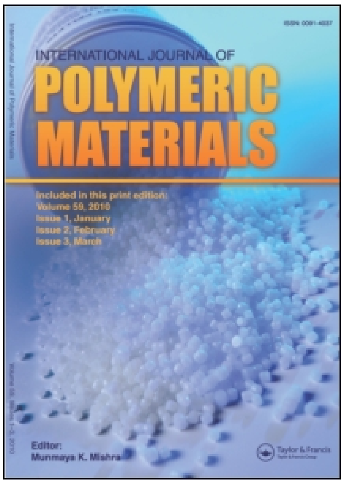

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New Polymer Syntheses Part 53. Novel Polyamides of Diarylidenecycloalkanone Containing Azo Groups in the Polymer Backbone: Synthesis and Characterization

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New Polymer Syntheses Part 53. Novel Polyamides of Diarylidenecycloalkanone Containing Azo Groups in the Polymer Backbone: Synthesis and Characterization

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A new interesting class of polyamides of diarylidenecycloalkanone containing azo groups in the polymer backbone $\mathbf{6_{a\text{-}d}}$ was synthesized by a solution polycondensation reaction of bis 2-aminoarylidene monomers $\mathbf{3_{a,b}}$ with 4,4′-azodibenzoyl dichlorides and 3,3′-azodibenzoyl dichlorides in NMP as a solvent, using anhydrous LiCl as a catalyst at room temperature. The model compounds **4, 5** were synthesized by the interaction of one mole of bis 2-aminoarylidene monomers $\mathbf{3_{a,b}}$ with two moles of benzoyl chloride using anhydrous LiCl as a catalyst in NMP at room temperature. The resulting polymers were characterized by elemental and spectral analyses, besides solubility and viscometry measurements. The thermal properties of those polymers were evaluated by TGA, DTG and DTA measurements and correlated to their structural units. X–ray analysis of the polymers showed that polyamides based on para-azo linkage have a higher degree of crystallinity than those based on meta-azo linkage in the region $2\theta = 5-60°$. In addition, the morphological properties of selected examples were tested by SEM.

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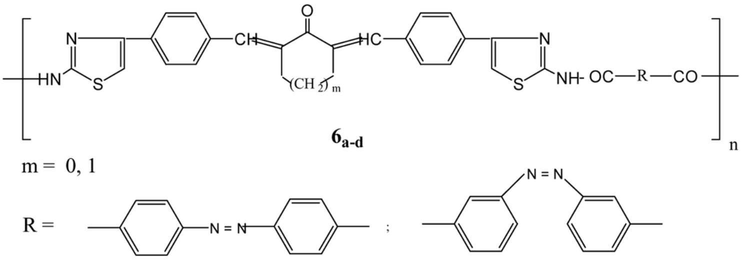


6a-d

Keywords aromatic azo chromophores, azo polymers, synthesis

INTRODUCTION

Polymers containing aromatic azo chromophores (azo polymers for short) have been extensively investigated in recent years [1–14]. Among various types of chromophores, azobenzenes were intensively studied. Azobenzenes when attached as side groups to main polymer chains show their photochromic properties, though the host polymer can seriously modify their properties. It is well-known and understood that the influence of polarized light, having a wavelength lying within an absorption band of the azo-benzene groups, induces photo-orientation [15–18]. It is widely accepted that the origin of all the effects is the multiple *trans–cis* photoisomerization process. Since the observation of the formation of holographic amplitude and phase gratings in those materials including surface relief gratings (SRG), the functionalized azo polymers are regarded as a new class of holographic materials [18]. It is expected that holography is one of the prospective techniques for establishing photonics as a future technology. There are few methods for preparation of chromophore functionalized polymers. Chromophores can be introduced into a polymer's main chain [19,20] or bonded as a side group [21–24] and can be dissolved in a polymer matrix [25,26]. Two main mechanisms are responsible for photo-induced anisotropy in polymers containing azo-groups: molecular reorientation and the presence of both *trans* and *cis* isomer populations. Molecular reorientation can be regarded as arising from the combination of three consecutive processes: the angular selective *trans* to *cis* photo-isomerization, the angular diffusion and the *cis* to *trans* relaxation. Depending on the structure and viscosity of the polymer matrix (mobility of polymers chains), the relaxation times of *cis* molecules and orientational relaxation times, different scenarios for the kinetics of photoinduced anisotropy in different polymers were observed [27].

The work reported in this paper outlines the synthesis and characterization of some new polyamides containing azo-groups and based on diarylidenecycloalkanones. The major aim of this work has been to investigate the effect of the inclusion of cycloalkanone and azo moieties on the polymer properties.

In addition other characteristics of these new polyamides, such as thermal stability, solubility, morphology and crystallinity, were discussed.

EXPERIMENTAL

Measurements

Elemental analyses were carried out using an Elemental Analyses system GmbH, VARIOEL, $V_{2.3}$ July 1998 CHNS Mode. IR spectra were recorded on IR-470, infrared spectrophotometer, Shimadzu by using the KBr pellet technique. The ^{1}H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature in DMSO or $CDCl_3$ using TMS as the internal reference. Mass spectra were recorded on a Jeol JMS600 mass spectrometer. Inherent viscosities of polymer solutions (0.5% w/v) in DMSO were determined at 30°C using an Ubbelohde suspended level viscometer. The solubility of polymers was examined using 0.02 g of polymer in 3–5 ml of solvent at room temperature. The X-ray diffractographs of the polymers were obtained with a Philips X-ray PW1710 diffractometer, and Ni – filtered CuKα radiations. The electronic spectra were scanned on a 2110 PC scanning spectrophotometer, Shimadzu in DMSO as a solvent. Thermogravimetric analysis (TGA) and differential thermal gravimetric (DTG) were carried out in air with Shimadzu DTG-60 at a heating rate of 10°C/min in air. The morphologies of polymers were examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument.

