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ORIGINAL ARTICLE

Synthesis and characterization of new poly(ester-amide)s containing diarylidenecyclohexanone in the main chain. Part: II

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Abstract A new category of poly(ester-amide)s based on diarylidenecyclohexanone in the main chain were synthesized via interfacial polycondensation of two monomers namely: 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** with diacid chlorides **IIIa–c**. The model compounds were synthesized by reacting one mole of compounds **IVa–c** with two monomers **I** and **II**. The structure of the model compounds was confirmed by correct elemental and spectral analyses. The various characteristics of the resulting polymers including: solubility, viscosity, thermal analysis, and X-ray diffraction analysis were determined and discussed. The majority of the polymers were insoluble in most common organic solvents. The viscosity measurements in dimethylsulfoxide showed the values 0.58–0.79 dl/g. Thermal analysis showed that they were thermally stable up to 500 °C. X-ray analysis showed that the polymers had some degree of crystallinity in the region $2\theta = 5–50°$.

1. Introduction

Recently much attention on high-performance polymers that have excellent thermal stability and solubility has provided researchers with the impetus that has led to the discovery of a variety of thermostable and processable polymers. Poly(ester-amide)s PEAs attracted scientific interest, since they may be designed to couple the excellent mechanical properties of polyamides and the biodegradability of polyesters (Okada, 2002). PEAs have found a wide range of applications, such as disposable bags, agricultural films, drug carriers and matrix resins for biomedical materials (Grigat et al., 1998). PEAs can crystallise

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rapidly if the amide segments have an ordered structure as in alternating PEAs (Qian et al., 2004b,c) and PEAs with uniform diamide segments (Qian et al., 2003a, 2004d). Several kinds of poly(ester-amide)s copolymers based on lactic acid, 3-caprolactone and amino acids have been studied previously (Qian et al., 2003b, 2004a). Another linear poly(ester-amide)s was derived from adipic acid, 1,4-butanediol, hexamethylene diamine and caprolactam, by emphasizing its thermal processing behavior and composites with inorganic fillers (Zou et al., 2004). The work reported in this paper outlines the synthesis and characterization of some new poly(ester-amide)s based on diarylidenecyclohexanone moiety in the main chain. The major aim of this work was to investigate the effect of the inclusion of cyclohexanone moiety on the polymer properties. In addition other characteristics of these new polymers such as thermal stability, solubility, and crystallinity were discussed.

2. Experimental

2.1. Instrumentation

Elemental analyses were carried out using an Elemental Analyses system GmbH, VARIOEL, $V_{2.3}$ July 1998 CHN. Melting points were determined on a Perkin–Elmer 240 °C electrothermal melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu 2110 PC spectrophotometer with KBr pellets. The ^{1}H NMR spectra were recorded on a GNM–LA 400 MHz NMR spectrophotometer at room temperature in DMSO or $CHCl_3$ using TMS as the internal reference. Viscosity measurements were made with 0.5% (w/v) solution of polymers in sulfuric acid (9M) at 25 °C using an Ubbelohde suspended level viscometer. The X-ray diffractograms of the polymers were obtained with a Phillips X-ray unit (Phillips generator Pw-1710) and Ni-filtered Cu Kα radiations. TGA and DTG measurements were performed on V 5.1 A Du Pont 2000 thermal analyzer at a heating rate of 10 °C/min in air. The solubility of the polymers was determined using 0.02 g of polymer in 3.5 ml of solvent. Electronic spectra were recorded for solutions in DMSO in the region 200–600 nm with a Shimadzu 2110 PC scanning spectrophotometer. The morphology of the polymers was examined by scanning electronic microscopy (SEM) using a Jeol JSM-5400 LV–ESM.

2.2. Reagents and solvents

Cyclohexanone (Merck), *p*-hydroxybenzaldehyde and vanilline were used without purification. Terephthaloyl chloride (Aldrich) was recrystallized from *n*-hexane (m.p 83–84 °C). Amino acids and all other solvents were of high purity and were purified further by standard method (Perrin et al., 1980).

2.3. Monomer synthesis

2.3.1. Synthesis of monomers I and II

2,6-Bis(4-hydroxybenzylidene) cyclohexanone **I** and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** were prepared as described in previous works (Aly, 1999, 1998a).

