New Polymer Syntheses. IX. Synthesis and Properties of New Conducting Polyazomethine Polymers Containing Main Chain Cycloalkanone and Pyridine Moieties

KAMAL I. ALY, ALI A. KHALAF

Polymer Laboratory 507, Chemistry Department, Assiut University, Assiut 71516, Egypt

ABSTRACT: Novel polyazomethines containing cycloalkanones or pyridine moieties were synthesized by the polycondensation of 2,5-bis(*m*-aminobenzylidene)cyclopentanone (BMAP, **IV**), 2,6-bis(*m*-aminobenzylidene)cyclohexanone (BMAH, **V**), 2,6-bis(*p*-aminobenzylidene)cyclohexanone (BPAH, **VI**), and 2,6-bis(*m*-aminostyryl)pyridine (BMAS, **VIII**) diamines with terephthalaldehyde in EtOH at 25°C. These polymers were yellow to orange in color, had reduced viscosities up to 1.42 dL/g, and had electric conductivities as high as 10^{-11}–10^{-12} S cm^{-1}. All the polyazomethines were insoluble in common organic solvents but dissolved completely in concentrated sulfuric acid. However, they were readily hydrolyzed in concentrated H_2SO_4. X-ray diffraction diagrams showed that the crystallinities of the polyazomethines were low. These azomethine polymers showed high thermal and thermooxidative stability and exhibited no appreciable decomposition up to 400°C in air. The electronic spectra of the polymers indicated a large bathochromic shift of the π–π* absorption band ($\sim$360 nm) that was due to the presence of C=N bonds in the polymer main chain. Doping with iodine dramatically raised the conductivity and produced dark brown to black colored semiconductive polymers with a maximum conductivity on the order of 10^{-7} S cm^{-1}. Furthermore, the morphology of selected examples of the four polyazomethines was examined by scanning electron microscopy. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1218–1229, 2000

Key words: polyazomethines; conjugated polymers; arylidene polymers; thermally stable polymers; semiconductive polymers

INTRODUCTION

Polyazomethines, which are also called polymeric Schiff bases, have been the subject of research beginning with D'Alelio et al.'s pioneering work.[1–3] These polymers have attracted much attention not only as high-performance fiber and film-forming polymers with remarkable thermal stability, high strength, and high modulus[4–8] but also as particularly promising electronic materials with semiconductive and piezoelectric properties.[9–11] They are generally synthesized by the simple solid-state or solution polycondensation of diamines with dialdehydes. Thus, polyazomethines containing heterocyclic nuclei, such as furan,[12,13] thiophene,[14] 1,3,4-thiadiazole,[15] and 1,3,4-oxadiazole,[16] have been synthesized from diamines or dialdehydes with these preformed nuclei. These polymers have a highly aromatic and widely conjugated heterocyclic system in the main chain.

In continuation of our interest in the study of the behavior of arylidene monomers,[17–24] in this article we report a route for the synthesis of some new polyazomethines containing cyclohexanone, cyclopentanone, or pyridine moieties in the main chain by simple solution polycondensation of dialdehyde with 2,5-bis(*m*-aminobenzylidene)-cyclopentanone (BMAP), 2,6-bis(*m*-aminobenzylidene)cyclohexanone (BMAH), 2,6-bis(*p*-aminobenzylidene)cyclohexanone (BPAH), and 2,6-bis(*m*-aminostyryl)pyridine (BMAS) under mild conditions. In addition, we also report on the characterization of these polymers, especially in regard to their thermal and electrical properties.

EXPERIMENTAL

Materials

The *p*- and *m*-nitrobenzaldyde (Fluka) were used as received. Cyclohexanone (bp 155°C) and cyclopentanone (bp 130–131°C; Merck) were freshly distilled. Terephthalaldehyde (mp 115–116°C, Merck) was recrystallized twice from water. The 2,6-dimethylpyridine and tetrahydrofuran (THF) from Merck were distilled under reduced pressure. Ethanol (99%) and all other chemicals were highly pure and were further purified by standard methods.[25]

Measurements

The IR spectra were recorded on a Shimadzu 2110 PC scanning spectrophotometer. 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) solutions of polymers in concentrated H$_2$SO$_4$ 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 CuKα radiations. DTA and TGA measurements were performed on a Du Pont 2000 thermal analyzer at a heating rate of 10°C/min in air and nitrogen. The solubilities of the polymers were determined using 0.02 g of polymer in 3–5 mL of solvent at room temperature. The morphologies of the polymers were examined by scanning electron microscopy (SEM) using a Jeol JSM-5400 LV instrument. The electrical conductivities were measured as follows: the sample was inserted in a home made holder between two copper disks (insulated with Teflon); then the sample resistivity was measured directly using a Keithly electrometer (610C) at 25°C with polymer disks (103.4 mm^3 diameter, 0.65–0.85 mm thickness), which were prepared by compressing the finely powdered polymers at 4000 kg/mL under a vacuum. We measured the conductivity (σ) from the Arrhenius equation. Iodine doping was carried out by exposing the disks to iodine vapor until the polymers were saturated, and the contents were calculated from their weight increase. Electronic spectra were recorded in concentrated sulfuric acid in the 200–500 nm range with a Shimadzu 2110 PC scanning spectrophotometer.

Monomer Synthesis

2,5-Bis(m-*nitrobenzylidene*)cyclopentanone (I)

A flask was charged with a mixture of *m*-nitrobenzaldehyde (40 mmol), cyclopentanone (20 mmol), and ethanol (95%, 100 mL). The mixture was heated at about 50°C to obtain a solution. A few drops of KOH (20%) were added as a catalyst during stirring. An exothermic reaction was observed while a highly yellowish solid separated. It was filtered off, washed thoroughly with water, and dried to afford monomer **I**. A purified sample (mp 215–217°C, 95% yield) was obtained by recrystallization from ethanol.

IR (KBr, cm^{-1}): 2980 (cyclopentanone C—H stretching); 1685 (C=O); 1610 (C=C); 1525, 1361 (NO$_2$); 1439 (cyclopentanone C—H deformation). ^{1}H-NMR (CDCl$_3$, ppm): 7.95–8.13 (m, 4H Ar-H *ortho* to NO$_2$); 7.60–7.85 (m, 4H of other Ar-H and 2H of 2CH=C); 3.15–3.30 (m, 4H of cyclopentanone).