Reagents and Solvents

Cyclopentanone (Merck, 99%), cyclohexanone (Merck, 99%), N-methylpyrolidone and anhydrous lithium chloride (Merck) were used without purification. Chloroacetyl chloride (Aldrich, 98%) and thiourea from El-Nasr Chemical Company, 95% (Egypt) were used. Benzoyl chloride from El-Nasr Chemical Company, 95% (Egypt), was freshly distilled (b.p. 183–184°C). All other reagents were of high purity and were further purified as reported in the literature [28] such as: for carbon disulphide, distillation of appreciable quantities of CS_2 should be carried out in a water bath at 55–65°C. The commercial substance may be purified by shaking for 3 h with mercury. It is then dried over anhydrous calcium chloride, and fractionated from a water bath at 55–65°C. The pure compound boils at 46.5°C/760 mmHg. N,N-dimethylformamide was dried over anhydrous calcium chloride for two days, then filtered and distilled at atmospheric pressure (b.p. 149–156°C). The distillate was best stored over 5°A molecular sieve. The commercial grade from DMSO may be dried by standing overnight over freshly activated alumina, barium oxide or calcium sulphate. The filtered solvent is then fractionally distilled over calcium hydride under reduced pressure (12 mmHg) and stored over a type 4°A molecular sieve. An additional stage involving cooling the solvent to about 5. The pure solvent has b.p. 75–76°C/12 mmHg.

Monomer Syntheses

All the pre-monomers, bis(4-chloroacetylbenzylidene)cycloalkanones $\mathbf{2_{a,b}}$ and monomers bis(2-aminothiazol-4-ylbenzylidene)cycloalkanones monomers $\mathbf{3_{a,b}}$ were synthesized as described in our previous work [29–31].

Synthesis of Model Compounds 4 and 5

General Procedure

A mixture of bis(2-aminothiazol-4-ylbenzylidene)cycloalkanone monomers $\mathbf{3_a}$ or $\mathbf{3_b}$ (0.004 mole), in LiCl/NMP (1 g in 20 ml), was stirred at room temperature. Benzoyl chloride (0.008 mole) diluted with NMP (8 ml) was added to the stirred solution under N_2 at 0°C. The mixture was subsequently stirred at room temperature in a steam of N_2 for 2 h. After that the stirring was continued for further 4 h. The solid product was filtered off, washed with dilute aqueous $NaHCO_3$, then with water, dried and recrystallized from the appropriate solvent.

Using the above general procedure, individual model compounds were synthesized.

2,5-Bis(2′-aminothiazol-4′-ylbenzylidene)cyclopentanone Dibenzamide 4

It was obtained by the reaction of 1.82 g (0.004 mole) 2,5-bis(2′-aminothiazol-4′-ylbenzylidene)cyclopentanone $\mathbf{3_a}$ with 1.21 g (0.008 mole) benzoyl chloride as brown crystals from bezene, yield 79%, m.p. 282°C.

Anal. Calc. for $\mathbf{C_{39}H_{28}N_4O_3S_2}$

Calcd. %: C, 70.48; H, 4.21; N, 8.43; S, 9.63.

Found %: C, 70.56; H, 4.34; N, 8.39; S, 9.56.

2,6-Bis(2-aminothiazol-4-ylbenzylidene)cyclohexanone Dibenzamide 5

It was obtained by the reaction of 1.88 g (0.004 mole) 2,6-bis(2′-aminothiazol-4′-ylbenzylidene)cyclohexanone $\mathbf{3_b}$ with 1.21 g (0.008 mole) benzoyl chloride as brownish crystals from benzene, yield 82%, m.p. 190°C.

Anal. Calc. for $\mathbf{C_{40}H_{30}N_4O_3S_2}$

Calcd. %: C, 70.79; H, 4.42; N, 8.26; S, 9.44.

Found %: C, 70.77; H, 4.44; N, 8.31; S, 9.37.

Table 1: Elemental analyses, yields and inherent viscosity of polyamides $\mathbf{6_{a\text{-}d}}$.

Polymer number	Yield (%)	η_{inh}* (dl/g)	Molecular formula (mol.Wt.)	Elemental analyses				
					C%	H%	N%	S%
$\mathbf{6_a}$	81%	1.08	$(\mathbf{C_{39}H_{26}N_6O_3S_2})_n$ (690)	Calcd	67.82	3.76	12.17	9.27
				Found	68.77	3.71	12.19	9.32
$\mathbf{6_b}$	78%	0.65	$(\mathbf{C_{39}H_{26}N_6O_3S_2})_n$ (690)	Calcd	67.82	3.76	12.17	9.27
				Found	67.16	3.79	12.21	9.09
$\mathbf{6_c}$	82%	1.02	$(\mathbf{C_{40}H_{28}N_6O_3S_2})_n$ (704)	Calcd	68.18	3.97	11.93	9.09
				Found	68.82	4.03	12.75	9.50
$\mathbf{6_d}$	79%	0.69	$(\mathbf{C_{40}H_{28}N_6O_3S_2})_n$ (704)	Calcd	68.18	3.97	11.93	9.09
				Found	67.94	4.04	10.99	9.32

*Measured in DMSO, with C = 0.5 g/100 ml at 30°C.

