POLY(ACYLSEMICARBAZIDE)S INCORPORATING FURANIC MOIETIES SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF A HOMOLOGOUS SERIES

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ABSTRACT: Solution polycondensation of furanic dihydrazides with different bridging groups, in conjunction with various aromatic diisocyanates, gave high yields of a novel series of furanic poly(acylsemicarbazide)s with high molecular weights. The polymers were characterized by solubility tests, viscosity measurements, ^{1}H NMR, ^{13}C NMR and FTIR spectroscopies and thermogravimetric analysis. The poly(acylsemicarbazide)s obtained had inherent viscosities in the range of 0.23-0.70 dL/g, and were easily dissolved in common organic solvents. The glass-transition temperatures of these polymers were recorded between 135 and 200°C. Decomposition temperature for 10% weight loss all occurred above 350°C in nitrogen atmosphere. Preliminary tests on films of all polymers indicated that these materials were flexible and tough.

Key words: Furan polymers; Poly(acylsemicarbazide)s; Diisocyanates; Polycondensation; Biomass

RESUME: La polycondensation en solution de dihydrazides bifuraniques avec divers dihydrazides aromatiques conduit aux poly(acylsemeicarbazide)s correspondants avec des rendements quantitatifs et des masses molaires assez importantes. Les propriétés de ces matériaux (test de solubilité, viscosimétrie, RMN 1H, RMN 13C et FTIR) sont examinées. Les viscosités ainsi obtenues sont comprises entre 0.23-0.70 dL/g. Les températures de transition vitreuses sont comprises entre 135 and 200°C et celles de décomposition sont supérieures à 350°C.

Mots clés: Polymère furanique, Poly(acylsemicarbazide)s, Diisocyanates, Polycondensation, Biomasse

INTRODUCTION

The growing interest in polymer based on renewable resources has stimulated the development of numerous classes of macromolecular materials possessing a variety of potential applications. Sugars, ubiquitous in nature in different forms (monomers, oligomers and polymers), constitute an interesting source for preparing bio-based monomers such as furan derivatives, dianhydrohexitols and lactic acid. In the past few decades, the synthesis of monomers bearing the furan heterocyclic has widely investigated using as starting materials two first-generation furan derivatives namely furfural and hydroxymethylfurfural obtained directly by acid-catalyzed depolymerization and dehydration of residues of agricultural or forestry activities [1-6].

In our previous work we have reported the synthesis, through a simple coupling procedure, of original bifuranic monomers bio-based ethyl 2-furoate and furfurylamine which constitute the starting point of an ambitious strategy that consists of (i) exploring their conversion into macromolecular materials in conjunction with other monomers such as diols, diamines, dianydrides and diisocyanates, to prepare several polyesters [7-10], polyamides [11-13], polyhydrazides [14-16], polyimides [17] and polyureas [18], (ii) characterizing the structure and properties of these materials and (iii) assessing their interest in order to give a sound appraisal of their possible applications as alternatives to existing

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fossil-based polymers. We recently started a systematic investigation of poly(acylsemicarbazide)s containing furanic moieties calling upon different strategies in order to optimize the rate of polycondensation of dihydrazide/diisocyanate system and the molecular weight of the ensuing material. Thanks to this preliminary study conducted on a model monomer namely 5,5'-isopropylidene bis(2-furoic acid hydrazide), it became clear that poly(acylsemicarbazide)s can be readily synthesized by solution polycondensation technique in high molecular weights [19]. It seemed therefore useful to pursue this investigation in order to establish both the applicability of this technique to a series of dihydrazides with different bridging groups in conjunction with various aromatic diisocyanates and to obtain correlations between the ensuing polymers and their properties.