2,6-Bis(m-*nitrobenzylidene*)cyclohexanone (II)

The procedure to procure the compound was essentially the same as that described for **I**. The crude yield was 97%. A sample recrystallized from dioxane gave the desired compound in the form of needles (mp 193°C).

IR (KBr, cm^{-1}): 2990 (cyclohexanone C—H stretching); 1680 (C=O); 1615 (C=C); 1365, 1532 (NO$_2$); 1443 (cyclohexanone C—H deformation). ^{1}H-NMR (DMSO-d_6, ppm): 8.12–8.26 (m, 4H of Ar-H *ortho* to NO$_2$); 7.55–7.80 (m, 4H of other Ar-H and 2H of 2CH=C); 2.85 (m, 4H of 2CH$_2$ of cyclohexanone); 2.01 (m, middle 2H of CH$_2$ cyclohexanone).

2,6-Bis(p-*nitrobenzylidene*)cyclohexanone (III)

Using a procedure similar to the one described for compounds **I** and **II**, an analytical sample of **III**

(mp 145–146°C, 87% yield) was obtained by recrystallization from methanol.

IR (KBr, cm^{-1}): 2995 (cyclohexanone C—H stretching); 1680 (C=O); 1610 (C=C); 1362, 1535 (NO$_2$); 1445 (cyclohexanone C—H deformation). ^{1}H-NMR (CDCl$_3$, δ, ppm): 7.80–8.15 (m, 4H of Ar-H *ortho* to NO$_2$); 6.95–7.60 (m, 4H of other Ar-H and 2H of 2CH=C); 2.25–2.45 (m, 6H of cyclohexanone).

BMAP IV

A flask was charged with a mixture of compound **I** (2.982 g, 8.52 mmol), ethanol (95%, 40 mL), and a catalytic quantity of 10% palladium on activated carbon. Hydrazine hydrate (4 mL) diluted with ethanol (10 mL) was added dropwise to the stirred mixture at 60°C. It was subsequently heated at this temperature for 30 min. The solid gradually dissolved during hydrogenation. The reaction mixture was filtered off and the filtrate was concentrated by rotary evaporation. The residue was dried in a vacuum oven to yield a compact pale yellow solid. An analytical sample was obtained by recrystallization from ether/THF (1:1, mp 101°C, 85% yield).

IR (KBr, cm^{-1}): 3460–3190 (NH stretching); 2950–2870 (cyclopentanone C—H stretching); 1660 (C=O of cyclopentanone); 695 (NH deformation). ^{1}H-NMR (DMSO-d_6, ppm): 6.39–7.04 (m, 8H of Ar-H and 2H of 2CH=C); 4.98 (s, 4H of 2NH$_2$); 3.10–3.45 (m, 4H of cyclopentanone).

BMAH V

Using a procedure similar to that for **IV**, a sample (mp 99°C, 85% yield) was obtained by recrystallization from THF/ether.

IR (KBr, cm^{-1}): 3390–3195 (NH stretching); 2850–2940 (C—H of cyclohexanone); 1685 (C=O of cyclohexanone); 1600–1610 (C=C); 695 (NH deformation). ^{1}H-NMR (DMSO-d_6, ppm): 6.39–7.04 (m, 8H of Ar-H and 2H of 2CH=C); 4.98 (s, 4H of 2NH$_2$); 1.45–1.90 [m, 2H of CH2 (middle) cyclohexanone]; 2.85–3.3 (m, 4H of 2CH$_2$ cyclohexanone).

BPAH VI

A procedure similar to that for **IV** and **V** was followed to obtain this compound. An analytical sample of **VI** (mp 145–6°C, 63% yield) was obtained from recrystallization from petroleum ether/THF.

IR (KBr, cm^{-1}): 3410–3190 (NH stretching); 2845–2960 (C—H of cyclohexanone); 1665 (C=O of cyclohexanone); 1590–1600 (C=C); 680 (NH deformation). ^{1}H-NMR (DMSO-d_6, ppm): 6.65–7.15 (m, 8H of Ar-H and 2H of 2CH=C); 4.65 (s, 4H of 2NH$_2$); 1.3–1.8 [m, 2H of CH$_2$ (middle) cyclohexanone]; 2.8–3.41 (m, 4H of 2CH$_2$ cyclohexanone).

2,6-Bis(m-*nitrostyryl*)pyridine (VII)

A mixture of *m*-nitrobenzaldehyde (40 mmol), 2,6-dimethylpyridine (20 mmol), and acetic anhydride (30 mL) was heated at 55°C for 1 h, at 85°C for 3 h, and at 150°C for 25 h. The reaction mixture was subsequently poured into water and stirred at ambient temperature for about 1 h to hydrolyze excess acetic anhydride. The solid thus obtained was filtered off, washed thoroughly with dilute aqueous NaHCO$_3$, washed with water, and dried to afford the compound **VII**. A purified sample was obtained by recrystallization from dioxane (mp 218°C, lit.[26] 217–219°C).

IR (KBr, cm^{-1}): 1605 (C=C stretching); 1465, 1490, 1530 (Ar-H and pyridine rings); 1540, 1370 (NO$_2$ groups); 745 (disubstituted pyridine ring). ^{1}H-NMR (DMSO-d_6, ppm): 8.25 (m, 4H of Ar-H *ortho* to NO$_2$); 7.25–7.65 (m, 7H of other Ar-H and pyridine ring); 6.75 (m of 4H of 2CH=CH—).

BMAS VIII

A procedure similar to that for **IV**, **V**, and **VI** was followed to produce BMAS **VIII**. An analytical sample of **VIII** was obtained by recrystallization from THF (mp 217°C, lit.[26] 218–220°C; 89% yield).

IR (KBr, cm^{-1}): 3460–3350 (NH stretching); 1640–1620 (NH deformation); 1570, 1515, 1475 (aromatic and pyridine ring); 820, 750 (2,6-disubstituted pyridine ring deformation). ^{1}H-NMR (DMSO-d_6, ppm): 4.35–4.45 (b, 4H of 2NH$_2$); 6.70 (m, 4H of 2CH=CH); 7.12–7.85 (m, 11H of aromatic and pyridine rings).