Polymer Syntheses

A solution polycondensation technique was used in the synthesis of these polyamides, described as follows.

General Procedure

In a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet and dropper, a mixture of bis(2-aminothiazol-4-ylbenzylidene)cycloalkanone monomers $\mathbf{3_a}$ or $\mathbf{3_b}$ (0.004 mole), in LiCl/NMP (1 g in 20 ml), and a solution of the diacid chlorides (0.004 mole) in NMP (15 ml) was added in a drop-wise manner while maintaining the stirred solution at 0°C under N_2. The mixture was subsequently stirred at ambient temperature in a steam of N_2 for 6 h, then it was poured into ice water to yield a yellowish to brown-colored solid. This was filtered off, washed with dilute aqueous $NaHCO_3$, then with water, ethanol, acetone and finally dried under reduced pressure (1 mmHg) at 70°C for two days.

The synthesized azo polymers, their yields, inherent viscosities, elemental analyses and some of their physical properties are listed in Table 1.

RESULTS AND DISCUSSION

The work described in this paper was focused on the synthesis of a novel interesting category of polyamides of diarylidenecycloalkanone containing azo groups in the polymer's main chain $\mathbf{6_{a\text{-}d}}$ using the solution polycondensation technique [32], and to study the various characteristics of the resulting polymers.

However, these new polymers necessitate the synthesis of monomers as precursors.

Preparation of Acid Chlorides

Acid chlorides were prepared as described in our previous work [33].

Monomer Synthesis

Synthesis of Bis(4-chloroacetylbenzylidene)cycloalkanones $2_{a,b}$

2,5-diarylidenecyclopentanone and 2,6-diarylidenecyclohexanone $\mathbf{1_{a,b}}$ were synthesized in good yield as reported in the literature [29] by the condensation of one mole of cyclopentanone or cyclohexanone with two moles of benzaldehyde in ethanol and in the presence of a few drops of potassium hydroxide as the catalyst, then recrystallized from ethanol as yellow crystals. Their structures were checked by elemental and spectral analyses as described in the experimental part. The title precursor monomers $\mathbf{2_{a,b}}$ were synthesized via Friedel–Crafts reaction by the interaction of the diarylidenecycloalkanone monomers $\mathbf{1_{a,b}}$, with chloroacetyl chloride using anhydrous aluminum chloride as a catalyst and in carbon disulphide as a solvent as presented in Figure 1. The structure of the precursor monomers $\mathbf{2_{a,b}}$ was confirmed by elemental and spectral analyses (including: IR, ^{1}H-NMR and mass spectra) as maintained in our previous work [29].

Synthesis of Bis(2-aminothiazol-4-ylbenzylidene)cycloalkanones Monomers $3_{a,b}$

These two monomers were synthesized by the interaction of bis(4-chloroacetylbenzylidene)cycloalkanone pre-monomers $\mathbf{2_{a,b}}$ with thiourea in absolute ethanol as shown in Figure 1. The structure of synthesized monomers $\mathbf{3_{a,b}}$ was confirmed by elemental and spectral analyses (including IR, ^{1}H-NMR and mass spectra) as described in our previous work [31].

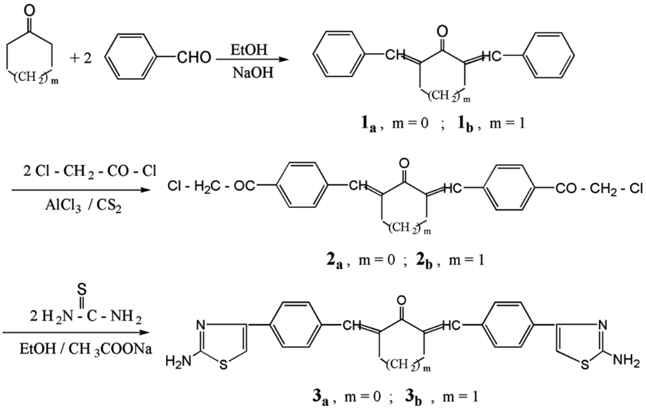


Figure 1: Synthesis of diarylidenecycloalkanone monomers $\mathbf{3_{a,b}}$.

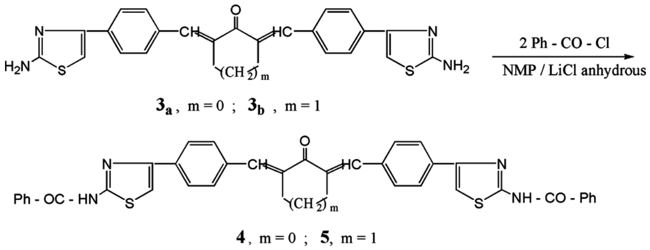


Figure 2: Synthesis of model compounds 4 and 5.

Synthesis of Model Compounds

Before attempting polymerization, model compounds **4** and **5** were synthesized by the interaction of one mole of diarylidenecycloalkanone monomers $\mathbf{3_a}$ or $\mathbf{3_b}$ with two moles of benzoyl chloride using LiCl anhydrous as a catalyst in NMP at room temperature as shown in Figure 2.

