% of the polymer the consistency was that of a semisolid mass and it was not possible to observe them under the microscope at room temperature. They were therefore heated to 50 °C and showed a very high degree of anisotropy with the characteristic polydomain texture of liquid crystals. These same solutions were heated to 65 °C between two microscope glass plates and then submitted to shearing in order to align the mesophase before cooling to room temperature. The result was the observation of a highly oriented birefringent pattern induced by shearing. The above features leave little doubt about the lyotropic liquid-crystal behavior of these systems above a critical concentration of about 12% at room temperature.

This conclusion was corroborated and quantified by low-shear viscosity measurements on the same solutions. Up to about 12%, the viscosity was found to be Newtonian for shear rates of less than 10 s^{-1}; at higher polyamide concentrations, a marked rheofluidification behavior (pseudoplasticity) took over and became more pronounced with higher concentrations. This is in tune with the formation of a mesophase (whose proportion relative to the isotropic phase increases with polymer concentration) because the liquid crystals formed align themselves in the direction of the shear stress and offer thereby a reduced frictional (viscous) resistance. The value of the viscosity at low shear rate was a further parameter that proved the formation of lyotropic liquid crystals: as shown in Figure 3 the appearance of the mesophase as observed at the microscope is accompanied by a decrease in viscosity. The critical concentration is about 13% at 40 °C. At 15% total alignment occurs; i.e., the anisotropy (mesophase) is at a maximum corresponding to a minimum viscosity. The subsequent increase in viscosity with increasing polymer concentration is simply due to the increase in concentration of liquid crystals.

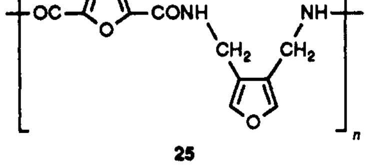
In order to establish a correlation between the critical concentration and the temperature of these solutions of **19**, i.e., a diagram linking the isotropic to the liquid crystal phase, both DSC (weak endotherm associated with the disappearance of the anisotropic phase) and microscopy under polarized light were used. Figure 4 shows the results obtained for such a phase diagram. The enthalpy change associated with the transition was found to be about 16 J/g, which is similar to values obtained from lyotropic mesophases of cellulose acetate.[14]

Obviously more work remains to be done on most of the aspects tackled here for furanic–aromatic polyamides, but it is already interesting to note that the presence of the furan ring in a macromolecular chain as part of the backbone in conjunction with aromatic rings allows a lyotropic liquid-crystal behavior above both a critical molecular weight and a critical concentration in NMP containing LiCl. The furan heterocycle with substituents at C2 and C5 is not in itself a mesogenic structure according to calculations and direct appraisal.[15] The high molecular weight character of polyamide **19** is therefore essential to the rigidity and association necessary to induce the formation (separation) of liquid crystals from solutions.

All-Furanic Polyamides. The three furanic diamines **10**, **15**, and **18** carry a methylene group between the furan ring and the NH_2 group. This is inevitable because furanamines tautomerize to the more stable imines in most cases. The basicity of **10**, **15**, and **18** is therefore higher than that of the aromatic amines used in the preceding section, and this precludes the use of the "direct" condensation technique, as mentioned above. All-furanic polyamides were therefore prepared by solution and interfacial polymerization. The following structures were obtained from the reaction of **3** + **10**, **3** + **15**, and **3** + **18**, respectively:



24



25

26

Table VI
100-MHz ^{1}H NMR Data for All-Furanic Polyamides

polyamide	δ (ppm relative to TMS)
24	DMF-d_7: 4.51 (s, 4 H, CH_2); 6.24 (s, 2 H, H3 and H4 Fu-CH_2); 7.21 (s, 2 H, H3 and H4 Fu-CO); 8.86 (s, 2 H, NH)
25	DMSO-d_6: 4.31 (s, 4 H, CH_2); 7.23 (s, 2 H, H3 and H4); 7.54 (s, 2 H, H2 and H5); 8.8 (s, 2 H, NH)
26	DMSO-d_6: 4.36 (s, 4 H, CH_2N); 4.43 (s, 4 H, CH_2O); 6.29 (m, 4 H, H3 and H4 Fu-CH_2); 7.17 (s, 2 H, H3 and H4 Fu-CO); 9 (s, 2 H, NH)