Syntheses of Model Compounds

All model compounds were prepared in a solution of EtOH (95%) or DMF as described below without any added catalyst and using the required stoichiometry between functional groups. In a typical experiment a solution of 10 mmol of BMAP **V** in about 30 mL of ethanol was placed in a 100-mL conical flask equipped with a magnettic stirrer. To this a solution of 20 mmol of benzaldehyde in 20 mL of ethanol was added dropwise over a period of 20 min with vigorous stirring at room temperature. At the end of the addition a highly yellowish precipitate separated out, which was filtered off, washed by ethanol, and recrystallized from ethanol (mp 148–149°C, 89% yield).

ANAL. Calcd for C$_{33}$H$_{26}$ON$_2$ (466): C, 84.98%; H, 5.58%; N, 6.01%. Found: C, 84.81%; H, 5.49%; N,
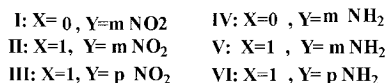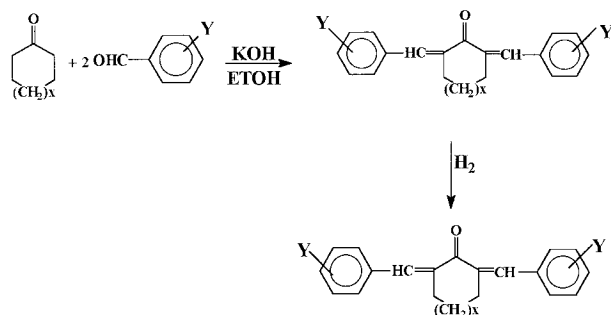
Scheme 1 The methods utilized for the preparation of the diarylidenecycloalkanone monomers BMAP **IV**, BMAH **V**, and BPAH **VI**.

5.7%. IR (KBr, cm^{-1}): 2860–2940 (C—H of cyclopentanone); 1685 (C═O of cyclopentanone); 1595–1610 (C═C and C═N stretching); 1210, 1395, 1500 (aromatic). ^{1}H-NMR (DMSO-d_6, ppm): 8.2–8.82 (m, 10H of Ar-H unsubstituted); 7.26–7.39 (m, 8H of Ar-H substituted); 6.44–6.93 (m, 4H of 2CH═C and 2CH═N); 3.36 (m, 4H of cyclopentanone).

Polycondensation of Polyazomethine-Containing Cyclohexanone XI from BMAH and Terephthalaldehyde

BMAH **V** (0.3045 g, 1 mmol) was dissolved in absolute ethanol (20 mL) and terephthalaldehyde was added to it (0.1341 g, 1 mmol) at 25°C. The mixture was then stirred at that temperature for
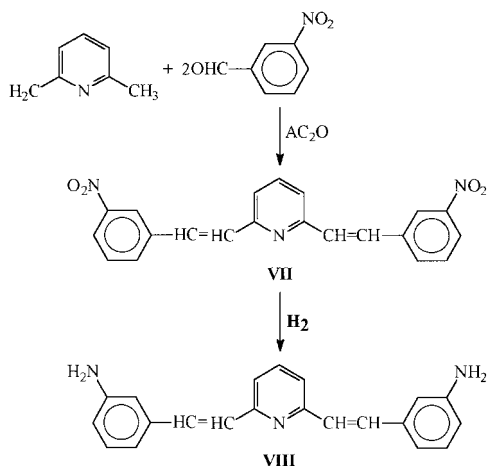
Scheme 2 The preparation of BMAS **VIII**.
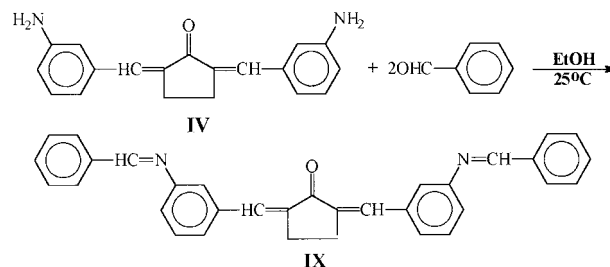
**Scheme 3** The synthesis of diazomethine compound **IX**.

20 min under dry nitrogen; the viscosity of the solution increased rapidly, and the polymer began to precipitate in the early stage of the reaction. The polymer was isolated by pouring the slurry into methanol (400 mL), followed by thorough washing with hot methanol and drying in a vacuum. The yield was 98%. The reduced viscosity was 1.42 dL/g, which was measured at a concentration of 0.5 g/dL in concentrated H$_2$SO$_4$ at 25°C.

IR (KBr, cm^{-1}): 1690 (C═O of cyclohexanone); 1620 (C═C of benzylidene).

All other polyazomethines were synthesized by an analogous procedure. The elemental analysis was not accurate, because these polymers burned incompletely.

RESULTS AND DISCUSSION

Scheme 1 outlines the methods utilized for the preparation of the diarylidenecycloalkanone monomers
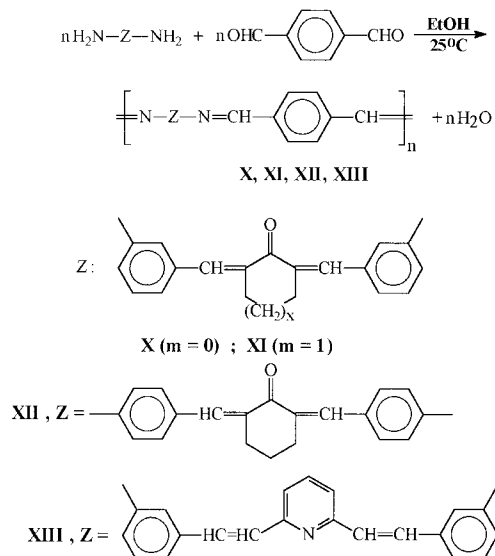
Scheme 4 The polycondensation of an equimolar mixture of terephthalaldehyde with diamines BMAP, BMAH, BPAH, and BMAS.

Table I   Synthesis of Polyazomethine Polymers X–XIII Containing Cycloalkanone and Pyridine Moieties

Polymer	Monomers		Reaction Conditions[a]		Polymer Yield	η_{red}[b] (dL/g)
	Diamine	Dialdehyde	Solvent	Time		
X	BMAP	TPA	EtOH	12 min	92	0.83
XI	BMAH	TPA	EtOH	5 min	98	1.42
XII	BPAH	TPA	EtOH	40 min	91	0.87
XIII	BMAS	TPA	EtOH	30 min	89	1.25

[a] Polymerization was carried out with 1 mmol of the monomers in 20 mL of ethanol at 25°C under nitrogen.