EXPERIMENTAL

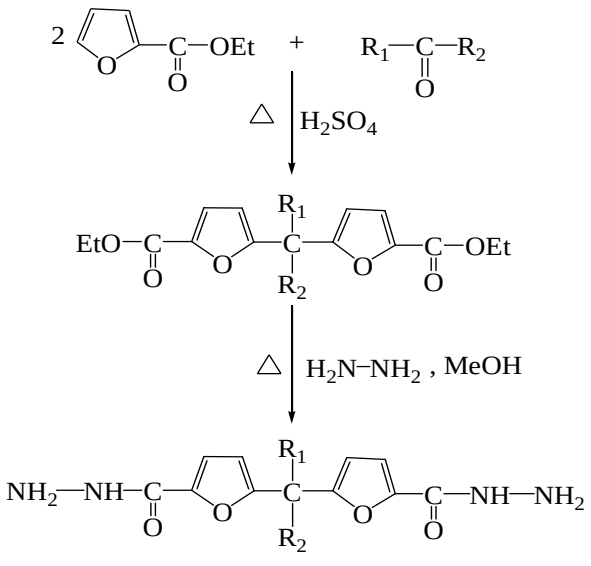
1. Materials

1,4-phenylene diisocyanate **a**, 2,4-diisocyanato-1-methyl-benzene **b** and 4,4'-oxybis(phenyl isocyanate) **c**, were high purity commercial products employed as received. N,N-dimethylacetamide (DMAc) was distilled from calcium hydride under reduced pressure. N,Ndimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dichloromethane (DCM), chloroform and m-cresol were dried and distilled as per literature procedures [20].

Dihydrazides **1**-**6** were synthesized in good yield from 2-ethyl furoate through a coupling procedure and subsequent treatment with hydrazine as previously reported [14] and as shown in Scheme 1.

2. Polymerization

All poly(acylsemicarbazide)s were prepared according to the following optimized solution polycondensation procedure **:** A mixture of 5 mmol of dihydrazide **1**-**6** and 5 mmol of diisocyanate **a**-**c** were introduced under nitrogen in 25 mL of DMAc and the resulting suspension was then stirred for 12 h before being poured into an excess of water in order to induce the precipitation of the ensuing polymer which was then washed thoroughly with water, acetone and ether and finally vacuum dried at 60°C to constant weight. The term « yield » will be used in this work to express the amount of material obtained following these operations.



1-**6**

R_1/R_2 : CH_3/CH_3 , CH_3/C_2H_5 , CH_3/C_3H_7 , CH_3/C_4H_9, CH_3/C_5H_{11} , CH_3/C_6H_5

Dihydrazides	**1**	**2**	**3**	**4**	**5**	**6**
R_1/R_2	CH_3/CH_3	CH_3/C_2H_5	CH_3/C_3H_7	CH_3/C_4H_9	CH_3/C_5H_{11}	CH_3/C_6H_5
Yield (%)	80	34	65	60	66	59
b.p. (°C) /0.07Torr	210	170	151	144	168	109

Scheme 1: synthesis of dihydrazides **1**-**6**

3. Characterization

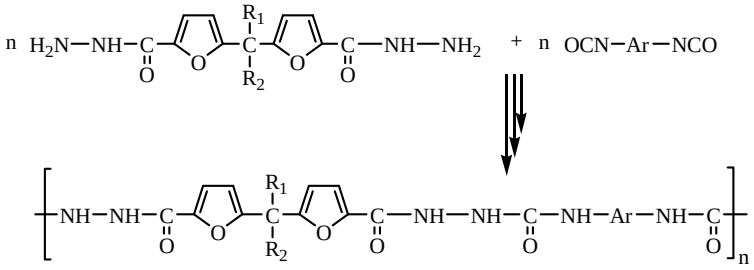
FTIR spectra were recorded on a Perkin-Elmer Infrared Spectrophotometer (FTIR 1650). The FTIR samples were prepared by casting films of the materials on KBr plates. ^{1}H NMR spectra were recorded on Bruker Avance 300 MHz spectrometers in DMSO-*6d* solutions (ref. d(DMSO) 2.48 ppm). The inherent viscosities (η_{inh}) were measured in DMSO (c = 0.1 g/dL) at 25±0.1 °C using Ubelohde capillary viscometer. The size exclusion chromatography (SEC) measurements were carried out with a modular chromatographic equipment containing a refractive index detector at ambient
temperature. A single column Hibar PS 40 (Merck) was used. The concentration of sample was c = 2 g/l (injection volume: 20 µl) and the flow rate was 1 ml/min. The molecular weights were evaluated by use of a polystyrene (PS) calibration determined with PS standards (KNAUER) using DMAc. Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent at room temperature after 24 h or on heating. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer differential scanning calorimeter DSC 7 at a heating rate of 10°C/min under flowing nitrogen. Tg was taken as the midpoint of the inflection observed on the curve of heat capacity versus temperature. Melting points were measured by DSC method. Thermogravimetric analyses (TGA) were conducted with a TA Instruments, and experiments were carried out on approximately 10 mg of samples under controlled flux of nitrogen at 50 mL/min at a heating rate of 10°C/min. Poly(acylsecarbazide) films were obtained according to the following procedure**:** polymer sample (0.5 g) was dissolved in 10 mL of DMF. This homogeneous solution was poured into a 9 cm glass Petri dish, which was placed in a 70°C oven for 4 h to remove most of the solvent and then the semidried film was further dried in vacuo at 130°C for another 2 h.

