New polyacylhydrazone dynamers incorporating furan moieties

Ichraf Jarraya, Imen Abdelhedi, Majdi Abid, Souhir Abid*and Rachid El Gharbi

Laboratory of Applied Chemistry HCGP, Faculty of Science, University of Sfax, 3000 Sfax Tunisia.

Abstract: Solution polycondensation of furanic dihydrazides with different bridging groups, in conjunction with terephthaldehyde or isophthaldehyde, gave high yields of a novel series of furanic polyacylhydrazones with high molecular weights. The polymers were characterized by solubility tests, viscosity measurements, ^{1}H and ^{13}C NMR, FTIR spectroscopies and thermogravimetric analysis. The polyacylhydrazones obtained had inherent viscosities in the range of 0.52-1.21 dL/g, and were easily dissolved in common polar solvents. The glass-transition temperatures of these polymers were recorded between 201 and 232°C. Decomposition temperature for 10% weight loss all occurred above 352°C in nitrogen atmosphere.

Keywords: Furan polymers, Polyaclhydrazone, Dynamers, Renewable, Dynamic covalent chemistry.

Introduction

Dynamic covalent chemistry[1-3] has recently attracted considerable attention as a powerful methodology for developing new functional materials[4,5] such as dynamic covalent polymers which are dynamic by nature (supramolecular) or by design (molecular)[3,6,7]. The performance of these polymers is driven by the ability to undergo exchange, incorporation or decorporation of their monomeric subunits, linked together by respectively labile non-covalent interactions or reversible covalent bonds, depending on the external conditions[8-12]. Particularly, the imine type bonds are formed by reaction of amino-containing groups with carbonyl groups, so that polycondensation of difunctional monomers yields molecular dynamers, such as polyacylhydrazones[13-15].

These polymers present particularly attractive features[16-21]: (i) they are strict alternating copolymers exhibiting physical properties different from those of the original unexchanged polymer; (ii) they are dynamic covalent polymers (molecular dynamers) due to the reversibility of the acylhydrazone bond, and (iii) they are therefore able to incorporate, decorporate or reshuffle their constituting monomers, in particular in response to external stimuli and environmental physical or chemical factors (heat, light, chemical entities, etc.). ; (iv) they form in high yield under mild and adjustable conditions by mixing different dynamers; (v) they contain an amide group providing hydrogen bonding interactions, as in polyamides. Thus, the features of polyacylhydrazone dynamers provide a powerful and easily implemented methodology for the generation of new materials presenting adaptive behaviour.

For instance, Qin Xu et al.[22] have recently described a pH-responsive drug carrier, poly (ethyleneglycol) (PEG)-hyperbranched polyacylhydrazone), which can form nanoscale micelles to be used as anti cancer drug carriers with pH-controlled drug release.

On the other hand, the synthesis of polymers bearing furan moieties constitutes an interesting way to exploit the vegetable biomass, as shown by the rich literature dealing with a large variety of structures and properties[23]. Given the extensive experience of our laboratories in the field of furan-based polymers[23-31], we decided to study the synthesis of a novel class of polyacylhydrazone dynamers incorporating 2,5-substituted furan moieties in their backbone.

To the best of our knowledge, no reports on furan polyacylhydrazone have appeared in the literature. In the present paper, we describe the synthesis of furan polyacylhydrazone by solution polycondensation of furan dihydrazides with aromatic dialdehydes (terephthaldehyd or isophthaldehyd). The choice of these two dialdehydes was based on their well-documented role in aromatic polyacylhydrazones.

Experimental Section

Chemicals

All chemicals were purchased from Aldrich Chemical Company. *N,N*-dimethyl-acetamide (DMAc), *N*-methyl pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), were treated with potassium hydroxide pellets for 24 h and distilled under reduced pressure over phosphorus pentoxide prior to their use.

The aromatic dialdehydes, terephthaldehyde (TPA), isophthaldehyde (IPA), 2-Furyl hydrazide (FH) and benzaldehyde (BA) presented high degree of purity and were used as received.

Synthesis of bifuranic dihydrazides

Bifuranic dihydrazides **DHF₁-DHF₇** were synthesized as already reported[27]. This synthesis involves the coupling reaction of bifuranic diesters obtained in turn by the condensation of ethyl 2-furoate with the corresponding aldehyde or ketone with hydrazine monohydrate in methanol reflux. These dihydrazides were purified by recrystalization in water and characterized by FTIR and ^{1}H and ^{13}C NMR spectroscopy.

| Dihydrazide	DHF$_1$	DHF$_2$	DHF$_3$	DHF$_4$	DHF$_5$	DHF$_6$	DHF$_7$
R$_1$/R$_2$	CH$_3$/CH$_3$	CH$_3$/C$_2$H$_5$	CH$_3$/C$_3$H$_7$	CH$_3$/C$_4$H$_9$	CH$_3$/C$_5$H$_{11}$	CH$_3$/C$_6$H$_5$	CH$_3$/H
Yields (%)	80	71	65	60	66	62	75
Tm (°C)	210	173	151	144	168	109	159