[b] Measured at a polymer concentration of 0.5 g/dL in concn H_2SO_4 at 25°C.

BMAP **IV**, BMAH **V**, and BPAH **VI**. The preparation of BMAS **VIII** is outlined in Scheme 2. According to Scheme 2, dinitrostyrylpyridine was prepared according to the method of Mikroyannidis[26] from the condensation of 2,6-dimethylpyridine with 2 mol of *m*-nitrobenzaldehyde in acetic anhydride. This was hydrogenated to the corresponding diamine by the reaction with hydrazine hydrate and palladium on activated carbon in ethanol.[26] Note that the hydrogenation step in Schemes 1 and 2 should not be excessively prolonged, because the benzylidene olefinic bonds, as well as the cyclohexanone or cyclpentanone carbonyl groups, might also be hydrogenated.

The IR and ^{1}H-NMR spectra of these three monomers did not show detectable hydrogenation
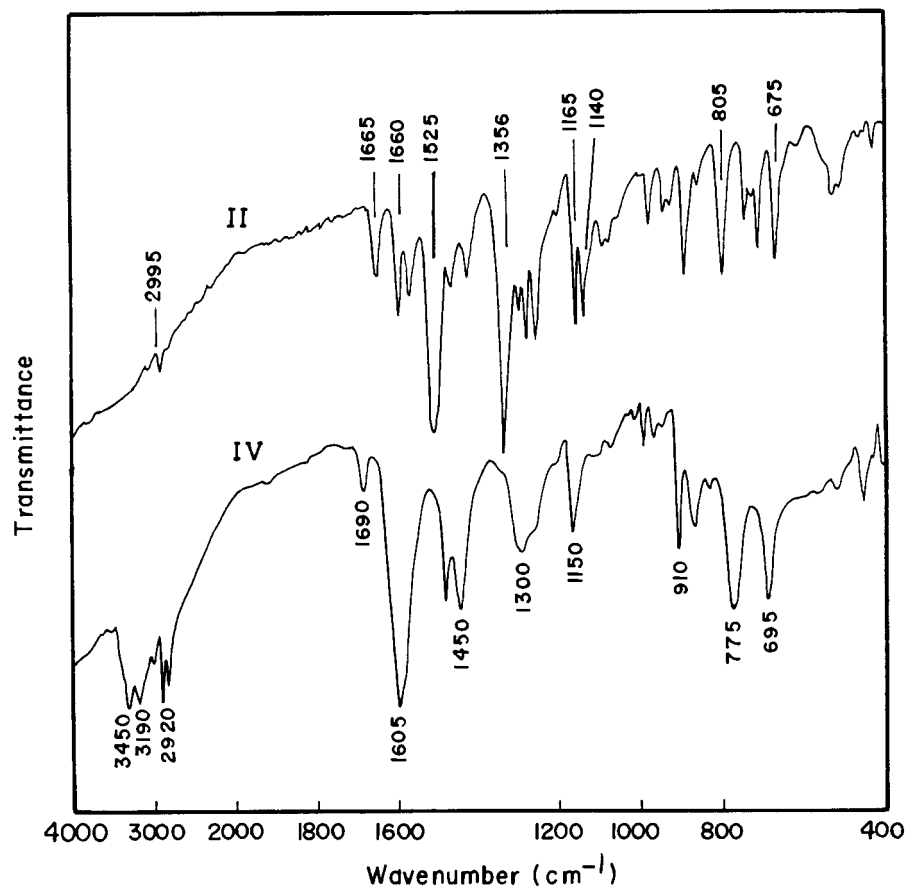

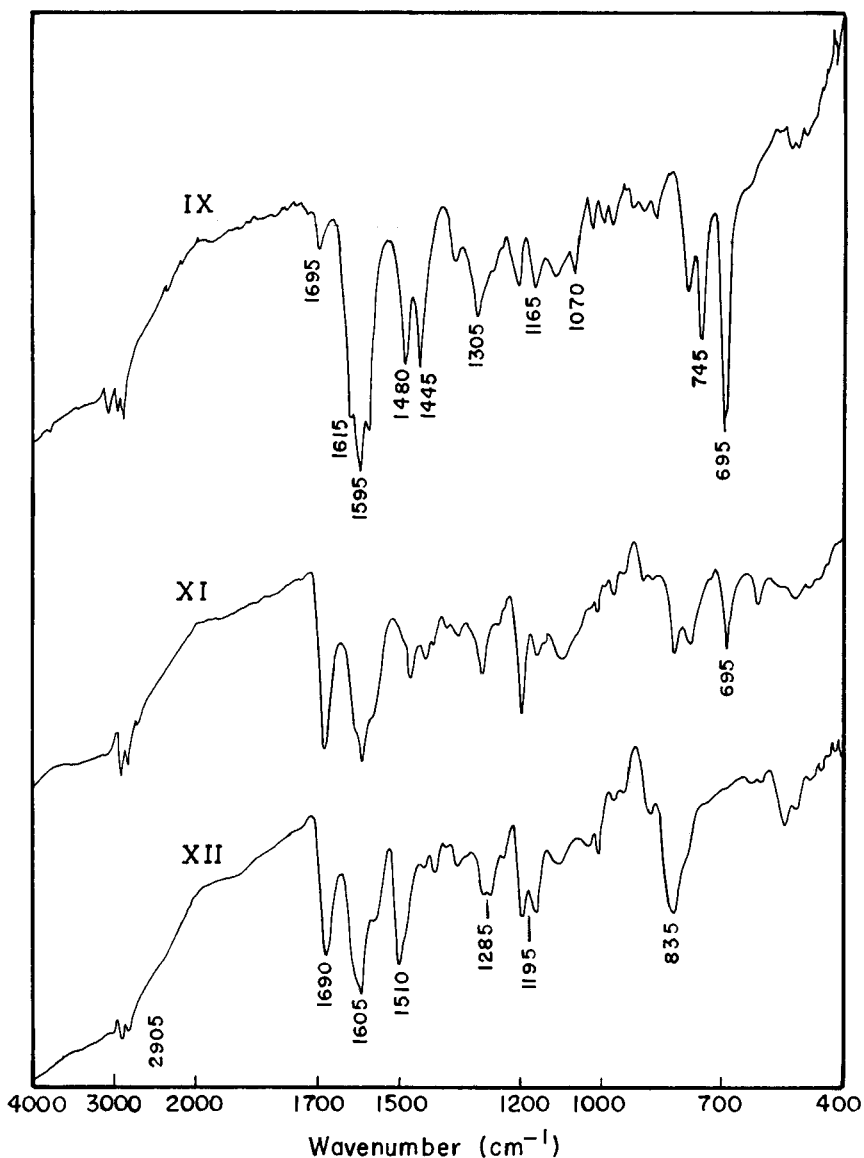**Figure 1**   IR spectra of dinitro-**II** and diamino-BMAH **V**.