RESULTS AND DISCUSSION

1. Poly(acylsemicarbazide)s synthesis

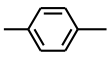
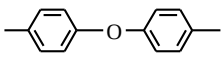
Scheme 2 illustrates the general reaction pathway for dihydrazide/diisocyanate condensations which led to the corresponding poly(acylsemicarbazide)s. As already started above, we adopted the solution polycondensation technique for these syntheses.

At first, the reaction medium was heterogeneous because of the insolubility of diisocyanates in DMAc. We noted a progressive disappearance of solid and the reaction mixture became after about 10 h a homogeneous viscous solution. Table I gives the two basic sets of data related to the optimized syntheses, ie. the yields of isolated polymers and their inherent viscosities. When reactions were conducted at 0°C, all obtained polymers, except **P_{10}**, were soluble in DMSO with inherent viscosities ranging between 0.23 and 0.70 dL/g indicating the formation of reasonably high molecular weight polymers. The molecular weights of these polymers obtained from SEC are given in Table 1. They are reasonable high for **P_1**, **P_2**, **P_4**, **P_6** moderate in the case of **P_3**, **P_5**, **P_4**, **P_8** and **P_{10}** relatively low for **P_7**. This decrease in molecular weight may be due to probably of premature precipitation polymer during the reaction, which limited further polymer growth.



P_1-P_{10}

R_1/R_2 : CH_3/CH_3 , CH_3/C_2H_5 , CH_3/C_3H_7 , CH_3/C_4H_9, CH_3/C_5H_{11} , CH_3/C_6H_5

Ar : **(a)** =  , **(b)** =  , **(c)** = 

Scheme 2: synthesis of polymers **P_1-P_{10}**

Table I. Yields and inherent viscosities related to $\mathbf{P_1}$ - $\mathbf{P_{10}}$

		T= 0°C			T= 20°C	
polymers	**monomers**	**yield (%)**	**η_{inh} (dL/g)[a]**	**Mn[c]**	**yield (%)**	**η_{inh} (dL/g)[b]**
$\mathbf{P_1}$	**1+a**	96	0,70	21300	98	0,55
$\mathbf{P_2}$	**2+a**	97	0,63	20400	93	0,38
$\mathbf{P_3}$	**3+a**	93	0,44	12600	95	0,26
$\mathbf{P_4}$	**4+a**	98	0,70	18900	92	0,34
$\mathbf{P_5}$	**5+a**	97	0,46	13500	98	0,28
$\mathbf{P_6}$	**6+a**	97	0,70	19600	98	0,21
$\mathbf{P_7}$	**1+b**	98	0,37	5700	94	0,30
$\mathbf{P_8}$	**4+b**	97	0,54	14700	98	0.23
$\mathbf{P_9}$	**1+c**	97	-	-	98	0,29
$\mathbf{P_{10}}$	**4+c**	95	0,53	11900	-	-

[a] inherent viscosities measured in DMSO (0.1g/dL) at 25°
[b] inherent viscosities measured in H_2SO_4 (0.1g/dL) at 25°C
[c] The weight molecular weight determined by SEC.

