

New Polyamides and Polyesteramides Incorporated with Bis(carboxy-substituted) Hydrazines: Synthesis and Characterization

Nadia G. Kandile, Abir S. Nasr

Chemistry Department, Faculty of Women, Ain Shams University, 11757 Heliopolis, Cairo, Egypt

Received 21 January 2011; accepted 26 January 2011

DOI 10.1002/app.34283

Published online 20 May 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The present article endeavors to synthesize new polyamides via direct polycondensation of various diamines [hexamethylene diamine, *p*-phenylene diamine, 2,5-bis(*m*-aminobenzylidene) cyclopentanone, and 2,6-bis(*m*-aminobenzylidene)cyclohexanone] with different bis(carboxy-substituted) hydrazines such as [1,2-bis(3-carboxy acrylyl)hydrazine and 1,2-bis(3-carboxybenzoyl) hydrazine]. The polycondensation reaction of 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine with the same bis(carboxy-substituted) hydrazines gave polyester amides. The poly-

condensation process was run in the presence of CaCl₂, triethylphosphite, and pyridine as a catalyst. These polymers were characterized by FTIR, ¹H-NMR, solubility, TGA, DSC, X-ray, mechanical properties, and electrical conductivity. The electrical conductivity measurements showed that all new polymers show promise as insulators. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1152–1161, 2011

Key words: polyamides; polycondensation; diamines; 1,2-bishydrazines; diacids

INTRODUCTION

The growth of modern technology has posed a constantly increasing need for materials that can perform well under harsh conditions, such as elevated temperatures.¹

The polyamides (PAs) are high-molecular weight materials containing intermittent amide units and the hydrocarbon segments that can be aliphatic, partially aromatic, or wholly aromatic. The type of hydrocarbon segment used has effects on the chain flexibility and structural regularity, with the latter's importance in the formation of crystalline phase. PAs are often called nylons, the trade name given to them by DuPont. Many types of PAs have been studied, for example, in one of the first patents on PAs almost 31 types are being described.² Since then, partially aromatic and wholly aromatic PAs have been successfully developed.^{3–6} They have good mechanical properties due to the formation of hydrogen bonding. The hydrogen bonding increases the chain interaction resulting in higher yield stress, fracture stress, impact strength, tear strength, and abrasion resistance.^{7–10} PAs are used essentially as fibers, films, and filler-containing engineering plastics for special applications.^{11,12} Most of the rein-

forced PAs are filled with glass fibers and to a lesser extent with particles, for example, talc, kaolin, and mica. For engineering plastics applications, dimensional stability at high temperatures is often sought. Wholly aromatic PAs can be processed from solution either into films or into fibers. These polymers have very good dimensional stability^{8,9} and excellent heat resistance.^{13,14} The PAs, (AA-BB)_{*n*}, can be prepared from diamines and diacids. The AB types of PAs are made from either ω -amino acids or cyclic lactams, which are the derivatives of the ω -amino acids. Partially, aromatic PAs have higher glass transition and melting temperatures compared to their aliphatic counterparts. They can be prepared by various methods, for example, mono-add systems, which both acid and amine functionalities are on the same molecule and diadd systems such as diacids, diacid chlorides, or diesters in combination with either aromatic or aliphatic diamines as well as the reactions between diisocyanates and diacids, which are commonly used for this propose.³ Wholly aromatic PAs have high-glass transition temperatures (>200°C), and, when crystalline, they show very high melting temperatures (>500°C). High-molecular-weight polymers cannot be prepared by melting or melt processing, because many aromatic diacids are decarboxylated, and the aromatic diamines are readily oxidized and have a tendency to sublime at elevated temperatures.¹⁵ Their synthesis is usually carried out in solution and due to the very low solubility, special solvents are required to obtain high-molecular-weight

Correspondence to: N. G. Kandile (nadiaghk@yahoo.com).

polymers. PAs are usually synthesized by the following methods.¹⁶ Described a novel procedure to prepare aromatic PAs. This reaction involved the complexation of an acid with triphenylphosphite in *N*-methylpyrrolidone (NMP) and pyridine (Py). CaCl₂ and LiCl were used along with NMP to improve the molecular weight of the polymer.

Polyesteramides (PEA) are copolymers of PA and aliphatic ester. Available since 1996, the commercial products are represented by the BAK grades from Bayer AG. According to Grigat,¹⁷ BAK is completely biodegradable under composting conditions. BAK provides lower water sensitivity than starch and seems to be suited for our purpose as the hydrophobic component. The preparation of biodegradable polymers is of considerable interest to many researchers. PEAs seem to be very promising materials combining good mechanical and processing properties of aliphatic PAs with well-known degradability of polyesters. A broad variety of biodegradable PEA has been already synthesized, as reviewed in Ref. 18. The majority of published works were dedicated to PEAs prepared by polycondensation, less concerned to preparation from depsipeptides by ring-opening polymerization or ring-opening copolymerization of lactams and lactones.

In continuation to our program for the synthesis of different polymers,^{19,20} the aim of the present work in this article was the synthesis of PAs and PEAs having hydrazo functionality in the main polymer chain by thermal polycondensation reactions of different diamines with different diacids. The synthesized new PA (3_{a-h}) and PEAs (4_{a-b}) were studied using elemental analysis, FTIR, ¹H-NMR, solubility, X-ray, thermal analysis, mechanical properties, and electrical conductivity.

EXPERIMENTAL

Materials

The chemicals were obtained from the following suppliers: maleic anhydride from Merck (Germany); phthalic anhydride from Aldrich (Egypt); acetic acid (glacial) and dimethylsulfoxide (DMSO) from G.P.R (Germany); thionyl chloride, NMP, and hydrazine hydrate (99%) from Fluka (Germany); Py and calcium chloride from EL-Nasr Pharmaceutical Chemicals Co. (Egypt); triethyl phosphate from BDH (Germany); methanol from Alpha (Germany), dimethylformamide (DMF), and tetrahydrofuran (THF) from Adwic (Egypt).

Measurements

Melting points were determined on a Boetius hot-stage apparatus. The elemental analyses were per-

formed on a Perkin-Elmer 240 C elemental analyzer. Infrared spectra were measured on IR-Atimattson-infinity series FTIR. Nuclear magnetic resonance spectra were recorded on Varian Genini-200 MHz spectrophotometer. Solubility of the polymers was examined using 0.02 g of polymer in 3–5 mL solvents at room temperature. X-ray diffractograms were obtained with a Phillips X-ray unit (Generator PW-1390) and a Ni-filtered Cu. Thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) were carried out under nitrogen atmosphere using a Shimadzu TGA-50H thermal analyzer. Pellets for electrical conductivity measurement were pressed at constant pressure 1000 psi. An IR die-silver paste was used to make contacts between the polymer pellets and the two graphite electrodes. Conductivities were measured at room temperature in air using a 610 Keithley Electrometer.