Synthesis of model compounds

The dimeric or trimeric acylhydrazone model compounds **MC₁-MC₃** was prepared as follows: a solution of 5 mmol of hydrazide or dihydrazide and the appropriate stoichiometric corresponding aldehyde or dialdehyde in 10 mL of DMAc was introduced in a 100 mL, two-necked, round-bottomed flask fitted with a gas inlet and outlet, condenser and a magnetic stirrer. This solution was stirred under nitrogen at 25°C for 6 h. The viscous reaction mixture was poured into 100 mL of water, with constant stirring to produce a precipitate that was washed with methanol and hot water, collected on a filter, and dried at 60 °C under vacuum for 12 h.
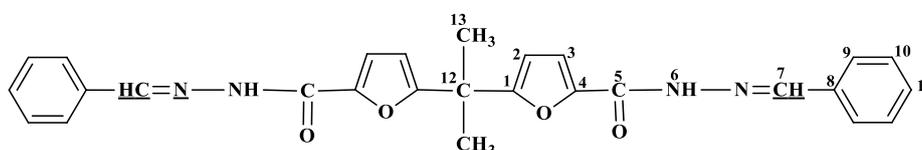
MC$_1$ ^{1}H NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 1.72(H^{13},6H) 6.42(H^2,2H), 7.23(H^3,2H), 7.42(H^{10},H^{11},6H), 7.68(H^9,4H), 8.43(H^7,2H), 11.59(H^6,2H). ^{13}C NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 40.96 ppm) δ = 26.30(C^{13},2C), 38.06(C^{12},1C), 107.98(C^2,2C), 116.18(C^3,2C), 127.55(C^{11},2C), 129.37(C^9,C^{10},8C), 130.57(C^8,2C), 134.72(C^7,2C), 145.92(C^1,2C), 148.43(C^4,2C), 162.16(C^5,2C),. Yield= 85%, Tm= 298°C.
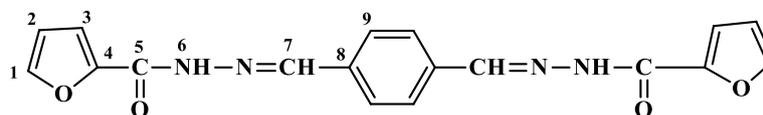
MC$_2$ ^{1}H NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 6.70(H^2,2H), 7.31(H^3,2H), 7.77(H^9,4H), 7.97(H^1,2H), 8.45(H^7,2H), 11.97(H^6,2H). ^{13}C NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 40.96 ppm) δ = 112.48(C^3,2C), 115.48(C^2,2C), 130.32(C^9,4C), 136.00(C^8,2C), 146.31(C^1,2C), 146.90(C^4,2C), 147.42(C^7,2C), 154.58(C^5,2C),. Yield= 81%, Tm>300°C.
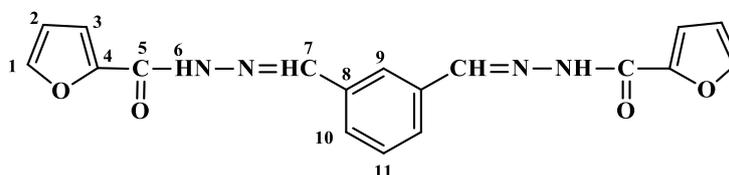
MC$_3$ ^{1}H NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 6.70(H^2,2H), 7.32(H^3,2H), 7.52(H^{11},1H) 7.75(H^{10},2H), 7.94(H^1,2H), 8.21(H^9,1H), 8.49(H^7,2H), 11.92(H^6,2H). ^{13}C NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 40.96 ppm) δ = 112.62(C^3,2C), 115.62(C^2,2C), 129.93(C^{11},1C), 130.26(C^{10},2C), 135.74(C^9,1C), 137.16(C^8,2C),146.44(C^1,2C), 147.05(C^4,2C), 147.69(C^7,2C), 154.81(C^5,2C),. Yield= 75%, Tm=146°C.