At 20°C, the reactions gave more encouraging results in terms of polymer molecular weights as suggested by the fact that polymers became insoluble in DMSO and had to be characterized by dissolving them in H_2SO_4.

2. Poly(acylsemicarbazide)s characterization

The FTIR spectra of all obtained poly(acylsemicarbazide)s were consonant with the corresponding expected structures. Table II gives the frequencies related to semicarbazide function and those arising from the furanic and aromatic moieties. The presence of NH and C=O stretching of semicarbazide linkage was confirmed by the presence of bands around 3300 and 1650 cm^{-1} respectively. Figure 1 shows a typical example of such a spectrum. These results were confirmed also by the ^1H NMR spectra which showed in particular the presence of three resonances around 8, 8.5 and 10 ppm related to the NH-NH-CO-NH group. The ^1H NMR chemical shifts and their assignments are summarized in Table III and Figure 2 shows a typical example of such a spectrum. The ^{13}C NMR spectra were also entirely consistent with the structures of the polymers (Table IV).

Table II. FTIR data ($\bar{\upsilon}$ cm^{-1}) related to $\mathbf{P_1}$ - $\mathbf{P_{10}}$ (KBr pellet).

	$\bar{\upsilon}$ (cm^{-1})									
	$\mathbf{P_1}$	$\mathbf{P_2}$	$\mathbf{P_3}$	$\mathbf{P_4}$	$\mathbf{P_5}$	$\mathbf{P_6}$	$\mathbf{P_7}$	$\mathbf{P_8}$	$\mathbf{P_9}$	$\mathbf{P_{10}}$
NH	3284	3296	3290	3300	3292	3277	3274	3282	3307	3307
CH= Furanic	3122	3113	3131	3141	3116	3120	3160	3112	3150	3154
CH= Aromatic	3040	3022	3026	3046	3011	3020	2960	2946	2973	2952
CH aliphatic	2984 2936	2977 2939	2960 2935	2954 2933	2950 2930	2950 2930	2955 2928	2952 2933	2953 2930	2950 2933
C=O stretching	1667	1665	1665	1663	1661	1654	1668	1669	1663	1664
C=C Aromatic	1602	1600	1601	1601	1600	1600	1601	1600	1600	1601
C=C Furanic	1516	1524	1517	1515	1517	1519	1532	1534	1522	1500
Fu breathing	1025	1024	1024	1022	1022	1022	1021	1024	1025	1023