SYNTHESIS OF THE MONOMERS

Synthesis of 1,2-bis(3-carboxyacrylyl) hydrazine²¹

A cold solution of hydrazine hydrate in acetic acid was prepared by slowly adding 5.00 g (0.1 mol) of 99% hydrazine hydrate to 25 mL of cold glacial acetic acid. This was then added to a solution of 19.6 g (0.2 mol) of maleic anhydride in 100 mL of glacial acetic acid. The temperature was maintained below 25°C throughout the addition, and then the reaction mixture was left stand at 25°C for 3 h. The crude hydrazide was filtered off and washed thoroughly with ethanol. After this, it was dried in a vacuum for 3 h to yield 19.9 g (85%) of product, mp 183–184°C (Ref. 21; mp 183–184°C).

Synthesis of 1,2-bis(2-carboxybenzoyl) hydrazine²²

Hydrazine hydrate (99%) 2.5 g (0.05 mol) in 10 mL of methanol was added to a solution of 14.8 g (0.1 mol) of phthalic anhydride in 75 mL of acetic acid and 50 mL of methanol and then cooled with an ice bath. After stirring with cooling for 1 h, a solid product was obtained by adding diethyl ether and filtering off to give colorless powder, yield 90%, m.p., 314°C (Ref. 22; mp 310°C).

Synthesis of 2,5-bis(*m*-nitrobenzylidene) cyclopentanone or cyclohexanone²³

A mixture of *m*-nitrobenzaldehyde (30.21 g, 0.2 mol) and cyclopentanone (8.41 g, 0.1 mol) or cyclohexanone (9.80 g, 0.1 mol) in ethanol (95%, 100 mL) was warmed at about 50°C to obtain a clear solution, and then few drops of catalytic KOH (20%) were added with stirring for 2 h. The yellow solid product

TABLE I
Yield and Elemental Analysis of Polymers
(3_{a-h}) and (4_{a-b})

Polymer no.	Yield %/color	Elemental analysis
		Calcd./found
		N
3 _a	72/brownish red	18.12/17.85
3 _b	70/brownish red	18.66/18.58
3 _c	75/brown	11.66/12.54
3 _d	80/brown	11.35/12.2
3 _e	69/colorless	13.72/13.7
3 _f	72/gray	14/13.2
3 _g	68/gray	9.62/8.75
3 _h	72/brown	9.3/8.5
4 _a	75/brown	13.95/13.95
4 _b	79/brown	11.96/12.5

formed was filtered off, washed with water, and crystallized from ethanol to give 2,5-bis(*m*-nitrobenzylidene) cyclopentanone, yield 95%, m. p. 216°C (Ref. 23; m.p. 215–217°C).

For 2,6-bis(*m*-nitrobenzylidene)cyclohexanone, the yellow solid product was filtered off, washed with

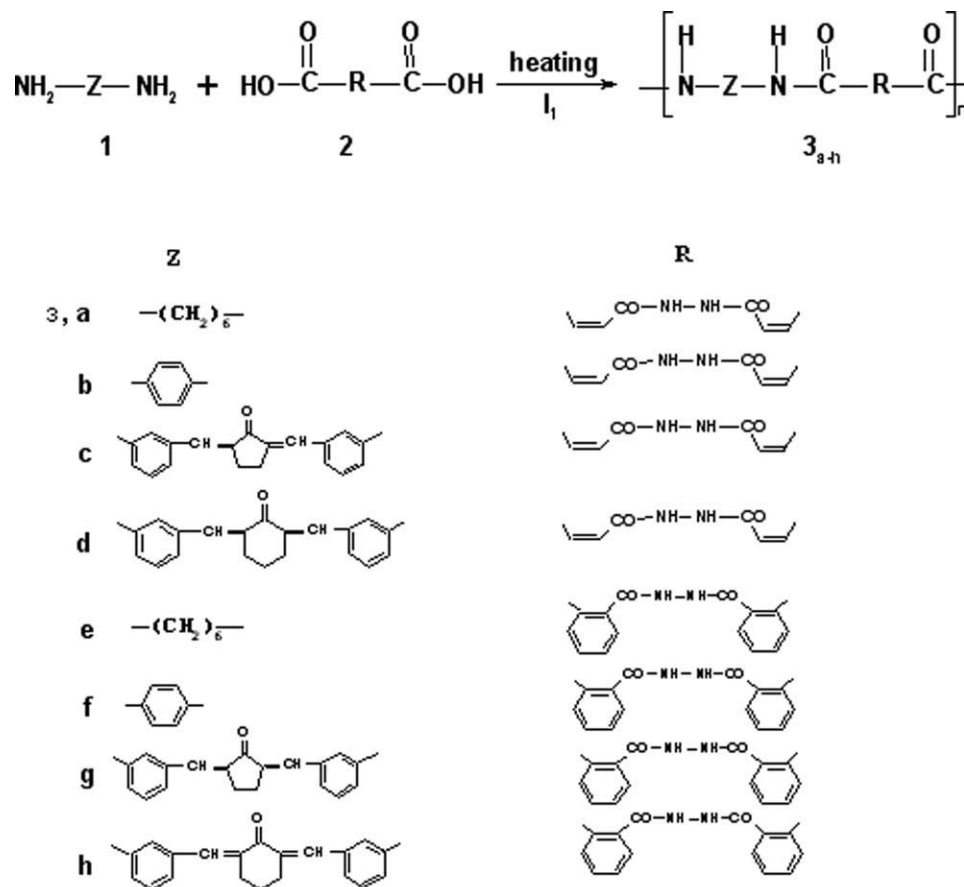
TABLE II
IR Spectra of Polyamides (3_{a-h}) and
Polyesteramides (4_{a-b})

Polymer code	IR spectra (ν_{\max} in cm^{-1})
3 _a	1562 (C–N), 1654, 1701 (C=O), 3391, 3517 (N–H)
3 _b	1516 (C–N), 1667, 1707 (C=O), 3277, 3360 (N–H)
3 _c	1528 (C–N), 1657, 1733 (C=O), 3391 (N–H)
3 _d	1530 (C–N), 1669, 1733 (C=O), 3250, 3364 (N–H)
3 _e	1555(C–N), 1660, 1706 (C=O), 3164(N–H)
3 _f	1517(C–N), 1667, 1725 (C=O), 3276, 3358 (N–H)
3 _g	1529 (C–N), 1662 (C=O), 3276, 3363 (N–H)
3 _h	1527 (C–N), 1662, 1720 (C=O), 3276, 3358 (N–H)
4 _a	1514 (C–N), 1661, 1734 (C=O), 3274, 3361 (N–H)
4 _b	1556 (C–N), 1660, 1712 (C=O), 3165, 3413 (N–H)

water, and crystallized from ethanol, yield 97%, m. p.: 193°C (Ref. 23; m.p. 193°C).