The structure of these model compounds was checked on the basis of good agreement between calculated and found analytical data, IR and ^{1}H-NMR.

The spectral data of the model compounds **4** and **5** showed new characteristic absorption bands at 3340 cm^{-1} for (NH) sec. amino group, at 1690 cm^{-1} for (C=O, amide), at 1640 cm^{-1} for (C=O, cycloalkanone), and at 1600 cm^{-1} for (C=C). In addition, other characteristic absorption bands, due to specific groups present in the various model compounds, were also evident in the IR spectrum.

The ^{1}H-NMR spectrum of model compound **4** (in $CHCl_3$, ppm) showed the following δ values: 9.8 (s, 2H, NH sec. amino group), 7.8-7.2 (m, 10H, aromatic protons and 2CH=C), and 3.0 (t, 4H, $2CH_2$ of cyclopentanone). Moreover, when the ^{1}H-NMR spectrum was carried out in (CF_3COOD) we obtained the same δ values except value for sec. amino group, which disappeared. The ^{1}H-NMR spectrum of model compound **5** (in DMSO-d_6, ppm) showed the following δ values: 10.1 (s, 2H, NH sec. amino group), 8.2-7 (m, 10H, aromatic protons and 2CH=C), 3.1 (t, 4H, $2CH_2$ of cyclopentanone), and at 2 (m, 2H of middle CH_2 cyclohexanone).

Synthesis of Polyamides

Polyamides were synthesized by a low-temperature solution polycondensation technique [34,35] in a solvent like NMP which dissolves the diamines and acts as a good acid acceptor for the HCl liberated during the polymerization reaction and also in the presence of LiCl, as the catalyst. LiCl-NMP solution is powerful enough to keep the growing polymer chain in solution as its molecular weight builds up.

Four novel polyamides based on diarylidenecycloalkanone moieties $\mathbf{6_{a\text{-}d}}$ were synthesized by polycondensation reaction of diaminoarylidene monomers $\mathbf{3_a}$ or $\mathbf{3_b}$ with 4,4′-azodibenzoyl, 3,3′-azodibenzoyl dichlorides in NMP as a

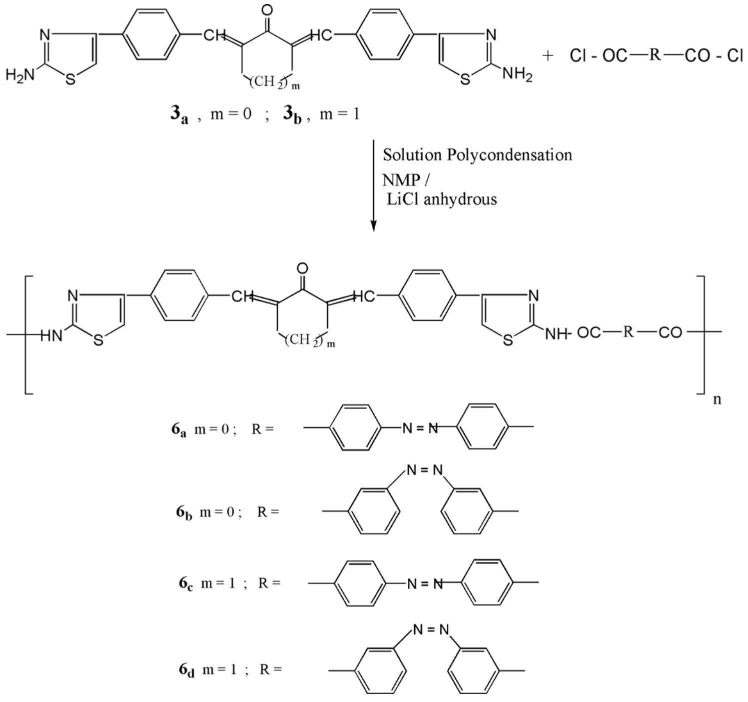


Figure 3: Synthesis of polyamides **$6_{a\text{-}d}$**.

solvent, using LiCl anhydrous as a catalyst at room temperature as shown in Figure 3.

Reaction times varied from 5–6 h. Polyamides were immediately isolated (see experimental part) when the reaction solution was poured into an ice/water mixture, with yields in the range of 78–82%.

The polymerization proceeded rapidly to yield high molecular weight polyamides with inherent viscosities in the range 1.08–0.65 dL/g. The resulting polyamides were characterized by elemental analysis, IR, solubility, absorption of water, viscometry, thermal analysis, and morphological properties. The elemental analyses of all the different polymers coincided with the characteristic repeating units of each polymer. It should be noted that the elemental analyses for the polymers deviated up to 1.12% from the theoretical values. However, it is not uncommon for polymers to trap solvents within the matrix, especially for polyamides of high molecular mass and those containing polar groups, which are capable of hydrogen bonding with solvent molecules [33].

Spectral data supported the structural assignments for the polymers and are in good agreement with spectral data obtained for the model compounds. The IR data obtained in KBr discs for all the polyamides showed the absorption band for N–H stretching at 3350-3200 $\mathrm{cm^{-1}}$ characteristic for the secondary amino group. The appearance of carbonyl absorptions at 1695-1680 $\mathrm{cm^{-1}}$, known as the amide I band, is due to carbonyl stretching vibration. A strong amide II band, due to the coupling of N–H bending and C–N stretching of the C–N–H group, was noted at 1535-1515 cm^{-1}. In addition, 1630–1645 cm^{-1} for (C=O, cycloalkanone), and at 1590–1600 cm^{-1} for (C=C) was noted.