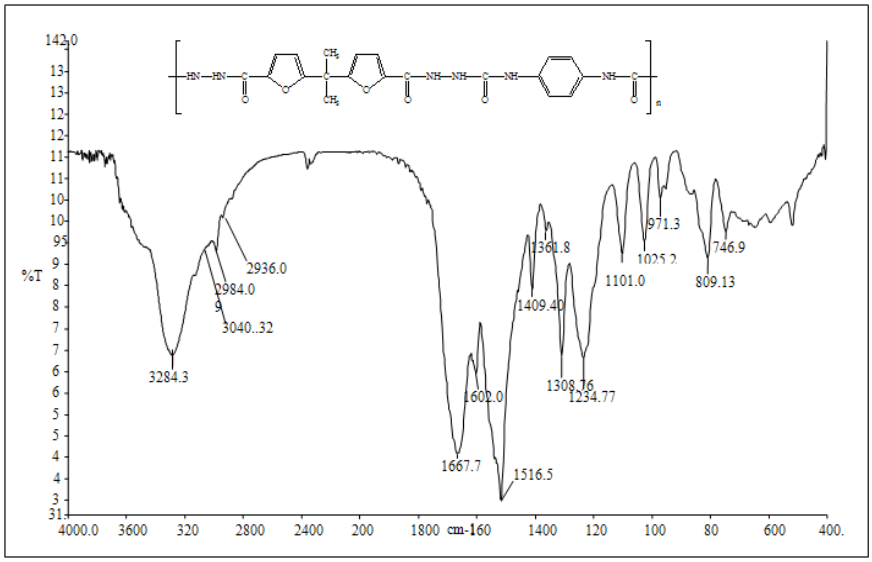


Figure 1. FTIR spectrum of $\mathbf{P_1}$

Table III . ^{1}H NMR data related to $\mathbf{P_1}$ **-** $\mathbf{P_{10}}$ in DMSO-*6d*

	δ (ppm)								
	$\mathbf{H_a}$	$\mathbf{H_b}$	$\mathbf{H_c}$	$\mathbf{H_d}$	$\mathbf{H_e}$	$\mathbf{H_f}$	$\mathbf{R_1}$	$\mathbf{R_2}$	**Ar**
$\mathbf{P_1}$	7.13	6.38	10.07	8.72	8.04	8.04	1.69	1.69	7.31
$\mathbf{P_2}$	7.14	6.41	10.05	8.71	8.03	8.03	1.94	0.75 - 2.13	7.31
$\mathbf{P_3}$	7.14	6.39	10.05	8.71	8.03	8.03	1.65	0.85 - 1.12 - 2.07	7.31
$\mathbf{P_4}$	7.13	6.39	10.05	8.71	8.03	8.03	1.65	0.85 - 1.08 - 1.25 - 2.05	7.32
$\mathbf{P_5}$	7.14	6.39	10.05	8.71	8.03	8.03	1.65	0.81-1.11-1.12-1.24-2.07	7.31
$\mathbf{P_6}$	7.21	6.34	10.11	8.71	8.03	8.03	2.09	7.07 - 7.27 - 7.31	7.34
$\mathbf{P_7}$	7.13	6.36	10.08	8.75	8.29	7.99	1.69	1.69	2.11 - 7.01 - 7.18 - 7.65
$\mathbf{P_8}$	7.13	6.38	10.08	8.75	8.29	7.99	1.65	0.83 - 1.09 - 1.26 - 2.11	2.11 - 7.02 - 7.20 - 7.67
$\mathbf{P_9}$	7.13	6.38	10.04	8.80	8.06	8.06	1.69	1.69	6.89 - 7.44
$\mathbf{P_{10}}$	7.14	6.39	10.04	8.80	8.05	8.05	1.66	0.84 - 1.10 - 1.24 - 2.07	6.89 - 7.44

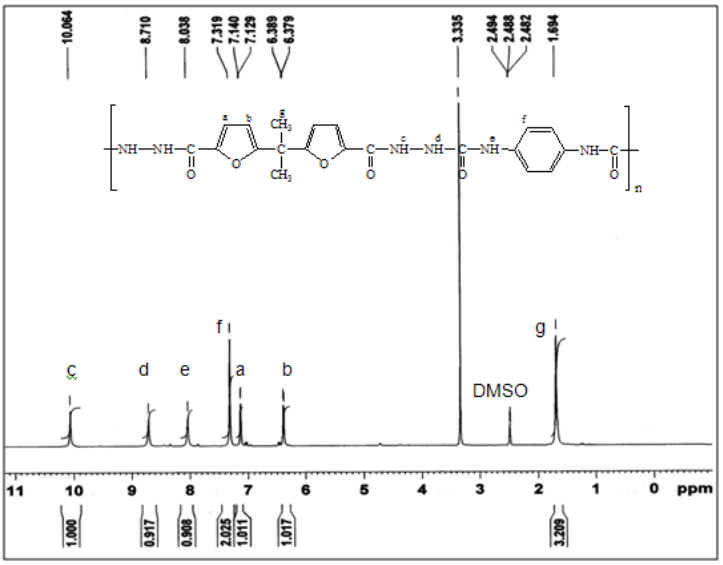


Figure 2. ^{1}H NMR spectrum of $\mathbf{P_1}$

Table IV. ^{13}C NMR data related to poly(acylsemicarbazide)s $\mathbf{P_1}$ - $\mathbf{P_{10}}$