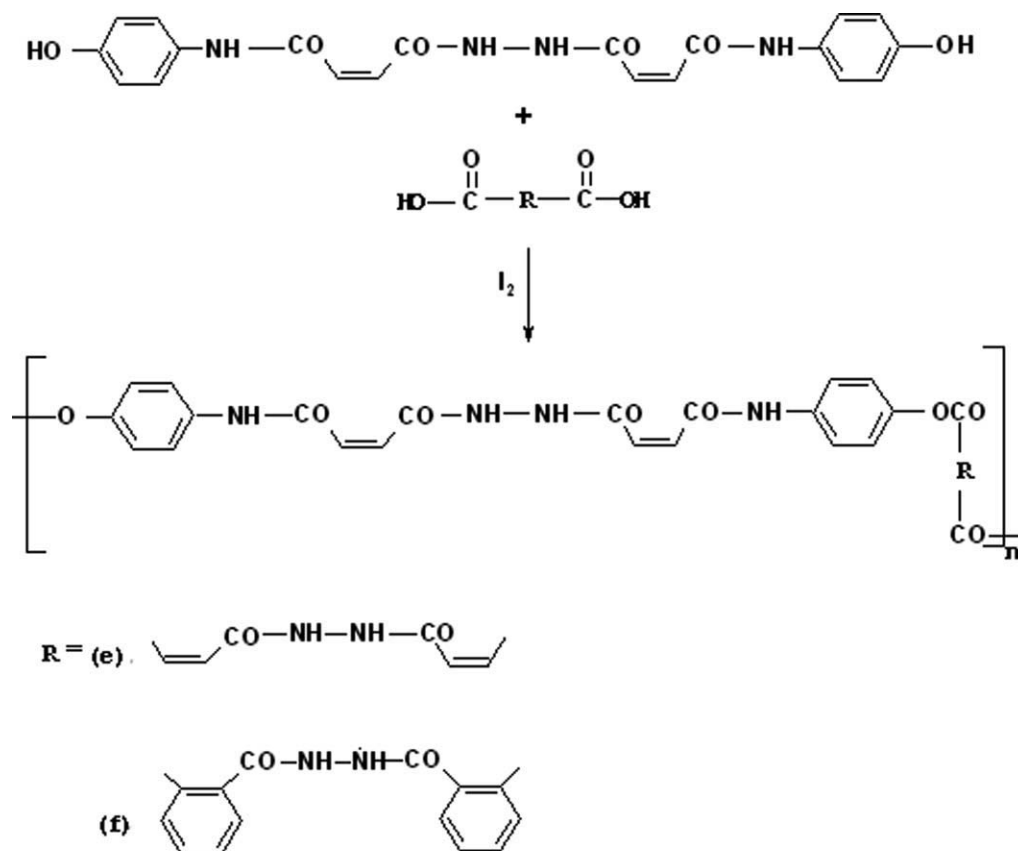
Synthesis of 2,5-bis(*m*-aminobenzylidene) cyclopentanone or cyclohexanone²⁴

The diamine monomers were prepared through the a catalytic reduction of 2,5-bis(*m*-aminobenzylidene)-cyclopentanone or cyclohexanone with hydrazine



I₁: CaCl₂, triethylphosphite, pyridine, NMP

Scheme 1 Synthesis of polyamides (3_{a-h}).



hydrate in the presence of Zn powder in NaOH in ethanol. The yields were very high. The structure of the diamine was designed to impart several desirable properties to polyimides.

A mixture of 2,5-bis(*m*-nitobenzylidene)cyclopentanone (1.75 g, 8 mol), or cyclohexanone (2.43 g, 8 mol), 1.2 g of Zn powder in 0.5 mL of 10% NaOH, and hydrazine hydrate (4 mL) were refluxed in

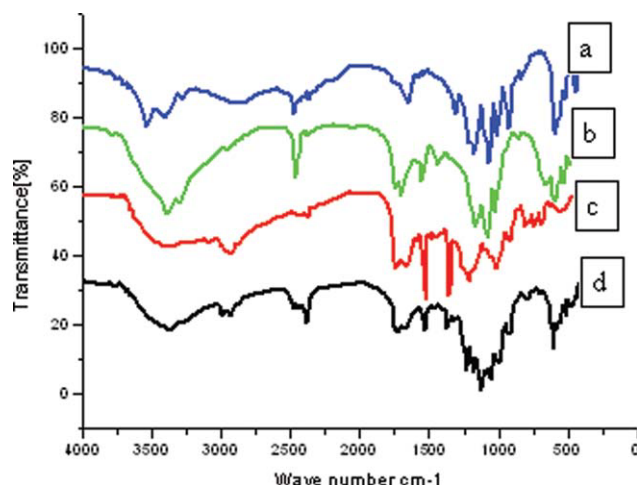


Figure 1 Infrared spectra of polyamides: (a) 3_a, (b) 3_b, (c) 3_c, and (d) 3_d. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

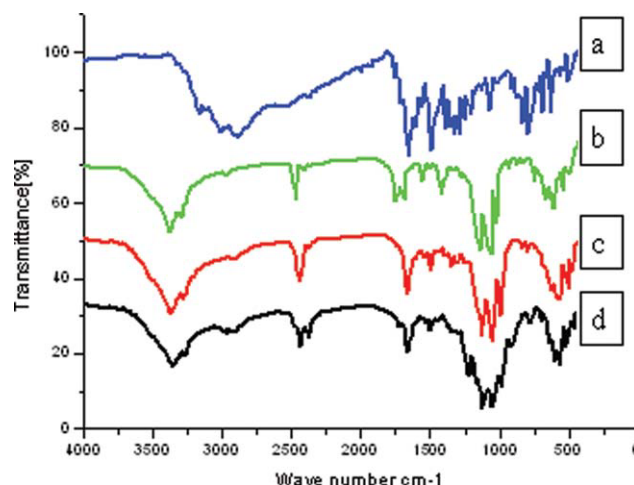


Figure 2 Infrared spectra of polyamides: (a) 3_e, (b) 3_f, (c) 3_g, and (d) 3_h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