Synthesis of polyacylhydrazones PAH$_1$-PAH$_{14}$

The synthesis of polyacylhydrazones typically was carried out as follows: a 100 mL, two-necked, round-bottomed flask equipped with a magnetic stirrer and nitrogen inlet and outlet, was charged with 2.5 mmol of the dihydrazide and 10 mL of dry DMAc, 2.5 mmol of dialdehyde then added in one portion. The mixture was stirred at 25°C. After 24 h, the reaction mixture was poured into 100 mL of water, with constant stirring to produce a precipitate that was washed with water, collected on a filter, and dried at 60°C under vacuum to constant weight. The term « yield » will be used in this work to express the amount of material obtained following these operations.
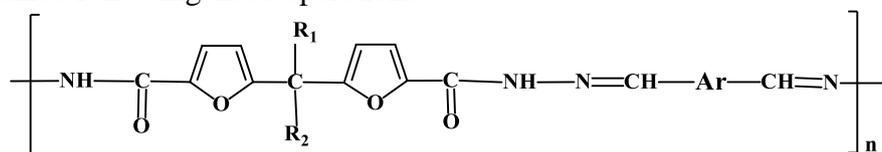
|	PAH$_1$	PAH$_2$	PAH$_3$	PAH$_4$	PAH$_5$	PAH$_6$	PAH$_7$
R$_1$/R$_2$	CH$_3$/CH$_3$	CH$_3$/CH$_3$	CH$_3$/C$_2$H$_5$	CH$_3$/C$_2$H$_5$	CH$_3$/C$_3$H$_7$	CH$_3$/C$_3$H$_7$	CH$_3$/C$_4$H$_9$
Ar							
	PAH$_8$	PAH$_9$	PAH$_{10}$	PAH$_{11}$	PAH$_{12}$	PAH$_{13}$	PAH$_{14}$
R$_1$/R$_2$	CH$_3$/C$_4$H$_9$	CH$_3$/C$_5$H$_{11}$	CH$_3$/C$_5$H$_{11}$	CH$_3$/C$_6$H$_5$	CH$_3$/C$_6$H$_5$	CH$_3$/H	CH$_3$/H
Ar							

Characterization methods

IR spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer (FTIR 1650). The FTIR samples were prepared by casting films of the materials on KBr pellets.

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 MHz spectrometers in DMSO solutions using solvent peaks as internal chemical shift reference (δ(DMSO-d_6) = 2.48 ppm (^{1}H) and 40. 96 ppm (^{13}C)).

Inherent viscosities were determined at 25°C from DMSO solutions with a polymer concentration of 0.15 g dL^{-1} using an Ubbelhode AVS-400 microviscosimeter.

Differential Scanning Calorimetry *(DSC)* analyses were carried out on a 2920 TA Instruments apparatus equipped with a liquid nitrogen cooling accessory, at cooling and heating rate of 20°C/min. Transition temperatures were measured on the second heating curves after a first heating at 150°C. Glass transition temperatures (Tg) were taken at the inflection point and melting points at the minimum of melting endotherms.

Thermogravimetric Analyses (TGA) were carried out on a TA instruments Q50 thermogravimetric analyzer system at heating rate of 20°C/min, under nitrogen atmosphere.
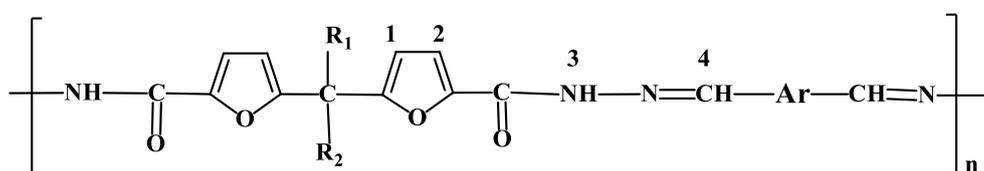
PAH$_1$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 1.78 (R$_1$/R$_2$ = CH$_3$/CH$_3$), 6.47 (H^1, 2H), 7.33 (H^2, 2H), 7.56,7.77,8.11 (CH Ar, 4H), 8.55 (H^4,2H) and 11.80 (H^3, 2H), ppm. Yield = 95%, η_{inh}=0.63 dL/g, Tg=228°C, Td=369°C.

PAH$_2$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 1.83 (R$_1$/R$_2$ = CH$_3$/CH$_3$), 6.48 (H^1, 2H), 7.29 (H^2, 2H), 7.89 (CH Ar, 4H), 8.58 (H^4,2H) and 11.82 (H^3, 2H) ppm. Yield = 99%, η_{inh} = 0.59 dL/g, Tg = 221°C, Td = 356°C.

PAH$_3$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.82 - 2.17 (R$_1$/R$_2$ = CH$_3$/C$_2$H$_5$), 6.46 (H^1, 2H), 7.29 (H^2, 2H), 7.51 - 8.23 (CH Ar, 4H), 8.50 (H^4,2H) and 11.68 (H^3, 2H) ppm. Yield = 90%, η_{inh} = 0.73 dL/g, Tg=216°C, Td = 344°C.

PAH$_4$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.81 - 2.20 (R$_1$/R$_2$ = CH$_3$/C$_2$H$_5$), 6.50 (H^1, 2H), 7.31 (H^2, 2H), 7.80 (CH Ar, 4H), 8.50 (H^4,2H) and 11.70 (H^3, 2H) ppm. Yield = 87%, η_{inh} = 0.54 dL/g, Tg = 219°C, Td = 358°C.