	δ (ppm)									
	C_1	**C_2**	**C_3**	C_4	**C_5**	**C_6**	**C_7**	**R_1**	**R_2**	**Ar**
P_1	161.7	158.5	156.1	115.7	107.6	145.7	37.9	26.2	26.2	119.7 ; 134.5
P_2	160.9	158.3	155.1	115.5	108.3	145.6	41.8	21.6	8.9 ; 31.2	119.6 ; 134.4
P_3	161.0	158.3	156.0	115.5	108.1	145.6	41.5	22.2	14.5;17.5;39.0	119.5 ; 134.4
P_4	161.0	158.3	156.02	115.5	108.1	145.5	41.4	22.0	14.3; 26.4;22.7; 38.1	119.5 ; 134.4
P_5	161.0	158.3	155.99	115.5	108.1	145.5	41.5	23.7	14.2 ; 22.1 ; 22.2 ; 31.7; 38.3	119.5 ; 134.4
P_6	159.8	158.2	155.93	115.5	110.2	146.2	46.8	25.5	127.0; 27.5; 128.8;144.1	119.5 ; 134.4
P_7	161.6	158.3	155.9	115.6	107.4	145.6	37.8	26.0	26.0	17.4;113.3;114.3;122.9 130.3;137.4;138.0
P_8	161.1	158.3	156.05	115.5	108.1	145.5	41.5	22.1	14.3 ; 22.9 ; 26.4 ; 38.2	17.4;113.2;114.3;122.9 130.3;137.4;138.0
P_9	161.6	158.3	156.03	115.6	107.4	145.63	37.7	26.0	26.0	119.1;120.4;135.4;152. 2
P_{10}	161.1	158.3	156.02	115.5	108.1	145.58	41.5	22.1	14.2;26.4;22.7;3 8.1	118.9;120.5;135.4;152. 2

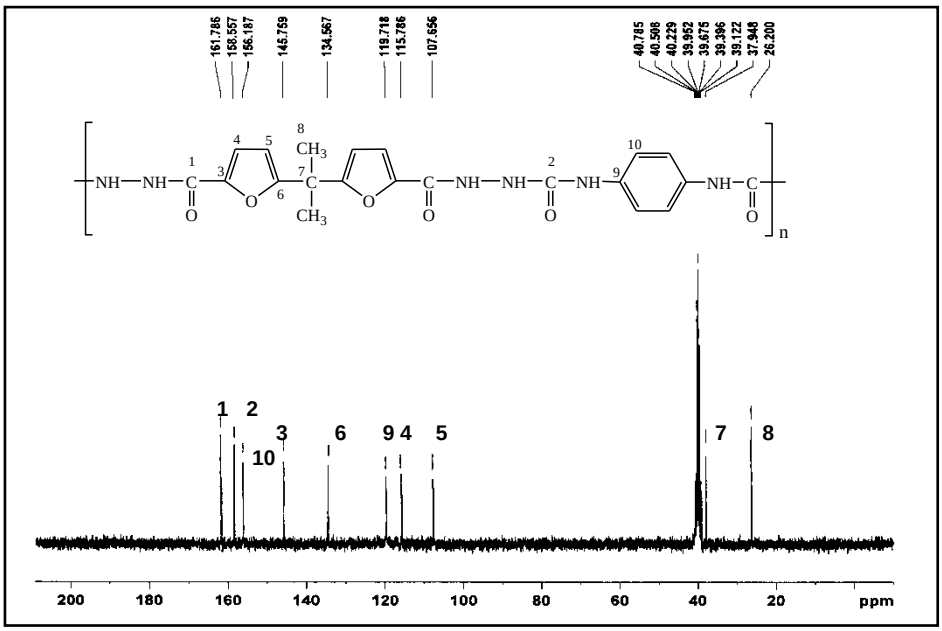


Figure 3. ^{13}C NMR spectrum of $\mathbf{P_1}$

3. Thermogravimetric Analysis

The thermal properties of the poly(acylsemicarbazide)s were evaluated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). The thermal behavior data of polymers are listed in Table V. DSC measurements were conducted with a heating rate of 15°C min^{-1} in nitrogen. Quenching from the elevated temperatures (approximately 200°C) to room temperature in air gave