The lowering of the usual carbonyl frequency from 1715 to 1690-1680 cm^{-1} is due to the resonance effect [36]. Because the polyamides were examined in the solid state, hydrogen bonding could be the major contributing factor in their lower carbonyl absorption frequency [37].

POLYMER CHARACTERIZATION

The various characteristics of the resulting polyamides, including solubility, viscometry, absorption of water, UV–visible spectra, X-ray diffraction analysis, thermal analysis, and morphological properties, were also determined and the data were discussed below.

The solubility characteristics of polyamides $\mathbf{6_{a\text{-}d}}$ were tested using the same solvents, under the same conditions A 0.5% (w/v), and solution was taken as a criterion for solubility (Table 2). Solubility measurement was determined for powdery samples in excess solvent including: concentrated sulfuric acid, formic acid, methylene chloride, chloroform acetone mixture (1:1), dimethylacetamide (DMA), tetrahydrofurane (THF), dimethylsulfoxide (DMSO), and dimethylformamide (DMF).

All the synthesized azo polymers had good solubility in polar aportic solvents such as DMSO, DMF and DMA. In THF, all the polyamides were partially soluble at room temperature. Neither solubility nor swelling was observed in common organic solvents like methanol, acetone or benzene; moreover in the chloroform acetone mixture and methylene chloride, the majority of polyamides were partially soluble except polymer $\mathbf{6_a}$, which was completely insoluble in both solvents. In concentrated H_2SO_4 and formic acid all the polyamides were readily soluble, giving an orange to yellowish color, except for polyamide $\mathbf{324_b}$ which gave a brownish color. These results clearly indicated

Table 2: Solubility characteristics of polyamides $\mathbf{6_{a\text{-}d}}$.

Polymer number	DMF	DMSO	DMA	THF	Chloroform + Acetone (1:1)	CH_2Cl_2	HCOOH	Conc. H_2SO_4
$\mathbf{6_a}$	++	++	++	+	−	−	++	++
$\mathbf{6_b}$	++	++	++	+	+	+	++	++
$\mathbf{6_c}$	++	++	++	+	+	+	++	++
$\mathbf{6_d}$	++	++	++	+	+	+	++	++

++: Soluble at room temperature (RT).
+: Partially soluble at (RT).
−: Insoluble.

that the presence of cyclohexanone moiety in the polymer backbone gave the polymers slightly more solubility than the presence of cyclopentanone moiety, which appeared clearly in the chloroform acetone mixture and methylene chloride. This may be attributed to the higher flexibility of the cyclohexanone moiety as described in our previous work [38]. More particularly, comparing the solubility of polymers containing 3,3′-azolinkage with those containing 4,4′-azolinkage, we found that the former possess slightly better solubility than the latter which appeared for polymer $\mathbf{6_b}$ than $\mathbf{6_a}$. This may be attributed to the close packing of the polymer chain in the latter polymers [39].

The inherent viscosities (ηinh) of polyamides $\mathbf{6_{a\text{-}d}}$ were determined in dimethylsulfoxide (DMSO) at 30°C with an Ubbelohde suspended level viscometer. The inherent viscosity value is defined as:

$$\eta_{\mathrm{inh}} = [2.3 \log \eta/\eta_{\mathrm{o}}]/\mathrm{C}$$

The solution concentration C is 0.5 g/100 ml, η/η_{o} = relative viscosity (or viscosity ratio). It can be shown from Table 1 that polyamide $\mathbf{6_a}$ had high viscosity (1.08 dL/g) and this may be attributed to the high molecular weight of the polymer. On the other hand, the inherent viscosity of the polyamides $\mathbf{6_b}$ and $\mathbf{6_d}$ is low (0.65, 0.69 dL/g, respectively) which may be attributed to the low molecular weight of these polymers.

An important characteristic of polyamides is the ability to absorb water. Generally moisture absorption is proportional to the frequency of amide groups [40]. The hydrophilicity of polyamides was estimated by measuring the isothermal water absorption as presented in Figure 4. Saturation in water absorption was observed for the selected polyamide $\mathbf{6_c}$ after a time exposure of

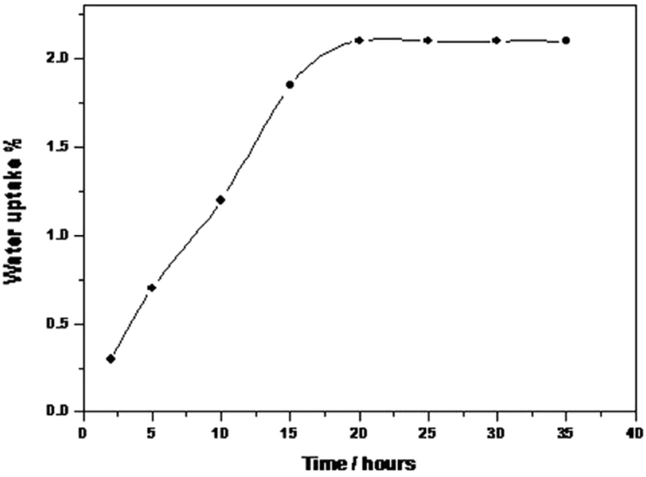


Figure 4: Water absorption (%) vs. time for polyamide $\mathbf{6_c}$.

about 35 h, which is dependent on the sample particle size. The water uptake for polyamide $\mathbf{6_c}$ (as a selected example) was 2.1%, after 35 h.