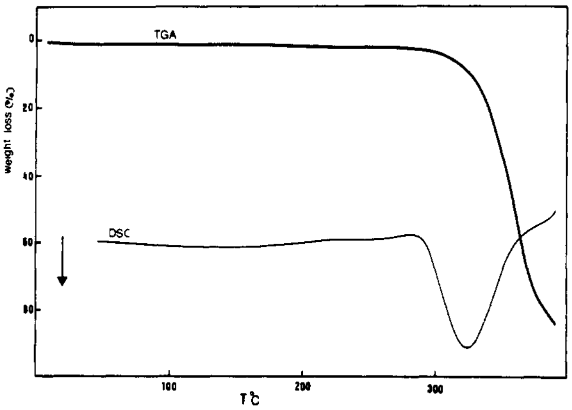


Figure 5. DSC and TGA tracings for polymer **24**. Heating rate: 10 °C/min for DSC and 5 °C/min for TGA.

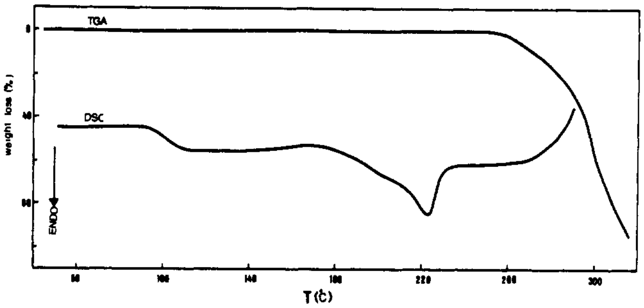


Figure 6. DSC and TGA tracings for polymer **26**. Heating rate: 10 °C/min for DSC and 5 °C/min for TGA.

Table V gives the results of some typical polycondensation experiments involving acid dichloride **3** and the three furanic diamines. Both yields and inherent viscosities were low. Table VI shows the ^{1}H NMR characterization of the resulting polymers. Their infrared spectra were consistent with the expected structure, with typical absorptions at 1650–1670 cm^{-1} (amide carbonyl) and 3300 cm^{-1} (amide N-H stretching) and the peaks specific to each polyamide (differently substituted furan rings, ether groups, ...).

DSC and TGA analyses for two of these polymers are given in Figures 5 and 6. Polymer **24** (Figure 5) shows melting with decomposition starting at about 325 °C. Polymer **25** gave a similar behavior (not shown here) but starting at 240 °C. Again, a major difference is encountered in the thermal response of two polymers bearing furan rings enchained in either 2,5- or 3,4-modes in the backbone as discussed above when discussing the different features of polymers **19** and **23**. This supports the postulate of a higher chain stiffness when the rings enter as 2,5-units. The diagrams for polymer **26** in Figure 6 show a clear T_g at about 100 °C and the melting of crystalline regions beginning at about 180 °C and ending at 225 °C. There is in this case a fairly wide temperature gap between the formation of the liquid polymer and its thermal degradation, which starts at about 260 °C.

It seems clear that the use of comonomers bearing the $FuCH_2NH_2$ group introduces some problems in terms of optimization of the yields and DPs of the resulting polyamides. This is most probably due to two causes: the first has to do with the difficulties associated with the purification of these monomers, which are prone to oxidation and resinification; the second involves the relative mobility of the hydrogen atoms of the CH_2 groups attached to the furan ring, which can give rise to side reactions during the polymer synthesis. These problems are being dealt with in order to assess the magnitude of the respective negative roles.

Conclusion

It has been shown that it is possible to synthesize furanic–aromatic polyamides possessing a regular structure, high molecular weights, and good thermal stability. In one instance, lyotropic liquid crystals were prepared. When both monomers are furanic, it is more difficult to attain satisfactory properties.

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