predominantly amorphous samples so that the glass transition temperatures (Tg) of all poly(acylsemicarbazide)s could be easily measured in the second heating traces of DSC. The Tg values were in the range of 135 - 242°C, depending on the structure of dihydrazide component and following with increasing stiffness of the polymer backbones. Insertion of flexible ether group increased the overall flexibility of the polymer chain and, thus, generally resulted in a decrease in Tg, as evidenced by Tg order shown in Table V: $\mathbf{P_1} > \mathbf{P_{10}}$.

All polymers $\mathbf{P_1}$-$\mathbf{P_{10}}$ lose weight during heating experiments due to loss of water (%H_2O) caused by the formation of the oxadiazole groups ring [21-22]. The TGA spectra of poly(acylsemicarbazide)s show distinct regions of weight loss. The first region was placed in the range of temperatures between 135 and 242°C and was associated with the loss of adsorbed water on the polymer. The second region was placed in the range of temperatures between 168 and 273°C and was associated with the loss of water produced during the formation of oxadiazole rings. The third region was associated with the loss of volatiles caused by the degradation of the polyoxadiazole thus obtained. Although it may be assumed that the loss of weight linked to the cyclization of polyhydrazide into polyoxadiazole occurs in a narrow temperature region, it must be pointed out that the literature [23-25] reports a large variation of values for the range of temperatures where hydrazide groups are converted into oxadiazole rings. Temperature ranges can depend on residual hydrazide contents and on the particular chemical group attached to the oxadiazole ring. Fig. 4 shows that the first derivative of the TGA spectrum of $\mathbf{P_4}$ can actually define Three distinct regions.

Table V. Thermal properties of $\mathbf{P_1}$-$\mathbf{P_{10}}$

	$\mathbf{P_1}$	$\mathbf{P_2}$	$\mathbf{P_3}$	$\mathbf{P_4}$	$\mathbf{P_5}$	$\mathbf{P_6}$	$\mathbf{P_7}$	$\mathbf{P_8}$	$\mathbf{P_9}$	$\mathbf{P_{10}}$
[a]**Tg (°C)**	165	242	188	180	148	135	140	139	178	189
[b]**Td_1 (°C)**	225	238	229	247	168	247	188	234	273	262
[c]**Td_2 (°C)**	335	378	380	386	314	386	320	330	377	378
[d]**Td_3 (°C)**	488	526	486	541	436	510	473	443	468	490

[a] *Glass transition temperature, from DSC curves.*
[b] *Temperature of degradation(*1st region*), from TGA curves.*
[c] *Temperature of degradation(*2nd region*), from TGA curves.*
[d] *Temperature of degradation(*3rd region*), from TGA curves.*