The ultraviolet and visible spectra of the synthesized azo polymers $\mathbf{6_{a\text{-}d}}$ were measured in dimethylsulfoxide (DMSO) at a concentration of 10^{-6} M. The UV spectra of these polyamides showed an absorption band with λ max near 263–277 nm, which was due to the $\pi-\pi^*$ transition within the benzenoid system for all the polyamides. All of these polymers showed an absorption band at λ max near 324–370 nm which was due to the $\pi-\pi^*$ and $n-\pi^*$ excitation of C=C and C=O groups. In addition, the polymers showed an absorption band with λ max near 460–475 nm, which was attributed to the presence of N=N group in the polymer backbone (cf. Figure 5).

The X-ray diffractograms of the prepared azo polymers $\mathbf{6_{a\text{-}c}}$ in (Figure 6a–c) were measured in the region $2\theta = 5\text{–}60^\circ$. Polyamide $\mathbf{6_b}$ showed an amorphous halo pattern in the selected region and this indicates that this polymer was amorphous (Figure 6b). Polyamide $\mathbf{6_a}$ showed few sharpness peaks with an amorphous background, indicating that there is a large class of structure in the same region. Polymer $\mathbf{6_a}$ was semicrystalline, which showed a few reflection peaks that are intermediate between crystalline and amorphous interference, which indicates that there is a large class of structures that are intermediate in the ordered states between crystals in the arrangement of their atoms and molecules (Figure 6a). More particularly, Figure 6c, showed that polyamide $\mathbf{6_c}$ became crystalline. On comparison between the crystallinity of the selected examples of polyamides, it should be noted that polyamides based on cyclopentanone have a low degree of crystallinity compared to those based on cyclohexanone, which may be attributed to the rigidity of the cyclopentanone moiety (shown in polyamides $\mathbf{6_{a,b}}$) as represented in our

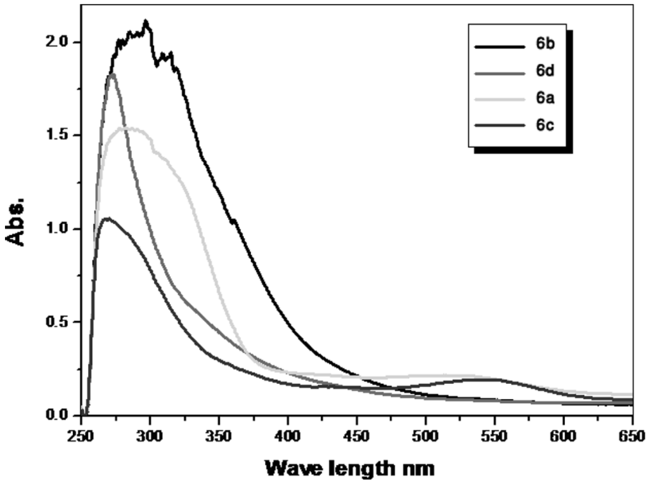
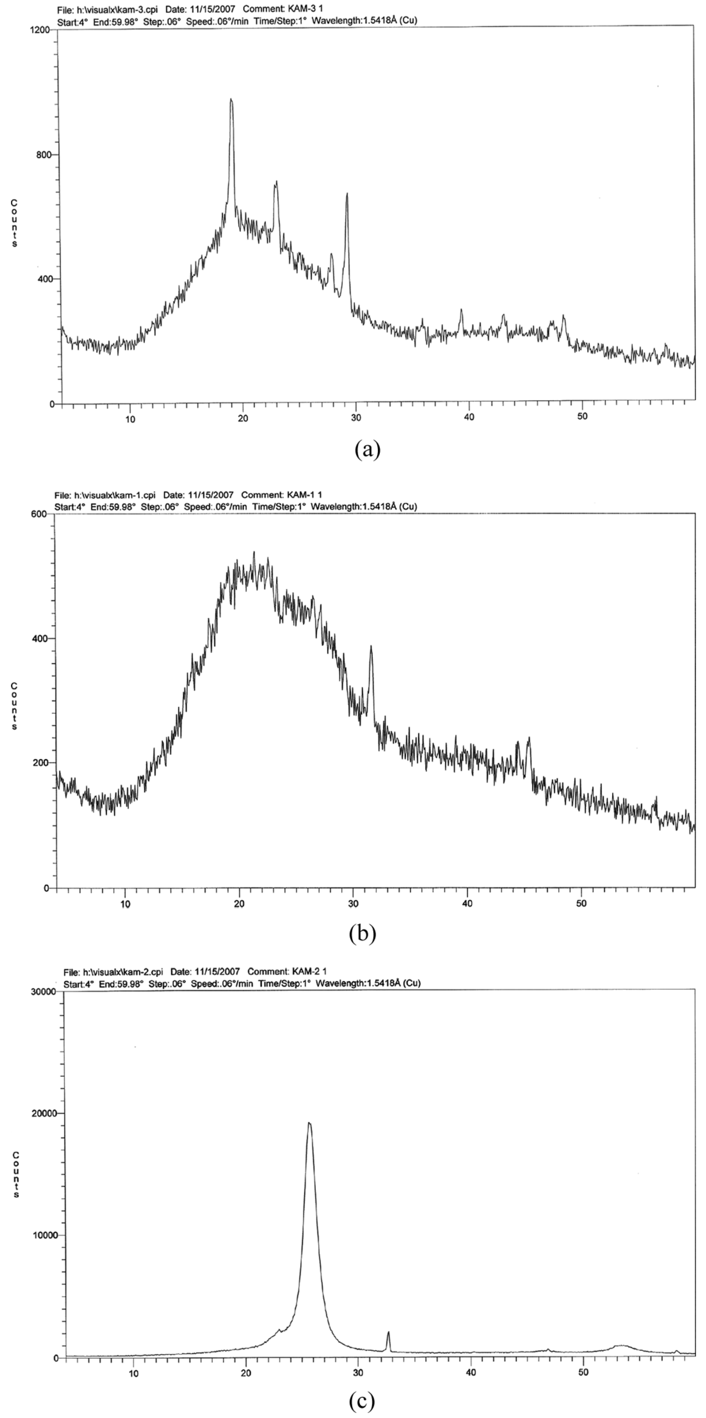