PAH$_5$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.85 - 2.10 (R$_1$/R$_2$ = CH$_3$/C$_3$H$_7$), 6.42 (H^1, 2H), 7.26 (H^2, 2H), 7.50 - 8.11 (CH Ar, 4H), 8.50 (H^4,2H) and 11.69 (H^3, 2H) ppm. Yield = 83%, η_{inh} = 0.52 dL/g, Tg = 217°C, Td = 356°C.

PAH$_6$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.87 - 2.50 (R$_1$/R$_2$ = CH$_3$/C$_3$H$_7$), 6.44 (H^1, 2H), 7.28 (H^2, 2H), 7.76 (CH Ar, 4H), 8.50 (H^4,2H) and 11.73 (H^3, 2H), ppm. Yield = 89%, η_{inh} = 0.55 dL/g, Tg = 214°C, Td = 352°C.

PAH$_7$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.80 - 2.10 (R$_1$/R$_2$ = CH$_3$/C$_4$H$_9$), 6.42 (H^1, 2H), 7.25 (H^2, 2H), 7.50 - 8.07 (CH Ar, 4H), 8.48 (H^4,2H) and 11.69 (H^3, 2H) ppm. Yield = 90%, η_{inh} = 0.53 dL/g, Tg = 211°C, Td = 365°C.

PAH$_8$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.81 - 2.05 (R$_1$/R$_2$ = CH$_3$/C$_4$H$_9$), 6.43 (H^1, 2H), 7.29 (H^2, 2H), 7.75 (CH Ar, 4H), 8.45 (H^4,2H) and 11.70 (H^3, 2H)ppm. Yield = 94%, η_{inh} = 0.52 dL/g, Tg = 211°C, Td = 362°C.

PAH$_9$ ^{1}H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.76 – 1.66 (R$_1$/R$_2$= CH$_3$/C$_5$H$_{11}$), 6.30 (H^1, 2H), 7.09 (H^2, 2H), 7.50 - 8.07 (CH Ar, 4H), 8.45 (H^4,2H) and 11.69 (H^3, 2H) ppm. Yield = 94%, η_{inh} = 0.53 dL/g, Tg=206°C, Td= 361°C.

PAH₁₀ ¹H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.79 - 2.11 ($R_1/R_2 = CH_3/C_5H_{11}$), 6.30 (H¹, 2H), 7.09 (H², 2H), 7.75 (CH Ar, 4H), 8.45 (H⁴,2H) and 11.69 (H³, 2H) ppm. Yield = 96%, η_{inh}=0.52 dL/g, Tg = 201°C, Td = 365°C.

PAH₁₁ ¹H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.76 - 2.10 ($R_1/R_2 = CH_3/C_6H_5$), 6.40 (H¹, 2H), 7.25 (H², 2H), 7.50 - 8.01 (CH Ar, 4H), 8.49 (H⁴,2H) and11.69 (H³, 2H) ppm. Yield = 94%, η_{inh} = 0.58 dL/g, Tg = 229°C, Td = 357°C.

PAH₁₂ ¹H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 0.79 - 2.10 ($R_1/R_2 = CH_3/C_6H_5$), 6.43 (H¹, 2H), 7.29 (H², 2H), 7.75 (CH Ar, 4H), 8.45 (H⁴,2H) and 11.67 (H³, 2H) ppm. Yield = 94%, η_{inh} = 0.55 dL/g, Tg = 232°C, Td = 362°C.

PAH₁₃ ¹H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 1.65 - 4.50 ($R_1/R_2 = CH_3/H$), 6.44 (H¹, 2H), 7.30 (H², 2H), 7.51 - 8.05 (CH Ar, 4H), 8.45 (H⁴,2H) and 11.75 (H³, 2H) ppm. Yield = 92%, η_{inh} = 0.59 dL/g, Tg = 230°C, Td = 352°C.

PAH₁₄ ¹H-NMR (300MHz, DMSO-d6, ref: δ(DMSO-d6) = 2.48 ppm) δ = 1.63 - 4.50 ($R_1/R_2 = CH_3/H$), 6.44 (H¹, 2H), 7.28 (H², 2H), 7.75 (CH Ar, 4H), 8.44 (H⁴,2H) and 11.76 (H³, 2H)ppm. Yield = 93%, Tg = 225°C, Td = 357°C.