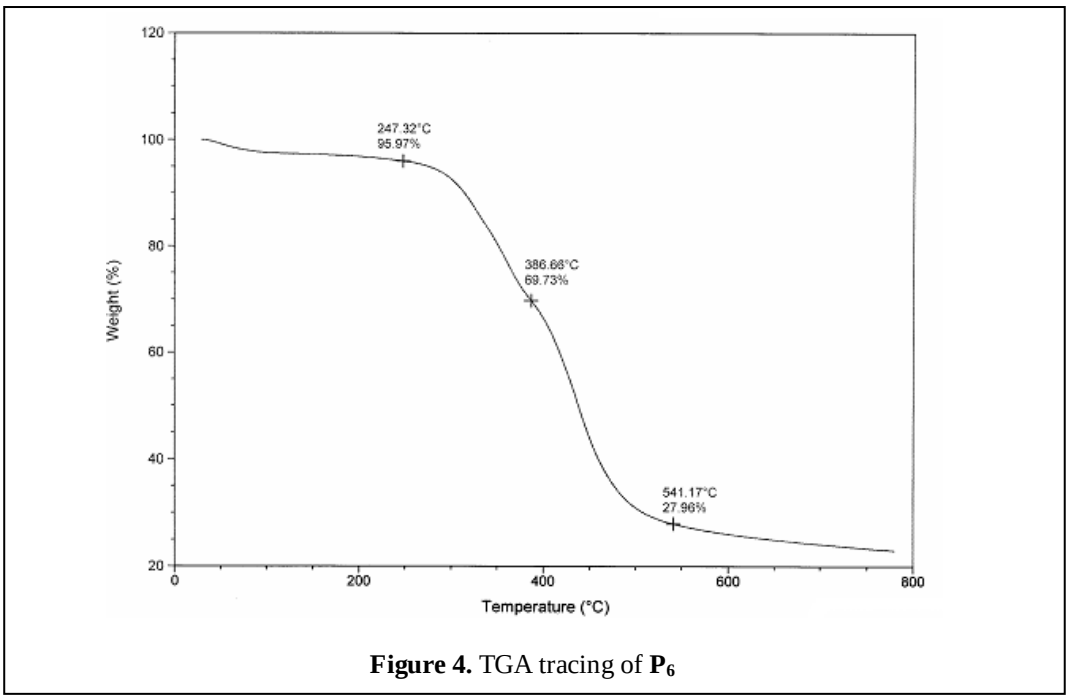


Figure 4. TGA tracing of $\mathbf{P_6}$

4. Solubility and film of polymers

The solubility of the poly(acylsemicarbazide)s were investigated for the samples in different organic solvents. All the present polymers exhibited good solubility in polar solvents such DMSO, DMF, NMP and DMAc. Analogous poly(acylsemicarbazide)s derived from isophthalic acid dihydrazide were not soluble in the above solvents [26-27]. It is obvious that introduction of flexible 2,5-bifuranic units into the polymer backbones weakened the intermolecular interactions and thus facilitate the diffusion of small molecules of solvent. The results reported in Table VI suggested that the solubility was somewhat influenced by the structure of the furan and the nature of aromatic units incorporated into the polymer chains. **P_9** showed limited solubility in high polar hot solvents probably due to the introduction of an aromatic unit.

Due to their good solubility these polymers were processed into thin films by casting their solutions onto glass plates. All the obtained films were flexible, tough, and in the case of **P_1** and **P_2** they were creasable which means that they preserved their integrity after repeated bendings. The free-standing films prepared from polymers **P_9** and **P_{10}** having a thickness in the range of 20–30 µm did not resist to repeated bendings, being less flexible, probably due to the lack of ether bridges.

Table VI. Solubility of the various poly(acylsemicarbazide)s[a]

Solvent	P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9	P_{10}
$CHCl_3$	-	-	-	-	-	-	-	-	-	-
CH_2Cl_2	-	-	-	-	-	-	-	-	-	-
m-cresol	±	±	+h	+h	±	±	±	+h	±	+h
NMP	+h	+h	±	+h	±	±	+h	+h	±	++
DMSO	++	+h	++	±	±	±	+h	±	±	±
DMAc	+h	±	++	±	±	±	+h	±	±	±
DMF	+h	+h	++	++	±	±	++	++	±	++
THF	-	-	-	-	-	-	-	-	-	-

++ , soluble at room temperature; +h , soluble on heating; ±, partially soluble on heating; -, insoluble
[a] Concentration : 10 mg/mL

CONCLUSION

2,5-bifuranic dihydrazides were firstly synthesized and characterized and then employed to polycondense with different aromatic diisocyanates to prepare a series of novel aromatic poly(acylsemicarbazide)s containing furan moieties. Experimental results indicated that the resulting poly(acylsemicarbazide)s exhibited a regular structure, high inherent viscosities and a good thermal stability and most of them were soluble in polar solvents. Preliminary tests on films of all polymers indicated that these materials were flexible and tough.

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