Figure 2 IR spectra of model **IX** and polymers **XI** and **XII**.

of these segments under the particular experimental conditions. Moreover, a literature survey revealed that hydrogenation of the cyclohexanone carbonyl group requires an acidic medium, a platinum catalyst, and a pressure of 30–45 psi to preferentially give the axial alcohol.[27]

Synthesis of Model Compounds

Before attempting the polymerization, the model compounds were prepared by the reaction of diamines with benzaldehyde. A typical example is the reaction of 2 mol of benzaldehyde with 1 mol of BMAP **IV** to afford the diazomethine compound

IX. Based on the good agreement between the calculated and found analytical data from IR and ^{1}H-NMR, this reaction is depicted in Scheme 3.

Synthesis of Polymers

The polycondensation of an equimolar mixture of terephthalaldehyde with diamines BMAP, BMAH, BPAH, and BMAS, which gives polyazomethines containing cycloalkanones or pyridine moieties in the main chain, proceeds according to Scheme 4.

To our knowledge, the first successful synthesis of high molecular weight wholly aromatic
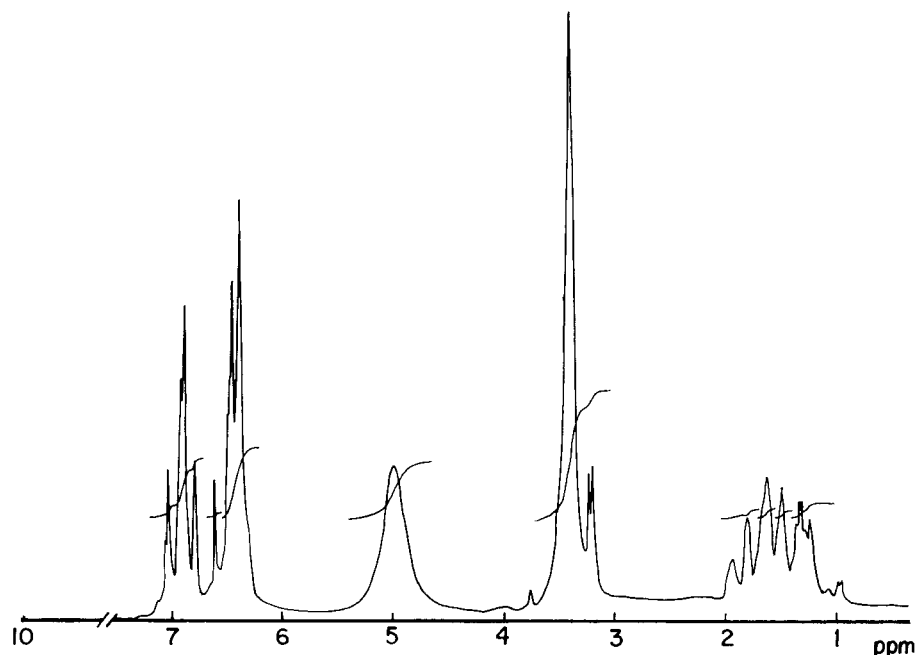
Figure 3   The ^{1}H-NMR of monomer **V**.

polyazomethines by the solution polycondensation technique was that reported by Suematsu and coworkers.[8,28,29] This was followed by the work of Saegusa and coworkers[15,16] who synthesized a series of polyazomethines containing heterocyclic moieties. Both research groups used *m*-cresol as the solvent. In this work *m*-cresol was not the solvent of choice, not only because it was

difficult to remove water during polymerization, but also because the heterogeneity of the reaction medium might have resulted in the formation of low molecular weight polymers. Experimentation led us to believe that ethanol is a better solvent for this purpose, because the monomers easily dissolve in it and polyazomethines with reduced viscosities up to 1.42 dL/g were readily obtained
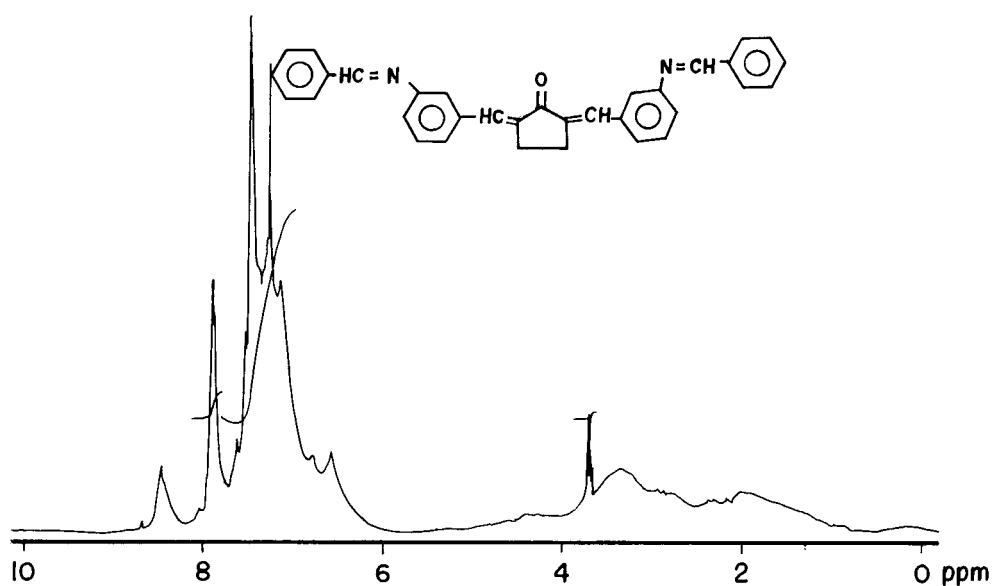

Figure 4   The ^{1}H-NMR of model **IX**.