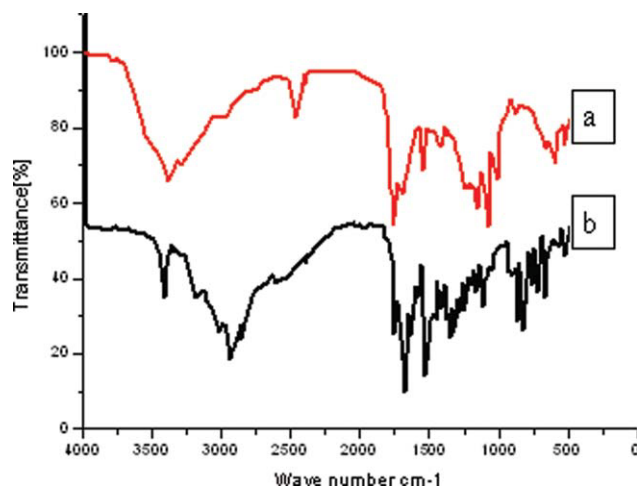


Figure 3 Infrared spectra of polyesteramides: (a) 4_a and (b) 4_b . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

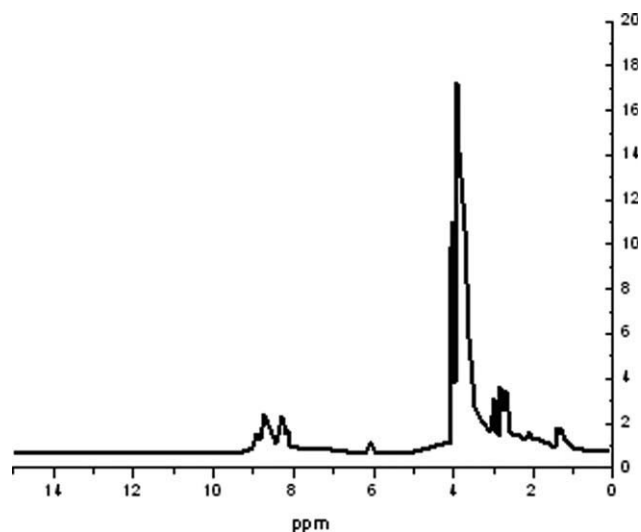


Figure 4 $^1\text{H-NMR}$ of polyamide: 3_c

ethanol for 30 min. The reaction mixture was cooled, filtered off, and dried to form a pale-yellow crystals of 2,5-bis(*m*-amino benzylidene) cyclopentanone, yield 90%, m.p. 102°C ([24] m.p. 102°C).

For 2,6-bis(*m*-aminobenzylidene)cyclohexanone, the reaction mixture was cooled, filtered off, and dried to give pale-yellow crystals, yield 93%, m.p.:100°C (Ref. 24; m.p. 100°C).

Synthesis of 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine²⁵

A mixture of *N,N'*-biisomaleimide (0.5 g and 2.5 mmol) and *p*-aminophenol (7.5 mmol) in 20 mL of glacial acetic acid was stirred at room temperature for 4 h. Excess ether was added, and the mixture was filtered off. The solid product was washed with ethanol and dried under reduced pressure and then

crystallized from dimethylformamide, yield 90%, m. p. 202°C (Ref. 25; m.p. 204°C).

POLYMER SYNTHESIS

Synthesis of polymers (3_{a-h}) and (4_{a-b})

General procedure

The synthesis of the polymers has been carried out by using a direct thermal polycondensation method.²⁶

A mixture of (0.001M) of diamine or 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine, (0.001M) of diacid, (0.2 g) of calcium chloride, 0.7 mL of triethyl phosphite, 0.8 mL of Py, and 4.0 mL of *N*-methyl-2-pyrrolidone was heated at 105°C with stirring for 3 h. The reaction mixture was slowly poured into 300 mL of methanol, and the precipitated solid was

TABLE III
Solubility Characteristics of Polyamides (3_{a-h}) and Polyesteramides (4_{a-b})

Polymer code	DMSO	DMF	NMP	Chloroform	Acetone	THF	Conc. H_2SO_4
3_a	±	–	–	–	–	–	+
3_b	–	–	–	–	–	–	+
3_c	+	±	+	±	±	±	+
3_d	±	±	±	–	–	–	+
3_e	±	–	–	–	–	±	+
3_f	±	±	±	–	–	–	+
3_g	–	–	–	–	–	–	+
3_h	–	–	–	–	–	–	+
4_a	±	±	±	–	–	±	+
4_b	±	±	±	–	–	±	+

+, soluble at room temperature (RT).

±, partially soluble at RT.

–, insoluble.

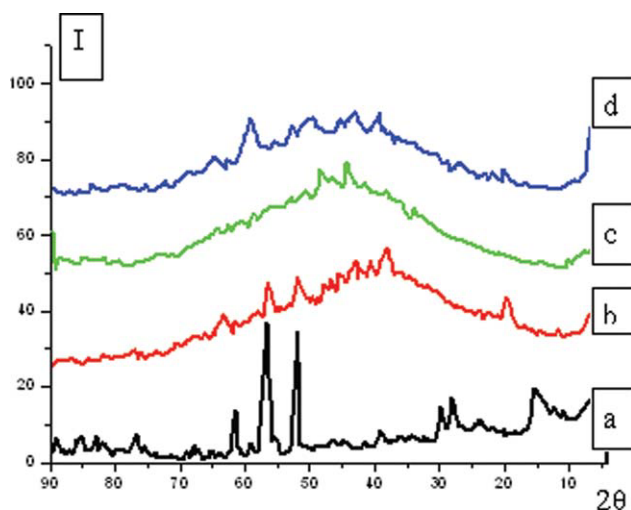


Figure 5 X-ray diffraction pattern of polyamides: (a) 3_a , (b) 3_b , (c) 3_c , and (d) 3_d . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

filtered off and washed with hot methanol to give the products (3_{a-h}) and (4_{a-b}), respectively, as shown in Table I

Reaction of different diacids with different diamines

Synthesis of PA polymers (3_{a-h})