2.3.2. Synthesis of diacid chlorides IIa–c

These monomeric compounds were prepared by methods that were similar to those used in the literature (Aly, 1998b). In a 250 ml conical flask, a mixture of 0.2 mol of ℓ-alanine was dissolved in 25 ml of 10% sodium hydroxide and then 0.1 mol of isophthaloyl was added in 1 h in five portions with vigorously shaking after each addition. At the end of the reaction time, 50 g of crushed ice was added and the reaction mixture was acidified with dilute HCl acid to Congo red paper. Whereas a white precipitate was isolated, washed well with water, dried and recrystallised from a mixture of 1:3 H_2O/ethanol to give white needle crystals.

2.4. Synthesis of model compounds Va,b

2.4.1. General method

In a 250 ml round-bottomed flask, 0.02 mol of compounds **III–V**, was dissolved in a 60 ml mixture of thionyl chloride–benzene at ratio 1:1, and refluxed for 1 h on water bath. After this, a few drops of pyridine were added and refluxed more for another hour. At the end of the reaction time, the mixture was evaporated under reduced pressure where a hemi-solid product and solid product were obtained and used without purification.

2.5. Polymer synthesis

2.5.1. General procedure

A three-necked flask, equipped with a mechanical stirrer (200 rpm/min) and dropper, was charged with a mixture of 0.02 mol monomer **I** or **II**, 50 ml methylene chloride and a suitable quantity of sodium hydroxide. A stoichiometric quantity of (0.04 mol) of the latter dissolved in 100 ml of water was also introduced. After mixing, 0.01 mol of acid chlorides **IIIa–c** dissolved in 25 ml methylene chloride was added over 2-min at 25 °C and vigorously stirred. After complete addition of the acid chloride, stirring was continued for 60 min whereby a highly yellowish solid separated out. The solid was filtered off, washed with water and hot ethanol and dried under reduced pressure of 1 mmHg at 90 °C for one day.

By using the above general procedure the following poly(ester-amide)s **VIa–c** and **VIIa–c** were obtained.

2.5.2. Poly(ester-amide) VIa

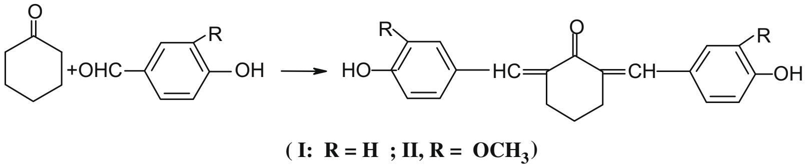
Obtained by the polymerization of 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** (0.002 mol) with acid chloride **IIIa** (0.002 mol) for 4 h as a yellow powder, yield 98% Anal. Calcd. for $C_{34}H_{30}N_2O_7$: C, 70.59; H, 5.19; N, 4.84. Found: C, 69.61; H, 5.02; N, 4.21.

2.5.3. Poly(ester-amide) VIb

Obtained by the polymerization of 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** (0.002 mol) with acid chloride **IIIb** (0.002 mol) for 4 h as a yellow powder, yield 92%. Anal. Calcd. for $C_{38}H_{38}N_2O_7$: C, 71.92; H, 5.99; N, 4.41. Found: C, 69, 90; H, 5.58; N, 4.18.

2.5.4. Poly(ester-amide) VIc

Obtained by the polymerization of 2,6-bis(4-hydroxybenzylidene) cyclohexanone **I** (0.002 mol) with acid chloride **IIIc** (0.002 mol) for 4 h as a yellow powder, yield 88%. Anal. Calcd. for $C_{46}H_{38}O_7N_2$: C, 75.62; H, 5.21; N, 3.84. Found: C, 75.01; H, 5.11; N, 3.32.



Scheme 1 Synthesis of monomers **I** and **II**.

2.5.5. Poly(ester-amide) ***VIIa***

Obtained by the polymerization of 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** (0.002 mol) with acid chloride **IIIa** (0.002 mol) for 4 h as a yellow powder, yield 95%.

Anal. Calcd. for $C_{36}H_{34}N_2O_9$: C, 67.71; H, 5.33; N, 4.39. Found: C, 68.69; H, 5.25; N, 4.16.