Figure 5: UV–visible spectra of polyamides $\mathbf{6_{a\text{-}d}}$.



(a)

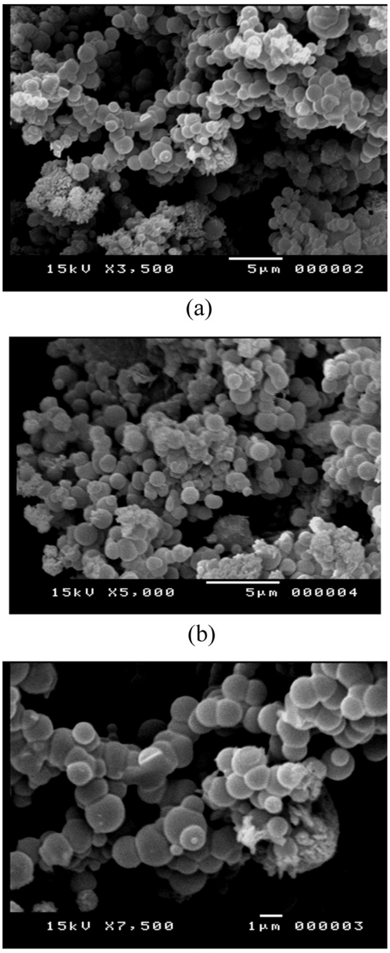
(b)

(c)

Figure 6: (a) X-ray diffraction patterns of polyamide $\mathbf{6_a}$; (b) X-ray diffraction patterns of polyamide $\mathbf{6_b}$; (c) X-ray diffraction patterns of polyamide $\mathbf{6_c}$.

previous publications [41]. Also polyamides based on 4,4′-azodibenzoylchloride $\mathbf{6_{a,c}}$ have a higher degree of crystallinity in compression with this derived from 3,3′-azodibenzoylchloride $\mathbf{6_b}$, which may be due to the more compact packing of the chain in the later polyamide.

The morphology of polymers was examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument as described in our previous work [32]. The morphological study of the selected example of azo polymers was examined using SEM measurement to show the surface of the polymer and to study the effect of substituent on the surface of the polymer molecules by comparison with the images in each case. The study of selected examples of polyamides showed that the surface of polyamide $\mathbf{6_a}$ (Figure 7a,