General procedure. A mixture of (0.001M) of diamine, diacid (0.001M), 0.2 g of calcium chloride, 0.7 mL of triethyl phosphite, 0.8 mL of Py, and 4.0 mL of *N*-methyl-2-pyrrolidone was heated at 105°C with stirring for 3 h. The reaction mixture was slowly poured into 300 mL of methanol; the precipitated

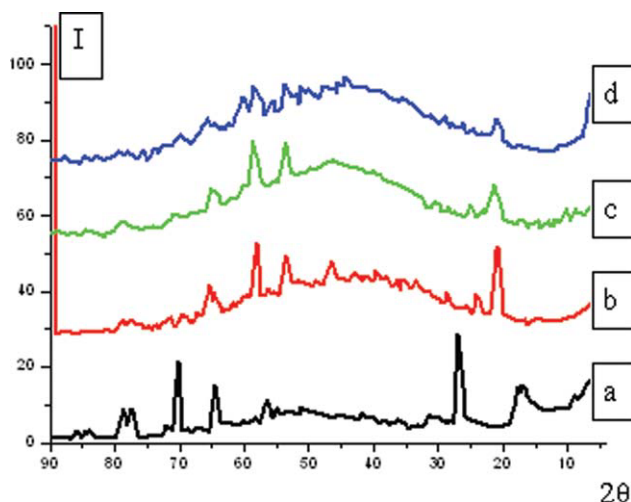


Figure 6 X-ray diffraction pattern of polyamides: (a) 3_e , (b) 3_f , (c) 3_g , and (d) 3_h . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

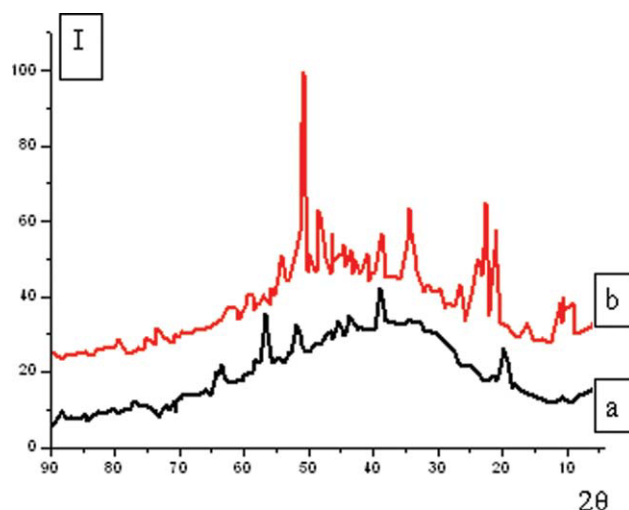


Figure 7 X-ray diffraction pattern of polyesteramides: (a) 4_a and (b) 4_b . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solid was filtered and washed with hot methanol to give the product Table I.

Reaction of 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine with different diacids

Synthesis of PEA polymers (4_{a-b})

General procedure. A mixture of (0.001M) of 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine, diacid (0.001M) (0.2 g) of calcium chloride, 0.7 mL of triethyl phosphite, 0.8 mL of Py, and 4.0 mL of *N*-methyl-2-pyrrolidone was stirred with heating at 105°C for 3 h. The reaction mixture was slowly poured into 300 mL of methanol, and the precipitated powder was filtered and then washed with hot methanol to give a brown powder Table II.

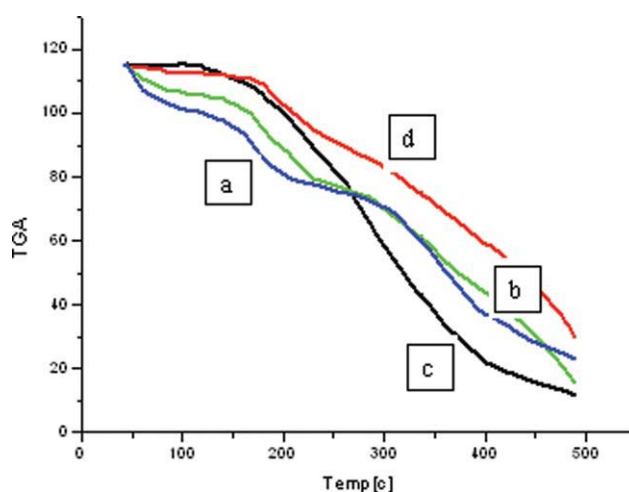


Figure 8 TGA for polyamides: (a) 3_a , (b) 3_b , (c) 3_c , and (d) 3_d . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

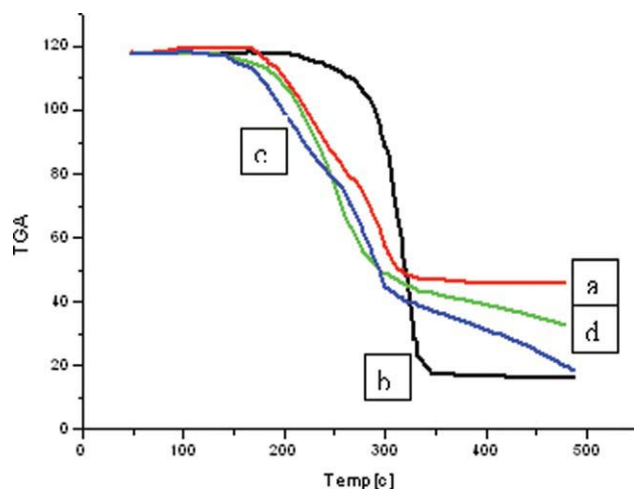


Figure 9 TGA for polyamides: (a) 3_e , (b) 3_f , (c) 3_g , and (d) 3_h . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

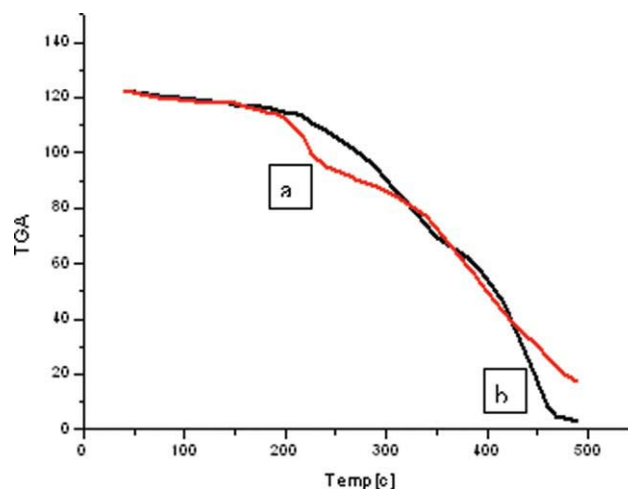


Figure 10 TGA for polyesteramides: (a) 4_a and (b) 4_b . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

As shown in Scheme 1, PAs 3_{a-h} having amide units were synthesized from the different diamine monomers **1** with one aliphatic and one aromatic dicarboxylic acid **2** in NMP and calcium chloride by the Guey–Sheng reaction conditions²⁶ by using triethyl phosphite and Py as condensing agents, and as shown in Scheme 2, PEAs 4_{a-b} were synthesized from 1,2-bis(3-*p*-hydroxyanilide acrylyl) hydrazine with one aliphatic and one aromatic dicarboxylic acid **2** under the same conditions.