2.5.6. Poly(ester-amide) ***VIIb***

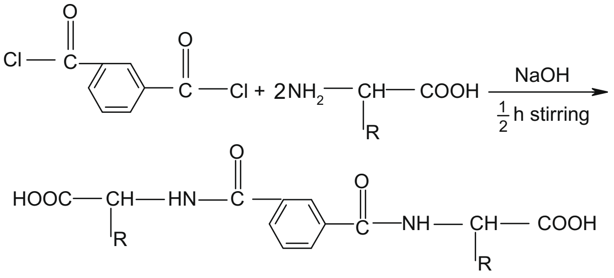
Obtained by the polymerization of 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** (0.002 mol) with acid chloride **IIIb** (0.002 mol) for 4 h as yellow powder, yield 96%.

Anal. Calcd. for $C_{40}H_{42}N_2O_9$: C, 69.16; H, 6.05; N, 4.03. Found: C, 69.14; H, 5.95; N, 4.21.

2.5.7. Poly(ester-amide) ***VIIc***

Obtained by the polymerization of 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** (0.002 mol) with acid chloride **IIIc** (0.002 mol) for 4 h as yellow powder, yield 90%.

Anal. Calcd. for $C_{48}H_{42}O_9N_2$: C, 75.49; H, 5.51; N, 3.67. Found: C, 74.48; H, 5.21; N, 3.04.



Scheme 2 Synthesis of diacid chlorides **IIIa–c**.

3. Results and discussion

3.1. Synthesis of monomers ***I*** *and* ***II***

The preparation of the poly(ester-amide)s **VIa–c** and **VIIa–c** was based on 2,6-bis(4-hydroxy benzylidene)-cyclohexanone **I** and 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II**. These monomeric units were synthesized by condensation of two moles of 4-hydroxy-benzaldehyde or 4-hydroxy-3-methoxy-benzaldehyde with one mole of cyclohexanone in the presence of ethanol and catalytic amount of conc. HCl as shown in Scheme 1.

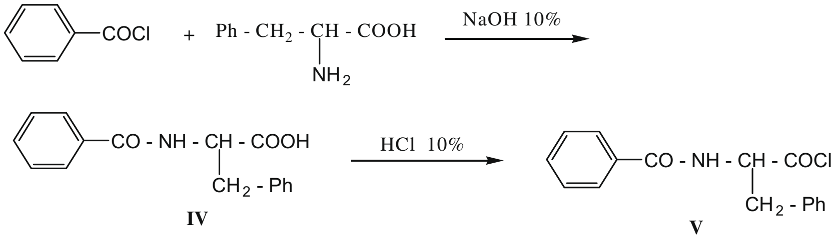
These monomeric units were purified by recrystallization twice before using in the polymerization. The structures of these compounds were elucidated by elemental and spectral analyses (IR and ^{1}H NMR).

3.2. Synthesis of diacid chlorides ***IIIa–c***

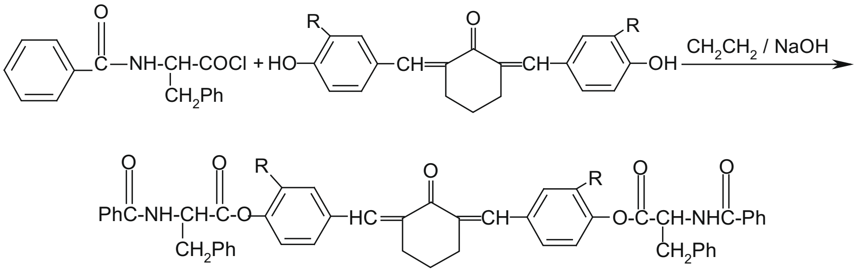
These monomeric units were prepared according to the literature (Vogel, 1978) by interaction of one mole terephthaloyl chloride with two moles of amino acid namely ℓ-alanine, ℓ-valine or ℓ-phenylalanine in the presence of 10% NaOH with vigorous shaking and 1/2 h stirring, as shown in Scheme 2.

3.3. Synthesis of model compounds ***Va,b***

Before attempting polymerization, the model compounds for the desired polymers were prepared. This was performed by interaction of one mole of any amino acid and ℓ-phenylalanine (as example) with one mole of benzoyl chloride to produce benzoyl ℓ-phenylalanine. The former was converted to acid chloride by dissolving the acid compound in a mixture of thionyl chloride – benzene and a few drops of pyridene as catalyst were added. At the end of the reaction time, the mixture was evaporated under reduced pressure, to give the acid chloride **IV** (Scheme 3).