Results and Discussion

Model compounds

In order to gain a useful insight into the feasibility of the corresponding polycondensations, three acylhydrazone model compounds **MC₁-MC₃** were prepared by stoichiometric addition reaction of DHF₁ with BA, TPA with FH and IPA with FH in DMAc as shown in Scheme 1.
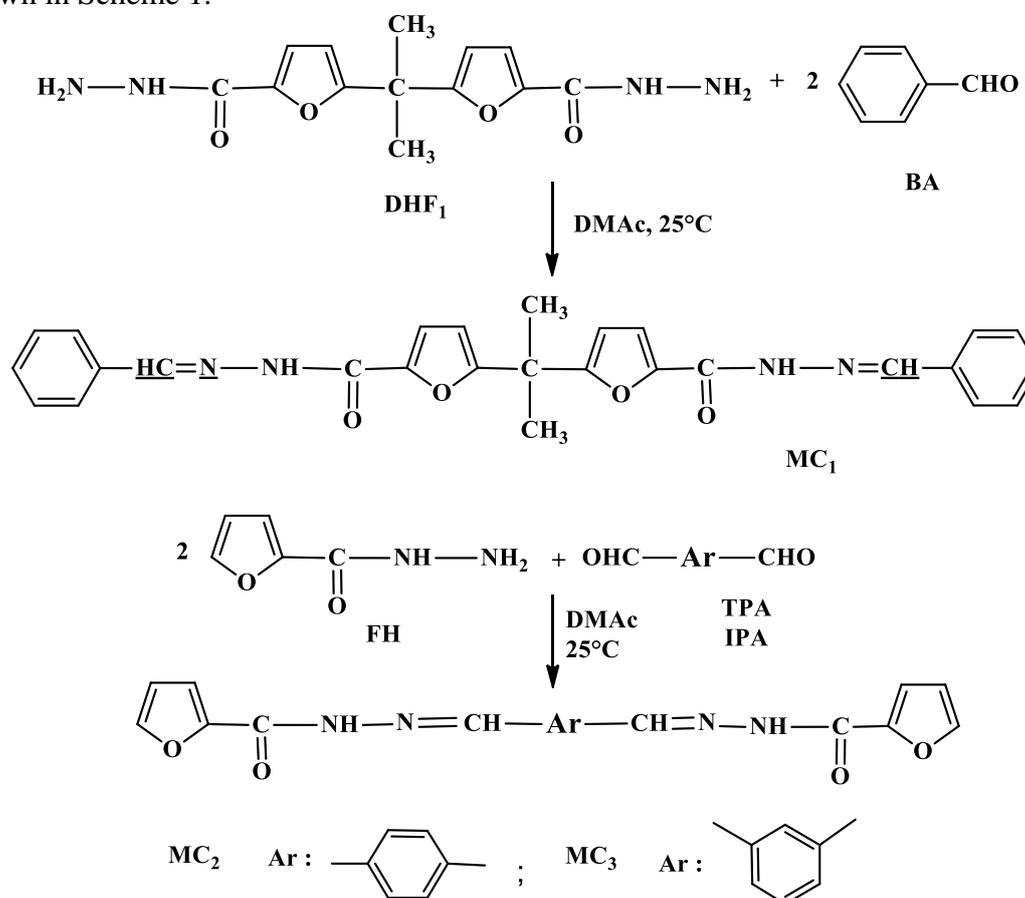
Scheme 1. Synthesis of the three model compounds **MC₁-MC₃**

The structures of **MC₁-MC₃** were confirmed by spectroscopic analyses, which showed the presence of acylhydrazone groups associated to furanic or aromatic moieties with disappearing of the –NH₂ peaks of hydrazine at 3300 cm⁻¹ and the C=O peaks of the aldehyde at 1640 cm⁻¹ used in the condensation reactions. In particular, FTIR spectra of these furanic acylhydrazones showed the presence of (cm⁻¹, KBr): C=O at 1643-1670 cm⁻¹, C=N at 1641-1666 cm⁻¹, NH at 3428-3443 cm⁻¹, C-H (aromatic) at 3035-3047 cm⁻¹, C=C (aromatic) at 1603-1613 cm⁻¹, C=C (furanic) at 1544-1560 cm⁻¹, furan ring breathing at 1010-1027 cm⁻¹.