The new PA (3_{a-h}) and PEAs (4_{a-b}) were characterized by elemental analysis, FTIR, ¹H-NMR, solubility, X-ray, thermal analysis, mechanical properties, and electrical conductivity.

The elemental analysis of all the polymers coincided with the characteristic repeating units of each polymer Table I.

The FTIR data for the PA polymers (3_{a-h}) showed the absorption band for (NH) stretching at 3015–3391 cm^{-1} , carbonyl absorptions at 1654–1733 cm^{-1} ,

and strong bands at 1516–1530 cm^{-1} due to C–N. The FTIR data for polymer (4_{a-b}) showed the absorption bands at 3165–3413 cm^{-1} for NH stretching characteristic for secondary amide linkages, absorption band at 1660–1734 cm^{-1} for carbonyl groups and at 1514–1556 cm^{-1} for the C=C skeletal in-plane vibrations as shown in Table II and Figures 1–3.

The ¹H-NMR spectrum in DMSO (6 d) for (3_c) showed a singlet at δ 8.1–8.2 (2H, 2NH), a multiplet at δ 8.9 (4H, Ar–H), a doublet at δ 3.7–4 (2H, 2 CH=C), and a triplet at δ 2.9–3 (4H, 2CH₂ cyclopentanone; Fig. 4).

Solubility characterization

The solubility behavior of the prepared PAs (3_{a-h}) and PEAs (4_{a-b}) in different solvents at room temperature is shown in Table III. The polymers had poor solubility in aprotic solvents such as chloroform, acetone, and were partially soluble in DMSO. All PA polymers were readily soluble in concentrated H₂SO₄, producing different colors probably

TABLE IV
Thermal Properties of the Polymers (3_{a-h}) and (4_{a-b})

Polymer code	T_g (°C)	T_m (°C)	Temp.	Wt. loss (%)	Temp.	Wt. loss (%)	Temp.	Wt. loss (%)
3_a	102.4	425.5	200	7.6	370	16	–	–
3_b	–	–	200	9.6	370	10.6	470	10.2
3_c	104.6	401.1	250	7.94	340	12.77	450	10.82
3_d	238.4	388.7	200	9.27	320	10.87	450	14.63
3_e	224.5	421.8	220	13.39	420	11.13	–	–
3_f	–	–	240	4.66	350	88.05	–	–
3_g	202.1	436.7	200	10.6	320	13.15	450	4.93
3_h	195	430.9	280	15.93	450	2.01	–	–
4_a	265	445.9	200	10.22	380	25.64	480	6.41
4_b	240	426.8	300	39.78	480	51.38	–	–

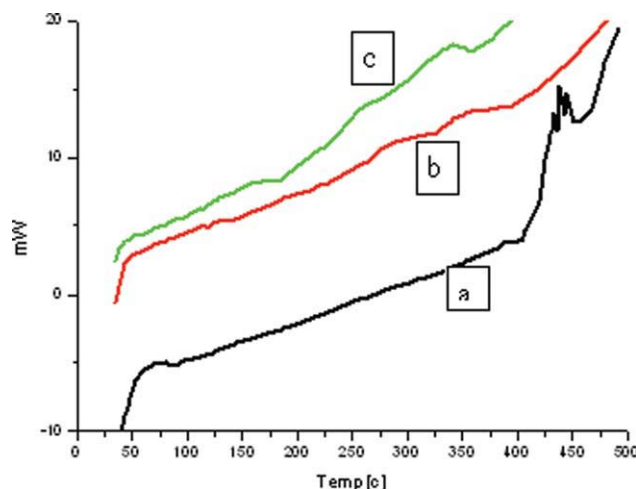


Figure 11 DSC of (a) 3_a , (b) 3_c , and (c) 3_d . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the presence of rigid planar different diamine units in the polymer main chain. This result indicated that all these PAs are organic insoluble in nature and can be prepared from the one-step high-temperature polycondensation method.

Thus, all the chemically PAs can be processed from solution. The less solubility of the polymers might be attributable to the better chain-packing and aggregation or partial crosslinking within polymer chains that occurred at elevated temperatures.

X-ray diffraction

X-ray diffraction studies of polymers (3_{a-h}) show few reflections of sharp peaks intermediate between crystalline and amorphous solids. The presence of the polar C=O groups in addition to the high con-

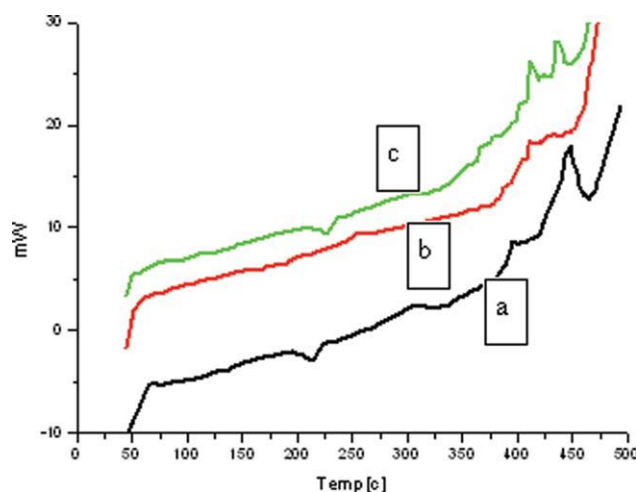


Figure 12 DSC of (a) 3_e , (b) 3_g , and (c) 3_h . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