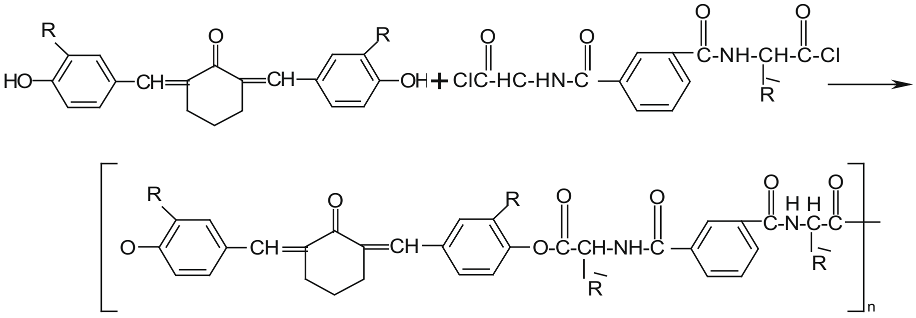


Scheme 3 Synthesis of precursor compound **IV**.



Va: R=H; Vb: R=OCH$_3$

Scheme 4 Synthesis of the model compounds **Va,b**.



VI a-c: (R=H): a: R'=CH$_3$; b: R'=CH (CH$_3$)$_2$; c: R'= -CH$_2$Ph.
VII a-c: (R=OCH$_3$): a: R'=CH$_3$; b: R'=CH (CH$_3$)$_2$; c: R'= -CH$_2$Ph.

Scheme 5 Synthesis of poly(ester-amide)s **VIa–c** and **VIIa–c**.

The model compounds **Va,b** were synthesized by interaction of the monomer **I or II** with the previous acid chloride **IV**. On the basis of the good agreement between calculated and found elemental analyses, IR, ^{1}H NMR spectra, the possible reaction is depicted in Scheme 4.

3.4. Synthesis of poly(ester-amide)s *VIa–c* and *VIIa–c*

One of the aims of studies presented in this work was to synthesize a new series of poly(ester-amide)s **VIa–c** and **VIIa–c** by using interfacial polycondensation technique which proved to be useful for the synthesis of polyesters and their analogues (Wittbecker and Morgan, 1959, Imai et al., 2003, Imai et al., 1980). These new polymers were synthesized by condensation of 2,6-bis(4-hydroxybenzylidene) cychohexanone **I** or 2,6-bis(4-hydroxy-3-methoxybenzylidene) cyclohexanone **II** with diacid chlorides **IIIa–c** as represented in Scheme 5.

The structure of these polymers was also established from elemental and spectral analyses. The elemental analyses of all the polymers coincided with the characteristic repeating units of each polymer; the data are included in the experimental part. It should be noted that the elemental analyses of these polymers deviated up to 1.12% from the theoretical values. However, it is not uncommon for polymers to trap solvent molecules within the polymer matrix (Aly and Khalaf, 2000).

Spectral data support the structural assignment of the poly(ester-amide). IR spectra recorded from pellets of KBr mixed with respective polymer showed characteristic absorption bands due to –NH groups at 3210–3250 cm^{-1}; C=O of esters at 1745–1735 cm^{-1}; C=O of cyclohexanone at 1690–1700 cm^{-1}; C=C stretching at 1590–1600 cm^{-1}; phenylene rings at 1590–1510 cm^{-1} and C–O–C bonds (ether linkage) at 1250–1260 cm^{-1}, and other characteristic bands appeared in the IR spectra.

Table 1 Solubility characteristics of poly(ester-amide)s **VIa–c** and **VIIa–c**.

Polymer	THF	DMF	DMSO	NMP	TCE*	CHCl$_3$ + acetone (1:1)	HCOOH + phenol (1:1)	Conc. H$_2$SO$_4$
VIa	±	±	±	+	−	−	−	+
VIb	±	±	+	+	−	−	−	+
VIc	−	±	+	+	−	−	±	+
VIIa	±	+	+	+	−	−	+	+
VIIb	±	+	±	+	−	±	+	+
VIIc	±	+	+	+	−	±	±	+

+, soluble at room temperature (RT); ±, partially soluble; −, insoluble; * tetrachloroethane.