The ¹H NMR spectra also agree with the structures proposed. In particular the -N**H₂** resonance of starting dihydrazide at 4.5 ppm and aldehyde function are no longer present and the NH resonance characteristic of the NH-CO group and imine proton appear. The ¹H NMR spectrum of model compound **MC₁** is given in Figure 1.
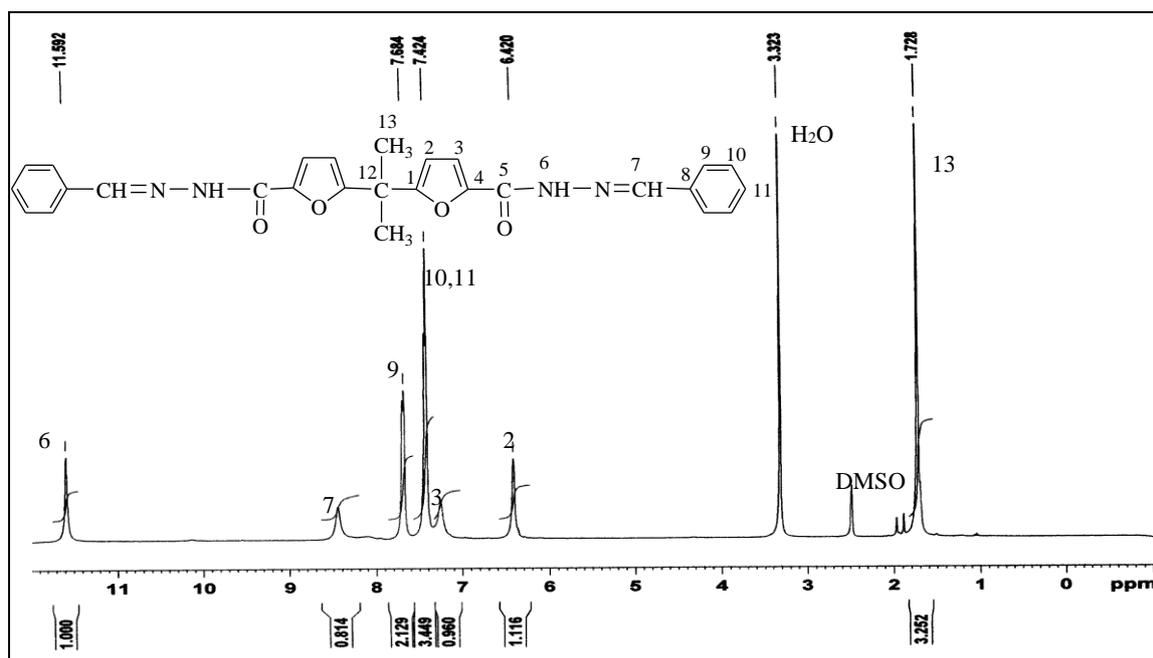

Fig.1. ¹H NMR spectrum (300MHz, DMSO-*d₆*) of **MC₁**

Polyacylhydrazones synthesis

By solution polycondensation of equimolar mixtures of bifuranic dihydrazide DHF₁-DHF₇ and dialdehydes TPA or IPA, fourteen polyacylhydrazones have been synthesized (Scheme 2). The reaction was carried out in a polar solvent (DMAc) at 25°C. The progress of the reaction was followed by the time evolution of both polymer yield and molecular weight (assessed in terms of inherent viscosity) by regular withdrawals from the reaction medium.
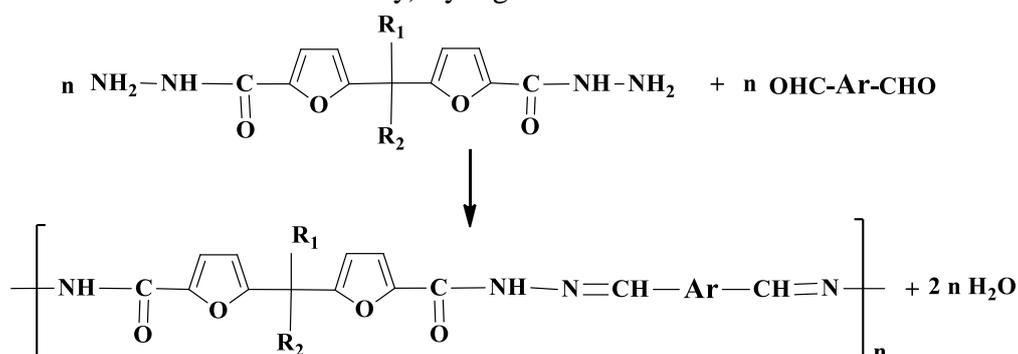
Scheme 2. Synthesis of polymers **PAH₁ – PAH₁₄**

Polymers were separated in high yields by precipitation in water. The yields refer to the amount of polymer isolated according to the procedure described above with respect to the total amount of monomers used, viz. the percentage of polyacylhydrazone insoluble in water. It is assumed that the soluble portion was in fact made up of oligomeric products. Inherent viscosity ranging from 0.52 to 0.73 dL/g indicated the formation of medium to reasonably high molecular weight polymers.