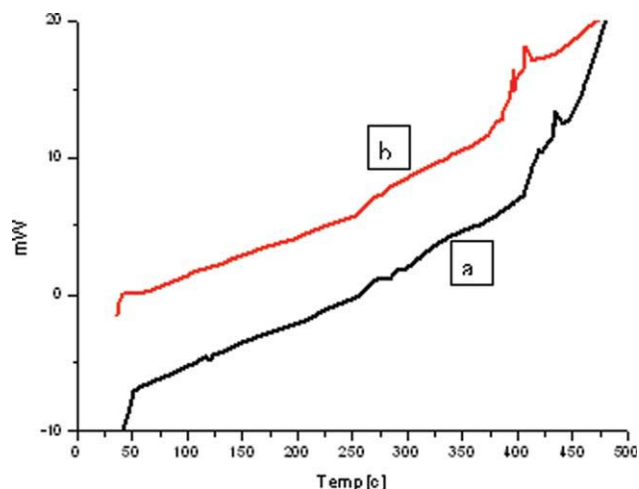


Figure 13 DSC of (a) 4_a and (b) 4_b . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

centration of C=C bonds induces some order between two adjacent chains in the polymer leading to some degree of crystallinity. On the other hand, the data show that PA polymers containing cyclohexanone moiety (3_d , 3_h) have a high degree of crystallinity in comparison with those containing cyclopentanone moiety (3_c , 3_g). PA polymers derived from aliphatic compound have a higher degree of crystallinity in comparison with those containing aromatic ring as shown in Figures 5 and 6. X-ray diffraction shows the crystallinity of the polymers (4_{a-b}) as shown in Figure 7. The PEA (4_b) obtained from the aromatic acids have sharper peaks than PEA (4_a) obtained from the aliphatic acids.

Thermal studies

The thermal properties of the PAs (3_{a-h}) and PEA (4_{a-b}) were investigated by the TGA and DSC.

Thermogravimetric analysis

The thermal stability of the PAs (3_{a-h}) and PEAs (4_{a-b}) was evaluated by thermogravimetric analysis (TGA) measurements in air at a heating rate of $10^\circ\text{C}/\text{min}$, and the thermograms are presented in Figures 8–10 and Table IV. These polymers exhibited

TABLE V
Mechanical Properties of 3_a , 0.4445 g in 15 mL Sulphuric Acid, Using Spindle 18, at Room Temperature

RPM	10	20	40	60	80	100
S.S (N/m ²)	3.37	6.77	14.5	21.6	28.2	35.3
S.R (1/s)	13.2	26.4	52.8	79.2	106	132
Viscosity (Pa s)	25.5	25.9	27.4	27.3	27.1	27.0
Torque (N m)	8.3	17.1	36.5	54.5	71.9	89.9

TABLE VI

Mechanical Properties of 3_c , 0.0192 g in 15 mL Sulphuric Acid, Using Spindle 18, at Room Temperature

RPM	10	20	40	60	80	100	150
S.S (N/m ²)	0.55	2.77	7.83	12.8	18.5	23.8	37.6
S.R (1/s)	13.2	26.4	52.8	79.2	106	132	198
Viscosity (Pa s)	3.0	10.0	15.8	16.2	17.6	18.2	19.1
Torque (N m)	1.20	6.90	19.2	32.0	46.0	59.8	95.0

reasonable thermal stability with weight loss up to 450°C (for the PAs) and 480°C (for the PEAs). The decomposition temperatures (T_d) for the PAs are 450°C at 4.9–14.6% weight loss and for the PEA is 480°C at 6.41%. Thus, the TGA data indicated that these polymers had fairly high thermal stability.

The thermograph of the polymers shows that the weight loss of the PAs in the low temperature range may be attributed to the ease of degradation of amide groups present in the PAs; however, the weight loss in the high temperature range is attributed to the degradation of the main chain.

From Table IV, it can be concluded that the PA-containing cyclopentanone ring with the aliphatic or aromatic compounds (3_c , 3_g) is more thermally stable than the other polymers, the PA-containing cyclopentanone ring with the aliphatic (3_c) component is more thermally stable than cyclopentanone ring with the aromatic component (3_g), and the PEA (4_a) is more thermally stable than (4_b).

Differential scanning calorimetry

The glass-transition temperatures (T_g) of PAs ($3_{a,c,d,e,g,h}$) and PEA (4_{a-b}) could be determined in the differential scanning calorimetry (DSC) thermograms; they were observed in the range from 102 to 265°C depending on the chemical structures of diacids and diamines used. The lowest T_g value of PA 3_a can be explained in terms of the flexibility and low rotation barrier of its diacid component, and the highest T_g of PEA 4_a may be due to the presence of long main chain of the component. All the polymers indicated melting endotherms (T_m) on their DSC traces, and they were observed in the range from 388 to 445°C supporting the semicrystalline nature of these polymers as shown in Figures 11–13 and Table IV.

TABLE VII

Mechanical Properties of 3_e , 0.3296 g in 15 mL Sulphuric Acid, Using Spindle 18, at Room Temperature

RPM	10	20	40	60	80	100
S.S (N/m ²)	3.92	7.01	14.0	20.6	28.0	34.5
S.R (1/s)	13.2	26.4	52.8	79.2	106	132
Viscosity (Pa s)	30	25.9	26.7	26.6	26.5	26.5
Torque (N m)	9.9	17.2	34.5	52.2	70.4	87.9

TABLE VIII

Mechanical Properties of 3_h , 0.0159 g in 15 mL Sulphuric Acid, Using Spindle 18, at Room Temperature

RPM	20	40	60	80	100	150
S.S (N/m ²)	2.06	7.09	12.1	17.3	22.9	36.5
S.R (1/s)	26.4	52.8	79.2	106	132	198
Viscosity (Pa s)	7.95	13.9	15.3	16.7	17.3	18.5
Torque (N m)	4.5	18.5	31.9	43.6	57.9	92.3

Mechanical properties

The results of the measurements of the mechanical properties for the polymers (3_{ar} , 3_c , 3_e , 3_h , 4_a) shown in Tables V–IX indicate that the values of the (shear stress, shear rate, viscosity, and torque) of all the studied polymers are promising. All the polycondensation reactions proceeded readily in a homogenous solution, and the reaction solutions generally became very viscous within 3 h. Viscosities of the resultant polymer solutions were normally very high. As shown in Tables V–IX, the obtained PAs (3_{a-h}) and PEA (4_{a-b}) had inherent viscosities in the range of 10–26.7 pa s.

The viscosity of all PAs was determined in concentrated sulfuric acid at room temperature. The data in Tables V–IX indicated that the PAs (3_e , 3_a) have a higher viscosity (30, 27 Pa s), respectively, than the others.

The value of the torque for the polymers (4_{ar} , 3_h) is greater than that for other PAs; the value of the shear stress for the polymers (4_{ar} , 3_e) is greater than other PAs, the values of the shear rate for the all polymers almost have the same value, and this data may attributed due to the molecular weight of the polymers.