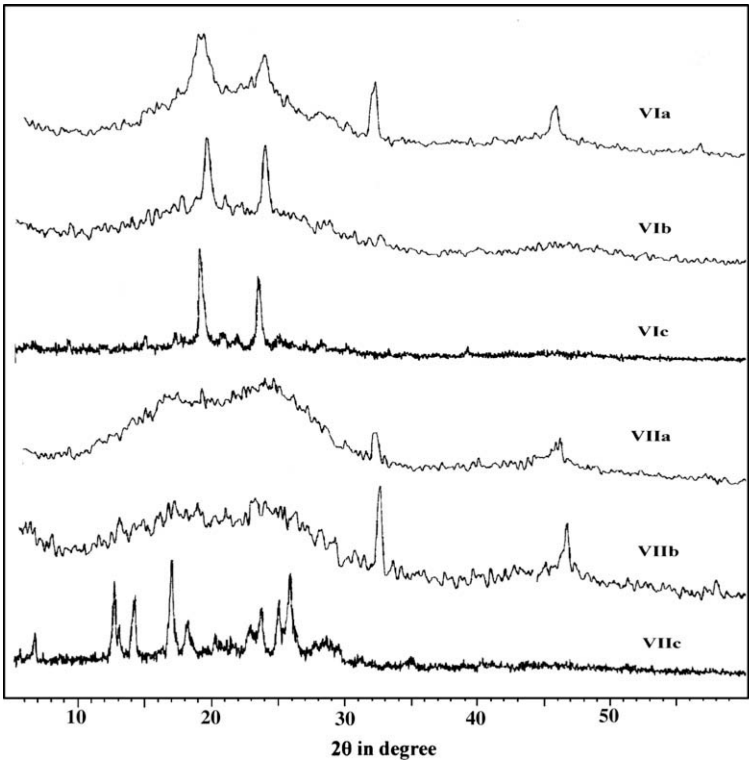


Figure 1 X-ray diffraction patterns of poly(ester-amide)s **VIa–c** and **VIIa–c**.

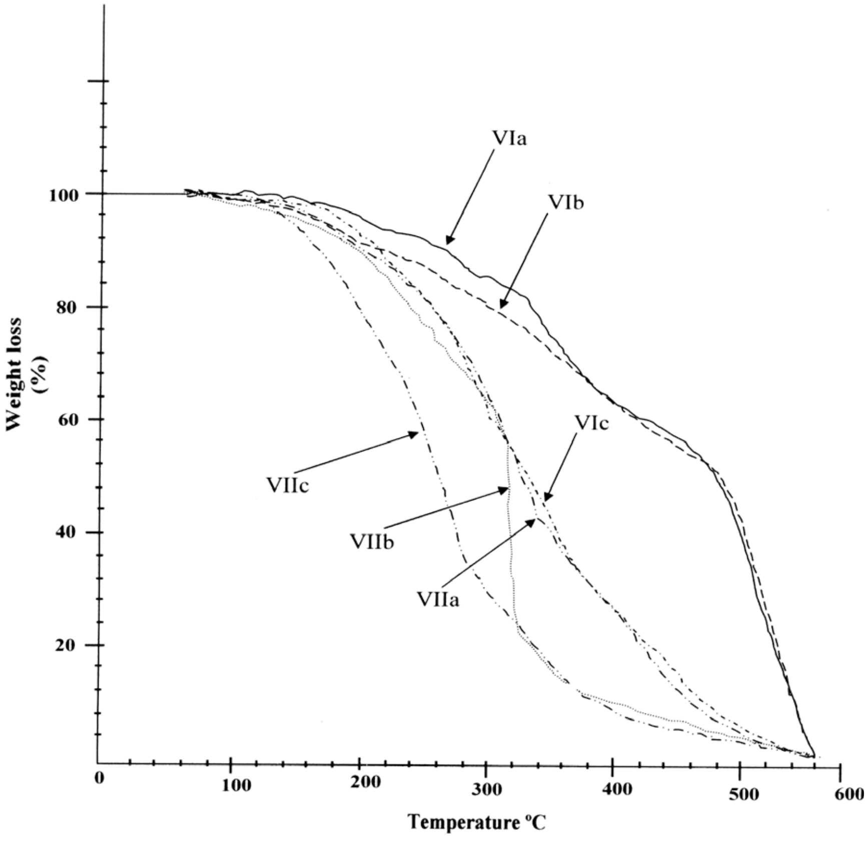


Figure 2 TGA traces of poly(ester-amide)s **VIa–c** and **VIIa–c** in air at a heating rate of 10 °C/min.