Table II   Solubility Characteristics of Polyazomethine Polymers X–XIII

Polymer	NMP	DMSO	DMF	THF	CHCl$_3$ + Acetone (1:1)	CH$_2$Cl$_2$	H$_2$SO$_4$	HCOOH
X	+	+	+	+	−	−	++	+
XI	++	+	+	−	+	−	++	++
XII	++	+	+	+	++	−	++	+
XIII	+	+	+	+	−	−	++	+

(++) Soluble; (+) moderately soluble; (−) insoluble; NMP, *N*-methyl-2-pyrrolidone; DMSO, dimethylsulfoxide; DMF, dimethylformamide; THF, tetrahydrofuran.

in high yields after a few minutes. The polycondensation results are summarized in Table I.

The structures of the monomers, model compounds, and polymer precursors were confirmed by IR (Figs. 1, 2) and ^{1}H-NMR spectroscopy (Figs. 3, 4; see Experimental section). The IR spectra of the polyazomethines were in agreement with those of model compounds. As an example, the IR spectra of polymers **XI** and **XII** and model **IX** are shown in Figure 2.
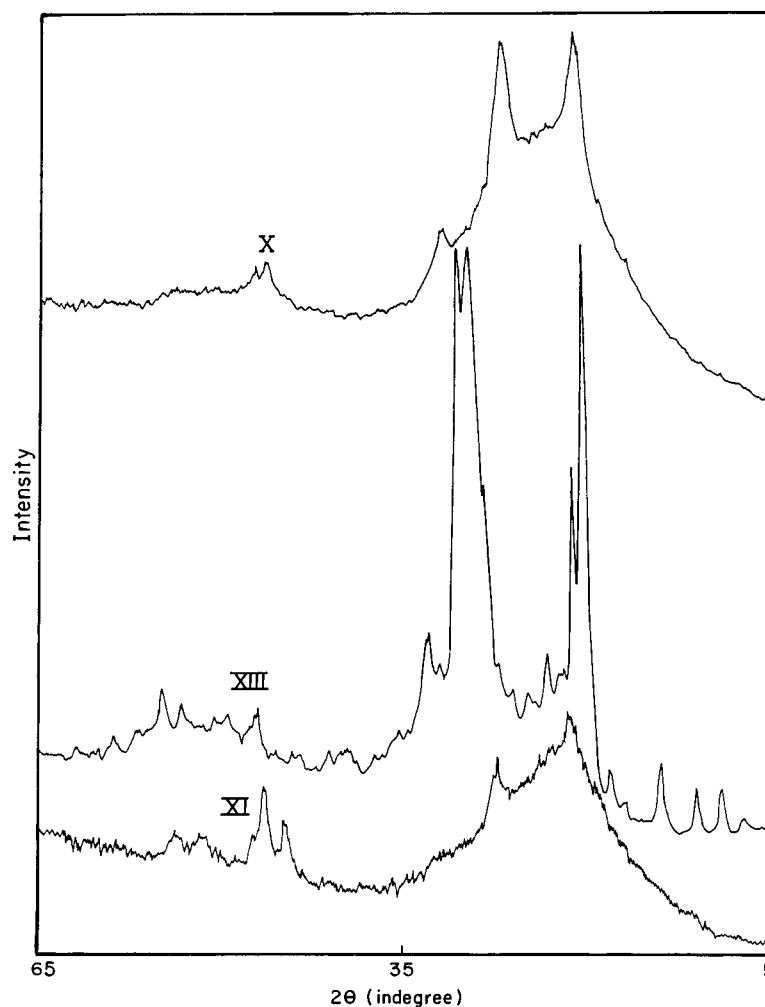

Figure 5   The X-ray diffraction patterns of polymers **X**, **XI**, and **XIII**.
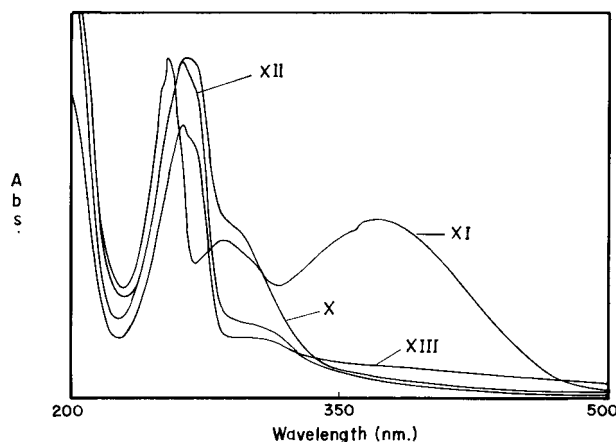
Figure 6 The electronic spectra of polyazomethine polymers **X–XIII**.

Polymer Characterization

Solubility

It is well known that azomethine polymers generally have limited solubility in most organic solvents because of their rigid chain structure.[14] However, several attempts have been made to obtain polyazomethines with improved solubility by introducing flexible bonding or bulky groups in the polymer backbone.[22] Our polyazomethines with cycloalkanones or pyridine moieties (**X–XIII**) were insoluble in common organic solvents like alcohol, benzene, acetone, methylene chloride, and so forth, but dissolved completely in concentrated sulfuric acid giving a deep brown color, except for polymer **XIII** that was a yellowish color. It is clear from Table II that polymers **XI** and **XII**, which contain a cyclohexanone moiety, are more soluble than polymers **X** and **XIII**, which contain cyclopentanone or pyridine moieties; this is attributed to the higher rigidity of the latter two. Generally, these polyazomethine polymers

were less soluble compared to those previously synthesized in our laboratory.[17–24]

X-Ray Analysis

The X-ray diffractograms of polyazomethine polymers **X**, **XI**, and **XIII** in Figure 5 show a few reflection peaks that are intermediate between crystalline and amorphous interference in the region $2\theta = 5$–$65°$. This indicates that there is a large class of structures that are intermediate in the ordered states between crystals (with pronounced long-range order) in the arrangement of their atoms and molecules. Moreover, the presence of C=N as polar groups in addition to high C=C bond levels induces some order between two adjacent chains in the polymer, leading to some extent of crystallinity.[30] Also, the diffractograms indicated that polyazomethine **XIII** has a high degree of crystallinity in comparison with polymers **X** and **XI**.