Tables V–IX show that as the molecular weight of the unit of polymers increased, the shear stress and the torque values are increased, where S.S is shear stress and S.R is shear rate.

Electrical conductivity

The electrical conductivity of the prepared PAs (3_{a-h}) and PEA (4_{a-b}) was measured and gave values in the range 10^{-10} – 10^{-11} (Ω cm⁻¹). This indicates that all the new polymers have insulating capabilities (Table X).

TABLE IX

Mechanical Properties of 4_{ar} , 0.0273 g in 15 mL Sulphuric Acid, Using Spindle 18, at Room Temperature

RPM	20	40	60	80	100	150
S.S (N/m ²)	4.24	8.63	14.1	19.5	24.7	39.2
S.R (1/s)	26.4	52.8	79.2	106	132	198
Viscosity (Pa s)	16.9	16.9	17.5	18.4	19.2	19.8
Torque (N m)	15.9	22.7	35.4	49.2	62.8	99.9

TABLE X
Electrical Conductivity of the Polyamides (3_{a-h}) and Polyesteramides (4_{a-b})

Polymer code	Electrical conductivity ($\Omega \text{ cm}^{-1}$)
3 _a	27.3×10^{-11}
3 _b	15.4×10^{-10}
3 _c	28.1×10^{-11}
3 _d	52.0×10^{-10}
3 _e	4.8×10^{-10}
3 _f	8.0×10^{-10}
3 _g	13.6×10^{-11}
3 _h	13.8×10^{-10}
4 _a	14.0×10^{-10}
4 _b	8.4×10^{-10}

CONCLUSIONS

Based on the above data, PAs with high insulating capacity can be synthesized from the polymerization of diacids with different diamines or different diols, respectively, using the polycondensation technique. Most of these polymers showed poor solubility in polar solvents such as DMF, NMP, chloroform, acetone, and THF.

The crystallinity of the new polymers showed that the polymers based on cyclohexanone moiety have a higher degree of crystallinity in comparison with those containing cyclopentanone moiety; however, polymers containing aliphatic moiety have a higher degree of crystallinity in comparison with those containing aromatic moiety.

The thermal properties of the polymers based on aliphatic or aromatic acids and polymers containing cyclopentanone moiety show greater thermally stability than the other polymers. The polymers based on aliphatic acids and containing the cyclopentanone ring are more thermally stable than the polymers based on aromatic acids and containing the cyclopentanone moiety.

The results of the measurements of the mechanical properties for the polymers indicated that the values of all the studied polymers (shear stress, shear rate, viscosity, and torque) are promising.

The electrical conductivity measurements showed that most of polymers possess values in the range $10^{-10} - 10^{-11} (\Omega \text{ cm}^{-1})$. These data indicate that all these polymers have electrical insulating properties, and the polymers prepared from aliphatic acids pos-

sess better insulating properties than the polymers prepared from the aromatic acids.

The authors are indebted to Dr. Salwa Abd-El Wahab, Department of Physics, Ain Shams University for her help with the electrical conductivity measurements.

References

- Willson, D. In *Polyimides*. Hergenrother, P. M., Stenzenberger, H. D., Eds.; Chapman & Hall: New York, 1990.
- Carothers, W. H. U.S. Pat.2,130,948 (1937).
- Gaymans, R. J. In *Synthetic Methods in Step-Growth Polymers*; Rogers, M. E., Long, T. E., Eds.; Wiley: Hoboken, NJ, 2003; Chapter 3, p 135–196.
- Lim, J. G.; Gupta, B. S.; George, W. *Prog Polym Sci* 1989, 14, 763.
- Yang, H. H. *Aromatic High-Strength Fibers*; Wiley: New York, 1989; p 70–111.
- Preston, J. In *Encyclopedia of Polymer Science and Technology*, 2nd ed; Wiley-Interscience: New York, 1988; p 265–278.
- Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*, Vol. 11; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; p 315.
- Preston, J. In *Encyclopedia of Polymer Science and Engineering*, Vol. 11; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley-Interscience: New York, 1989; p 381.
- Garcia, J. M.; Garcia, F. C.; Serna, F.; de la Pena, J. *Prog Polym Sci* 2010, 35, 623.
- Gaymans, R. J.; Sikkema, D. J. In *Step Polymerization*, Vol. 5; Allan, G., Bevington, J. C., Eastmond, G. C., Ledwith, A., Russo, S., Sigwald, P., Eds.; Pergamon: Oxford, 1989; p 357–373.
- Suh, D. H.; Ju, S. Y.; Park, S. H.; Lee, J. W. *J Macromol Sci Pure Appl Chem* 2001, 38, 751.
- Kohan, M. I. *Nylon Plastics Handbook*; Hanser-Gardner: Munich, NY, 1995; p 844–857.
- Deopura, B. L.; Alagirusamy, R.; Joshi, M.; Gupta, B. *Polyesters and Polyamides*; CRC Press, Cambridge, UK, 2008; p 126–134.
- Morgan, P. W. *Macromolecules* 1977, 10, 1381.
- Lin, J.; Sherrington, D. C. *Adv Polym Sci* 1994, 111, 176.
- Yamazaki, N.; Higashi, F.; Kawabata, J. *J Polym Sci Polym Chem Ed* 1974, 12, 2149.
- Grigat, E.; Koch, R.; Timmermann, R. *Polym Degrad Stab* 1998, 59, 223.
- Okada, M. *Prog Polym Sci* 2002, 27, 87.
- Kandile, N. G.; Mohamed, M. I.; Zaky, H. T.; Nasr, A. S.; Abdel-Bary, E. M. *Carbohydr Polym* 2009, 75, 580.
- Kandile, N. G.; Nasr, A. S. *Carbohydr Polym* 2009, 78, 753.
- Feuer, H. C.; Rubinstein, H. *J Am Chem Soc* 1958, 80, 5873.
- Kealy, T. J. *J Am Chem Soc* 1962, 84, 966.
- Aly, K. I.; Khalaf, A. A. *J Appl Polym Sci A* 2000, 37, 2118.
- Mikroyannidis, J. A. *Eur Polym J* 1992, 28, 439.
- Hedaya, E.; Hinman, R. L.; Theodoropoulos, J. *J Am Chem Soc* 1966, 31, 1311.
- Guey-Sheng, L.; Sheng-Huei, H. *J High Perform Polym* 2001, 13, S137.