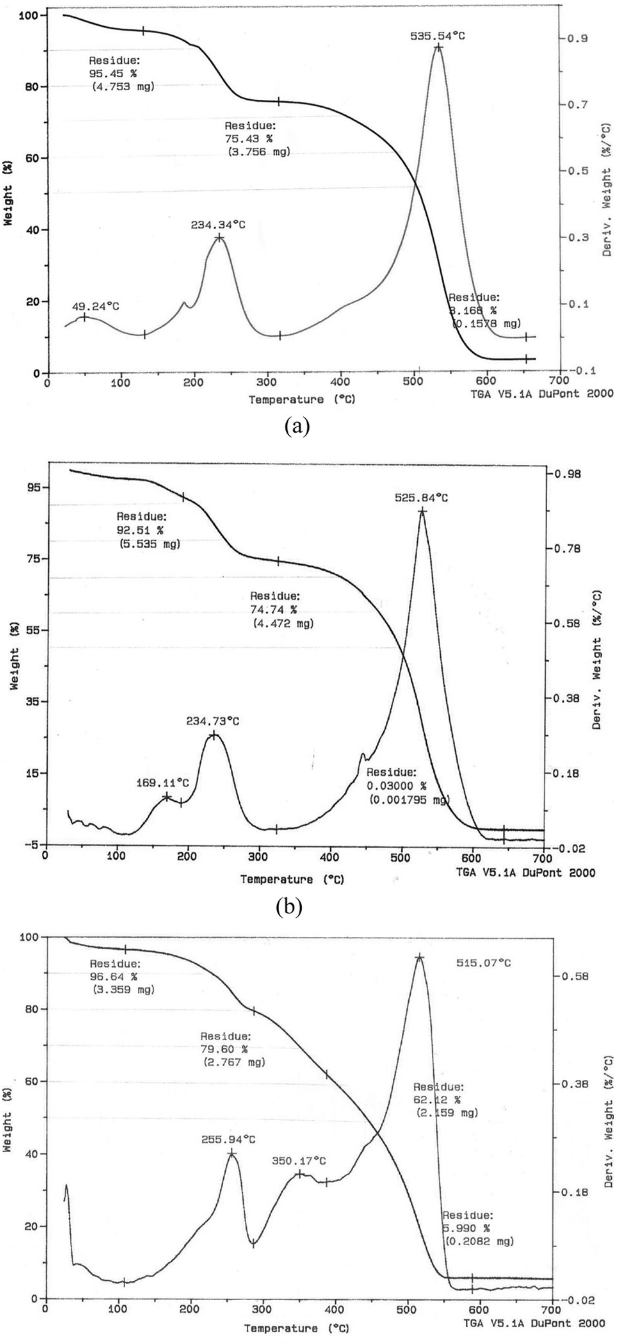


(a)

(b)

(c)

Figure 7: SEM images of polymer 6_a surface at different magnifications, a: X = 3500; b: X = 5000 and c: X = 7500.



(a)

(b)

(c)

Figure 8: (a) The TGA and DrTGA trace of polyamide $\mathbf{6_a}$ in air at a heating rate of 10°C/min; (b) The TGA and DrTGA trace of polyamide $\mathbf{6_b}$ in air at a heating rate of 10°C/ min; (c) The TGA and DrTGA trace of polyamide $\mathbf{6_c}$ in air at a heating rate of 10°C/min.

magnification X = 3500 and Figure 7b, X = 5000) consisted of globular grains with coalescence, while higher magnification X = 7500 (Figure 7c) showed accumulative particles with globular and semi-globular grains.

The thermal behavior of polyamides containing diarylidenecycloalkanone $\mathbf{6}_{\mathbf{a\text{-}d}}$ was evaluated by thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) in air at a heating rate of 10°C min^{-1}. TGA curves show a small weight loss in the range 3–5% starting at 50°C until 115°C, which may be attributed to loss of moisture and entrapped solvents. The thermographs of these polymers are given in Figures 8a–c, while Table 3 gives the temperatures for various % weight losses. All the polyamides showed similar decomposition patterns (two main degradation steps), except polyamide $\mathbf{6}_{\mathbf{c}}$ showed different decomposition patterns (three decomposition steps). The initial decomposition of these polymers (10% loss) is considered to be the polymer decomposition temperature (PDT) [30,42] which occurred in the range 215°C to 239°C for the synthesized polyamides.

In Figures 8a,b, for polyamide $\mathbf{6}_{\mathbf{a,b}}$ (two degradation steps) the mass loss is between ~195–265°C (−23.54%) in the first region; rapid mass loss is between ~275–580°C (−98.76%) in the second region. In addition, for polyamide $\mathbf{6}_{\mathbf{c}}$ (three degradation steps) the mass loss is between ~170–275°C (−20.27%) in the first region; rapid mass loss is between ~285–395°C (−39.67%) in the second region; and finally mass loss is between ~400–545°C (−97.59%) in the third region. These results indicate that the degradation is maximum at around 5345–580°C, and the rate of degradation in the second and in the third stage is somewhat faster than in the first stage. A comparison of the T_{10}% values of polymer $\mathbf{6}_{\mathbf{c}}$ showed better thermal stability than others, and the thermal stabilities of the obtained polyamides (at T_{10} %) are in the order $\mathbf{6}_{\mathbf{c}} > \mathbf{6}_{\mathbf{d}} > \mathbf{6}_{\mathbf{a}} > \mathbf{6}_{\mathbf{b}}$. More particularly, polyamides which are based on the cyclopentanone ring $\mathbf{6}_{\mathbf{a,b}}$, were slightly more thermally stable than the polyamides that contain the cyclohexanone moiety $\mathbf{6}_{\mathbf{c,d}}$ which appeared clearly in T_{30} %. This was attributed to the flexibility of the latter moiety [38]. Meta-azo-linked are also thermally stable, but not rigid which is clearer in T_{40} and T_{50} %.

Table 3: Thermal properties of polyamides $\mathbf{6}_{\mathbf{a\text{-}d}}$.

Polymer code	**Temperature (C) for various percentage decompositions***				
	10%	**20%**	**30%**	**40%**	**50%**
$\mathbf{6}_{\mathbf{a}}$	223	256	419	480	507
$\mathbf{6}_{\mathbf{b}}$	215	253	422	470	496
$\mathbf{6}_{\mathbf{c}}$	239	290	350	409	448
$\mathbf{6}_{\mathbf{d}}$	227	250	391	471	503

*The values were determined by TGA at a heating rate of 10°C/min.

CONCLUSIONS

A new interesting class of polyamides of diarylidenecycloalkanone containing azo groups in the polymer backbone was synthesized by room temperature solution polycondensation technique. All the synthesized polyamides had good solubility in polar aportic solvents. Neither solubility nor swelling was observed in common organic solvents and the majority of polyamides were partially soluble in a chloroform acetone mixture and methylene chloride. The water uptake for polyamide **6$_\mathbf{c}$** (as a selected example) was 2.1%, after 35 h. Polyamides based on 4,4′-azodibenzoylchloride have a higher degree of crystallinity in compression with those derived from 3,3′-azodibenzoylchloride. Polyamides which are based on the cyclopentanone ring **6$_\mathbf{a,b}$**, were slightly more thermally stable than the polyamides that contain the cyclohexanone moiety.

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