Electronic Spectra

The electronic spectra of models and undoped polyazomethines were obtained in sulfuric acid at a concentration of 2.6×10^{-6} M. These displayed two absorption bands with λ_{max} near 260 nm, which was due to the π–π^* transition within the benzenoid system, and with λ_{max} near 360 nm, which was due to the π–π^* excitation of C=N groups. The electronic spectra of polymers **X–XIII** in Figure 6 show broadening absorption bands and a small bathochromic shifting of both bands, indicating a highly conjugated system. Moreover, the electric conducting properties of the undoped and doped polymers are therefore related to the presence of extensively delocalized π electrons along the polymer chain, and the delocalization of π electrons also contributes to the formation of the polymer-iodine adducts.

Table III   Thermal Stability of Polyazomethine Polymers X–XIII

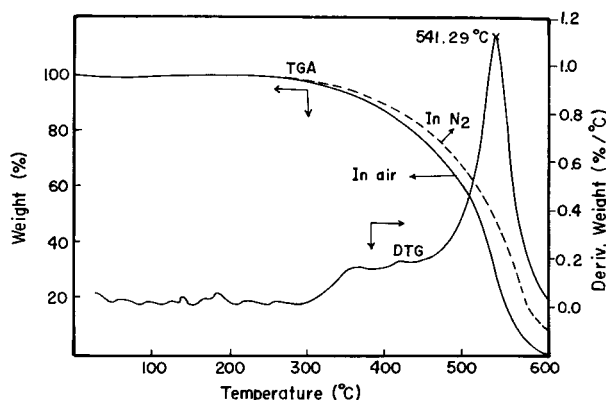| Polymer	5% Weight Loss Temp. (°C)		10% Weight Loss Temp. (°C)		Weight Residue at 600°C (%)	
	In Air	In Nitrogen	In Air	In Nitrogen	In Air	In Nitrogen
X	391	395	415	419	2.6	2.8
XI	379	382	402	406	2.5	2.7
XII	375	378	408	412	3.1	3.8
XIII	402	405	427	433	4.3	4.5

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

Figure 7 The TGA and DTA traces of polyazomethine **XI** in air and N$_2$ at a heating rate of 10°C/min.

Thermal Properties

The thermal behavior of polyazomethine polymers **X–XIII** was examined by TGA in air and nitrogen atmospheres. They were stable to thermal and thermooxidative degradation up to around 400°C. As shown in Table III and Figure 7, the decomposition temperatures were little affected by the atmosphere in air and in nitrogen, suggesting that oxygen does not participate in the degradation of polyazomethine polymers **X–XIII**. A comparison of the T_{10} values of polymer **XIII** derived from styrylpyridine showed better thermal stability than others based on cycloalkanones (**X**, **XI**, **XII**). This might be attributed to the high rigidity of the pyridine moiety as a heterocyclic ring in the polymer chain. More particularly, polyazomethine **X**, which was based on the cyclopentanone ring, was slightly more thermally stable than polyazomethines **XI** and **XII** that contain the

Table IV   Electrical Conductivity of Polyazomethine Polymers X–XIII

Polymer	Affinity Toward I$_2$ (wt %)[a]	Electrical Conductivity[b] (S cm^{-1})	
		Undoped	I$_2$ Doped
X	82	3.6×10^{-12}	5.3×10^{-8}
XI	73	4.1×10^{-12}	1.2×10^{-7}
XII	69	1.8×10^{-12}	3.6×10^{-8}
XIII	72	2.9×10^{-11}	1.8×10^{-8}

[a] The iodine content was calculated from the weight increase.
[b] Measured by dc electrical conductivity at 25°C.

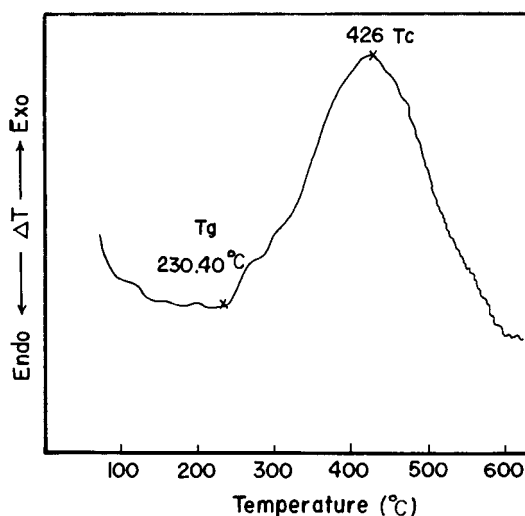**Figure 8** The DTA curves of polymer **XI** with a heating rate of 10°C/min in N$_2$.

cyclohexanone moiety. This was attributed to the flexibility of the latter moiety.