The FTIR, ^{1}H NMR spectra of all these polymers confirmed their regular linear structure, devoid of detectable anomalies. Figure 2 shows the ^{1}H NMR spectrum of furanic–aromatic polyacylhydrazone **PAH₁₄** as example of satisfactory structural features. The ^{1}H NMR spectra showed no signals to hydrazide or aldehyde functions and two singlet signals at 11.67-11.80 and 8.44-8.55 ppm corresponding respectively to N**H** and N=C**H** proton. No resonances arising from endgroups or side-reactions are detected in these spectra, showing that the expected high molecular weight polymers were obtained.
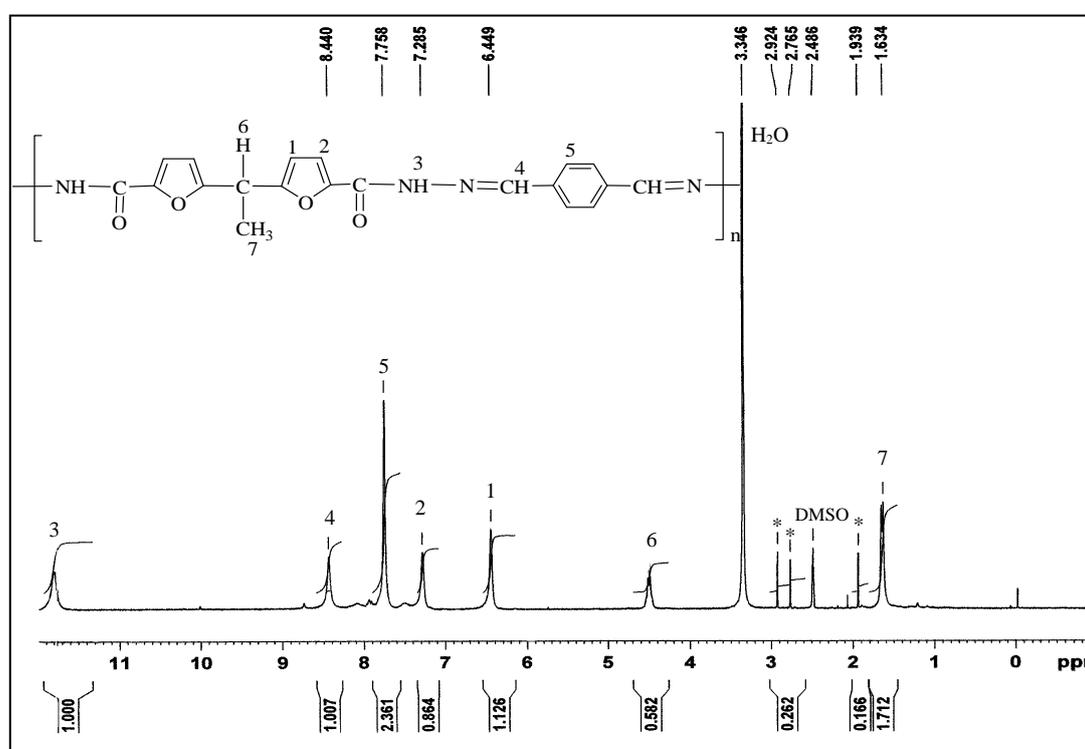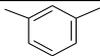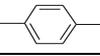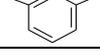

Fig.2. 1H NMR spectrum (300MHz, DMSO-*d₆*) of **PAH₁₄** *DMAc

The major FTIR features (Table 1) include a carbonyl peak varying in the spectral range 1651-1662 cm^{-1}, absorption at about 1641-1654 cm^{-1} characteristic for C=N, absorption at 3200-3235 cm^{-1} characteristic NH of the acylhydrazone function, the vibrations arising from the furanic ring at 3129, 1514, 1023 cm^{-1} and those characteristic of 2,5-disubstituted furanic rings at 956, 806 and 749 cm^{-1}. Fig. 3 provides a typical example of such a spectrum.

Table 1. FTIR spectral data of the synthesized compounds

Comp.	C=N	C=O	NH libre	C=C(aromatic)	CH(furanic)	C=C(furanic)	furan ring breathing	2,5-disubstituted furan ring
PAH₁	1648	1656	3221	1543	3129	1514	1023	954, 802, 749
PAH₂	1649	1656	3200	1543	3141	1511	1025	953, 805,750
PAH₃	1648	1651	3213	1542	3139	1512	1023	952, 804, 749
PAH₄	1650	1656	3219	1544	3143	1516	1022	951, 806, 751
PAH₅	1647	1654	3235	1542	3147	1515	1023	955, 808,749
PAH₆	1651	1662	3200	1547	3129	1514	1023	956, 806,749
PAH₇	1644	1654	3220	1542	3133	1516	1024	959, 801,749
PAH₈	1651	1655	3222	1544	3145	1511	1020	951, 804,749
PAH₉	1643	1655	3210	1549	3210	1511	1021	957, 798, 750
PAH₁₀	1651	1659	3210	1548	3182	1514	1019	950, 803, 750
PAH₁₁	1644	1652	3226	1540	3133	1516	1022	956, 802, 749
PAH₁₂	1654	1661	3226	1546	3133	1511	1023	954, 807, 750
PAH₁₃	1641	1651	3200	1547	3141	1514	1019	958, 803, 750
PAH₁₄	1647	1653	3200	1542	3177	1517	1018	953, 809, 749

Furanic polyacylhydrazone **PAH₁ – PAH₁₄** solubilities were studied qualitatively in various solvents at room temperature and upon heating. It can be seen as shown in Table 2 that all these polymers were easily dissolved both in polar solvents such as DMAc, DMF, NMP, DMSO and m-cresol and in less polar solvents such as CHCl₃, and THF. Their solubility was the higher, the longer the aliphatic moieties R_1 and R_2.