Table 2 Decomposition temperature of poly(ester-amide)s **VIa–c** and **VIIa–c**.

Sample	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)
VIa	196	289	455
VIb	142	250	440
VIc	203	301	493
VIIa	208	304	495
VIIb	250	384	570
VIIc	283	410	575

[a] Initial decomposition temperature.
[b] Polymer decomposition temperature.
[c] Maximum polymer decomposition temperature.

3.5. Characterization of poly(ester-amide)s *VIa–c* and *VIIa–c*

The various characteristics of the resulting poly(ester-amide)s **VIa–c** and **VIIa–c** including: solubility, X-ray diffraction analysis, TGA and DTA were also determined and all the data are discussed below.

3.5.1. Solubility

Room temperature solubility characterizations of poly(ester-amide)s **VIa–c** and **VIIa–c** were tested using various solvents including: THF, DMF, DMSO, NMP tetrachloroacetylene, chloroform – acetone (1:1; v/v), formic acid + phenol (1:1; v/v), and conc. H_2SO_4. A 5% (w/v) solution was taken as a criterion for solubility. All the poly(ester-amide)s **VIa–c** were insoluble in most simple organic solvents such as: alcohols, benzene, and acetone. It can be clarified from Table 1 that the majority of the polymers were completely soluble in polar aprotic solvents such as DMSO, DMF and NMP except polymers **VIa–c** which were partially soluble. In a strong protic solvent such as H_2SO_4, all the synthesized poly(ester-amide)s were freely soluble and gave reddish color. From these data it is revealed that the incorporation of $R' = CH_2ph$ in poly(ester-amide)s **VIc** and **VIIc** backbone induces higher solubility to some extent.

Moreover, it was found that all the polymers **VIa–c** were completely insoluble in chloroform – acetone mixture and TCE except polymers **VIIb,c** which were partially soluble. On comparison of the solubility of the polymers based on divanilyidenecyclohexanone with that of those based on diarylidenecyclohexanone, it was found that the latter series are more soluble in most solvents than the former polymers. This may be attributed to the higher flexibility of the cyclohexanone moiety as described in our previous works (Aly, 1989, 2002).

3.5.2. Determination of viscosity

The reduced viscosity of poly(ester-amide)s **VIa–c** and **VIIa–c** was determined by Ubbelohde suspended level viscometer using dimethylsulfoxide (DMSO) at 25 °C ± 0.5 °C, and this gave the values, 0.58 dl/g, 0.65 dl/g, 0.75 dl/g and 0.79 dl/g, respectively.

3.5.3. X-ray analysis

The X-ray diffractograms of poly(ester-amide)s **VIa–c** and **VIIa–c** are shown in Fig. 1. It can be clarified from this figure that the majority of the polymers showed few reflection peaks in the region $2\theta = 5–60°$, this indicates that these polymers are semicrystalline except the polymer **VIc** which showed a halo pattern in the same region. Also diffractographs indicated that the polymers **VIa–c** have a high degree of crystallinity in com-