Electrical Conductivity

The electrical conductivity of the azomethine polymers ranged from 10^{-11} to 10^{-12} S cm^{-1} at 25°C (Table IV). Polymers **X** and **XI**, which contain cyclopentanone and cyclohexanone, respectively, were the most conductive among these examined polymers. The doping with iodine as an electron acceptor was performed until the polymer was saturated with iodine. The doped polyazomethines (**X–XIII**), which had an affinity (absorbed amount) of circa 12 wt % toward iodine, were light to dark brown in color. Those with more than 65 wt % were black after being left overnight whereas the undoped ones were yellow to orange solids. Polymers **X** and **XI** absorbed 82 and 73 wt % of iodine per polymer, respectively. As can be seen from Table IV, the electric conductivities were successfully raised by iodine doping and reached as high as 10^{-7}–10^{-8} S cm^{-1} upon iodine doping of circa 65 wt %. Thus, the polyazomethine polymers with cycloalkanones or pyridine moieties are good insulators, but they are converted into semiconductors by doping with iodine. Moreover, the study of the electrical conductivity temperature dependence, curing, and irradiation of these polymers is in progress and the results will be published in the near future.
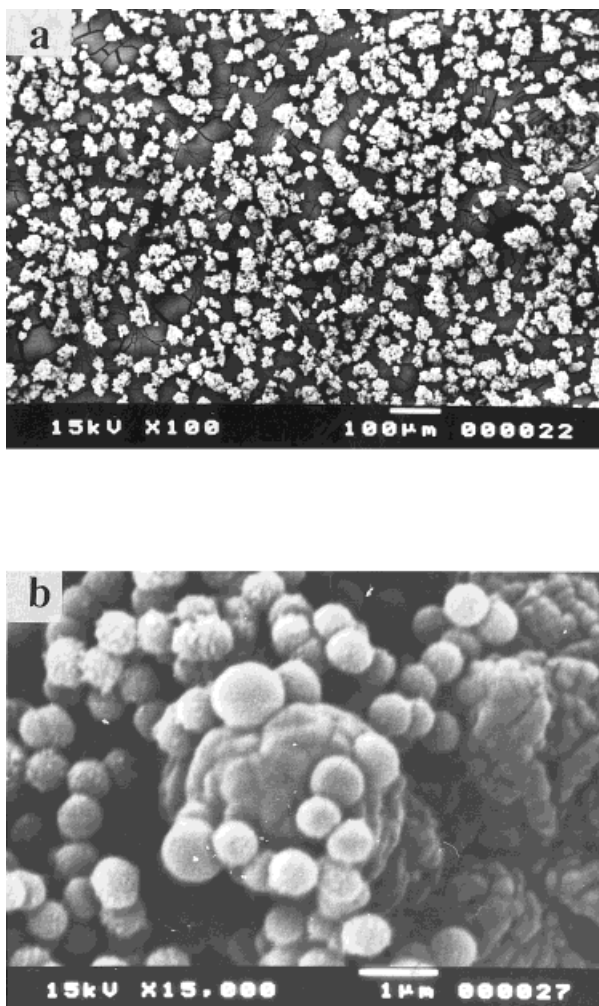
Figure 9 The SEM images of the polymer surface of **XI**.

Morphological Properties

The morphology of the synthesized polyazomethine **XI** (Fig. 9) was examined by SEM (Jeol JSM-5400 LV instrument). The SEM sample was prepared by evaporating a dilute solution of polymer **XI** on a smooth surface of aluminum foil and coating it with gold-palladium alloy. The SEM images were taken on a Pentax Z-50P (Camera) with Ilford film at an accelerating voltage of 15 kV using a low-dose technique.[31]

The SEM study of polymer **XI** [Fig. 9(a)] shows that the polymer has a polymorph globular structure with some coalescence present. The higher magnifications in Figure 9(b) show that the globular and subglobular structures appeared in a continuous chain with some coalescence present.

CONCLUSIONS

Novel polyazomethine polymers based on diarylidenecycloalkanones or styrylpyridine were prepared in quantitative yield by the solution polycondensation technique. TGA showed that these polymers are stable to thermal and thermooxidative degradation up to around 400°C. Upon doping with iodine, the synthesized polymers became semiconductors (10^{-7}–10^{-8} S cm^{-1}). SEM images of polymer **XI** revealed that the examined polymer surface possessed a globular structure.

REFERENCES

1. D'Alelio, G. F.; Crivello, J. V.; Schoenig, R. K.; Huemmer, T. F. J Macromol Sci Chem 1967, A1, 1161.
2. D'Alelio, G. F.; Schoenig, R. K. J Macromol Sci Chem 1968, A2, 979.
3. D'Alelio, G. F. J Macromol Sci Rev C 1969, 3, 105.
4. Millaud, B.; Strazielle, C. Polymer 1979, 20, 563.
5. Millaud, B.; Strazielle, C.; Weill, G. Polymer 1980, 21, 639.
6. Morgan, P. W.; Pletcher, T. C.; Kwolek, S. L. Polym Prepr Div Polym Chem Am Chem Soc 1983, 24(2), 470.
7. Preston, J. Angew Makromol Chem 1982, 109/110, 1.
8. Suematsu, K.; Nakamura, K.; Takeda, J. J Synth Org Chem Jpn 1983, 41, 84.
9. Patel, M. S.; Patel, S. R. J Polym Sci Polym Chem Ed 1982, 20, 1985.
10. Patel, M. V.; Patel, S. H. J Macromol Sci Chem 1981, A16, 1429.
11. Suematsu, K.; Nakamura, K.; Takeda, J. J Pharm Soc Jpn 1983, 103, 250.
12. Chundury, D.; Szmant, H. H. Polym Prepr Div Polym Chem Am Chem Soc 1983, 24(2), 50.
13. Patel, A. A.; Patel, S. R. Eur Polym J 1983, 19, 561.
14. Imai, Y.; Maldar, N. N.; Kakimoto, M. J Polym Sci Polym Chem Ed 1984, 22, 371.
15. Saegusa, Y.; Takashima, T.; Nakamura, S. J Polym Sci A Polym Chem 1992, 30, 1375.
16. Saegusa, Y.; Takashima, T.; Nakamura, S. J Polym Sci A Polym Chem 1992, 30, 1369.
17. Aly, K. I. Polym Int 1998, 47, 483.
18. Aly, K. I. High Perform Polym 1998, 10, 353.
19. Aly, K. I. High Perform Polym 1994, 6, 149.
20. Aly, K. I.; Abd-Alla, M. A. Polym J 1992, 24, 164.
21. Aly, K. I.; Abd-Alla, M. A. Polym Int 1993, 30, 313.

22. Abd-Alla, M. A.; Aly, K. I.; Geies, A. A. J Macromol Sci Chem 1991, A28, 269.
23. Abd-Alla, M. A.; Aly, K. I. J Macromol Sci Chem 1991, A28, 251.
24. Abd-Alla, M. A.; Aly, K. I. High Perform Polym 1990, 2, 235.
25. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. Purification of Laboratory Chemicals, 2nd ed.; Pergamon: New York, 1980.
26. Mikroyannidis, J. A. Eur Polym J 1989, 25, 557.
27. Augustine, R. L. Catalytic Hydrogenation; Dekker: New York, 1981; pp 58, 87.
28. Suematsu, K.; Nakamura, K.; Takeda, J. Colloid Polym Sci 1983, 261, 493.
29. Suematsu, K.; Takeda, J. J Synth Org Chem Jpn 1983, 41, 972.
30. Mandelkern, L. Crystallization of Polymers; McGraw–Hill: New York, 1964.
31. Tager, A. Physical Chemistry of Polymers; Mir: Moscow, 1972.