Figure 3. FTIR spectrum of **PAH₃**

Table 2. Solubility of the various polyacylhydrazones

PAH	R_1/R_2	-Ar-	DMSO	DMAc	DMF	m-crésol	THF	CH_2Cl_2	$CHCl_3$	EtOH
PAH₁	CH_3 / CH_3		±	+	+	+	-	-	-	-
PAH₂	CH_3 / CH_3		++	+	+	++	±	-	±	-
PAH₃	CH_3 / C_2H_5		+	+	+	++	-	-	±	-
PAH₄	CH_3 / C_2H_5		+	+	+	++	±	-	±	-
PAH₅	CH_3 / C_3H_7		+	++	+	++	+	-	+	-
PAH₆	CH_3 / C_3H_7		+	++	+	++	+	-	+	-
PAH₇	CH_3 / C_4H_9		+	+	+	++	+	-	+	-
PAH₈	CH_3 / C_4H_9		+	+	+	++	+	-	+	-
PAH₉	CH_3 /		+	+	+	++	+	-	+	-
PAH₁₀	CH_3 /		+	+	+	++	+	-	+	-
PAH₁₁	CH_3 / C_6H_5		+	+	+	+	±	-	-	-
PAH₁₂	CH_3 / C_6H_5		+	+	+	+	±	-	±	-
PAH₁₃	CH_3/ H		+	+	±	±	±	-	±	-
PAH₁₄	CH_3/ H		++	+	±	±	±	-	±	-
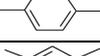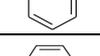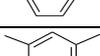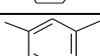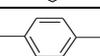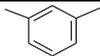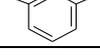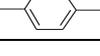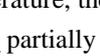
++ soluble at room temperature, the solid polymer was completely dissolved in the solvent to afford a clean.

+ soluble upon heating, ± partially soluble, − insoluble; the solid polymer did not dissolve in the solvent.
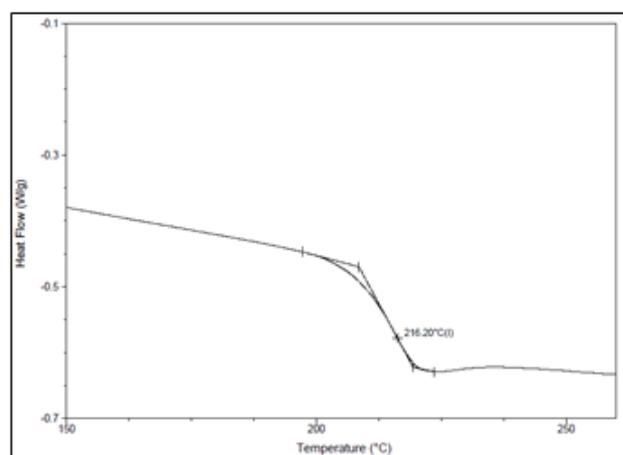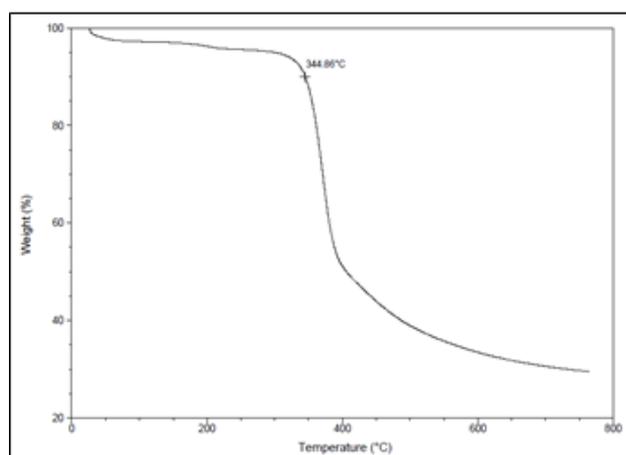

Figure 4. TGA thermogram of polymer **PAH₃** **Figure 5.** DSC thermogram of polymer**PAH₃**

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to evaluate the thermal properties of the polyacylhydrazones, TGA and DSC curves of the polyacylhydrazone **PAH₃** are shown in Figure 4 and 5 respectively. The values of their glass transition temperature (Tg) and thermal decomposition (Td) are given in experimental part.

For the latter data, the small weight loss of 3–5%, recorded between 100 and 200 °C, was attributed to the evaporation of the residual water remaining in the polymer after precipitation and drying, as previously observed with other amide group-containing polymers such as polyamides. After this first step, all polyacylhydrazones present a good thermal stability.

Conclusion

2,5-bifuranic dihydrazides were firstly synthesized and characterized and then employed to polycondense with different aromatic dialdehydes to prepare a series of novel aromatic polyacylhydrazones containing furan moieties. Experimental results indicated that the resulting polyacylhydrazones exhibited a regular structure, high inherent viscosities and a good thermal stability and most of them were soluble in polar solvents. Work is in progress to assess the properties and possible applications of these materials.

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