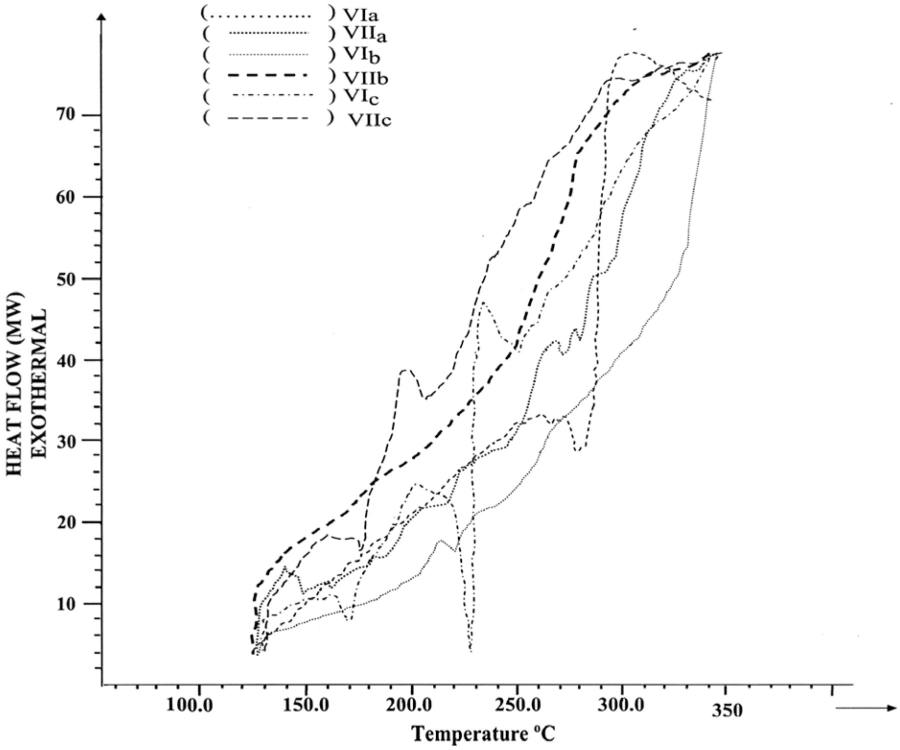


Figure 3 DSC curves of polymers (**VIa–c** and **VIIa–c**).

parison with the polymers **VIIa–c**. Moreover, the presence of C═O, C═C, polar groups, induces some order between two adjacent chains of the polymers, leading crystallinity to some extent (Mandelkern, 1964). On comparison between all the poly(ester-amide)s **VIa–c** and **VIIa–c**, it was found that the presence of methoxy group as a substituent in the polymers backbone caused some hindering between the repeating units and enforced it to unsymmetrical orientation in the polymers chain and reduced the crystallinity.

3.5.4. Thermal analyses

The thermal stabilities of poly(ester-amide)s **VIa–c** and **VIIa–c** were evaluated by TGA and DSC. Fig. 2 presents typical TGA traces of poly(ester-amide)s in N_2. The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT) and the maximum polymer decomposition temperature (PDT_{max}) are listed out in Table 2. The PDT corresponds to the temperature at which a weight loss of 10% was recorded. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred. In Fig. 2, the TGA curves show a small weight loss in the range 1–2% starting at 125 °C up to 180 °C, which may be attributed to loss of absorbed moisture and entrapped solvent, respectively. All the poly(ester-amide)s showed similar decomposition pattern. The expected nature of decomposition of these polymers are the scission of many bonds of olefinic groups and ester groups and a pyrolytic oxidation of amidic bonds. The PDT for all poly(ester-amide)s ranged from 276 to 465 °C. Therefore, the data given in Table 2 indicate that the thermal stabilities of these poly(ester-amide)s are in the order: **VIa** > **VIIa** > **VIc** ≈ **VIIc** > **VIIb** > **VIb**.

Fig. 3 shows typical DSC traces of poly(ester-amide)s **VIa–c** and **VIIa–c**. Poly(ester-amide)s **VIIa** and **VIIb** showed large ascending exothermic curves without definite T_g, T_c and T_m and may be attributed to curing reactions involving the olefinic bonds. Polymer **VIIc** shows a broad exotherm with T_c from 125 to 148 °C and T_m at 160 °C and this reflects the existence of some degree of crystallinity inside the polymer bulk and this is confirmed by the data of X-ray shown in Fig. 1.

The DSC curves of **VIa**, **VIc** showed different broad exotherms with T_c from 215 to 225 °C followed with T_m at 230 °C and T_c from 117 to 150 °C accompanied by T_m at 175 °C, respectively, and this indicates the presence of some degree of crystallinity order in polymer backbone, see X-ray in Fig. 1.

4. Conclusions

A new series of poly(ester-amide)s **VIa–c** and **VIIa–c** were synthesized using interfacial polycondensation technique. The various characteristics of the resulting polymers were tested. The presence of methoxy group as a substituent in the polymer backbone reduced the crystallinity and caused some hindering between the repeating units and enforced it to unsymmetrical orientation in the polymers chain. All the poly(ester-amide)s were yellowish to pale-yellow, and had inherent viscosity in the range 0.56–0.79 dl/g. They were soluble in polar aprotic solvents such as DMSO and NMP. X-ray diffractograms of poly(ester-amide)s showed some degree of crystallinity in the region $2\theta = 5–50°$.

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