

New Polymer Syntheses. V. Synthesis, Characterization, and Morphology of New Conjugated Polymers, Copolymers, and Terpolymers Containing Piperidone Moiety in Main Chain

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ABSTRACT: A new interesting category of polyconjugated polymer, poly(3,5-benzylidene)isopropylpiperidone, was obtained by condensation of isopropylpiperidone with terephthalaldehyde. Copolymerization and terpolymerization with cyclopentanone and/or cyclohexanone were also carried out. The model compound was prepared by the condensation of 2 mol benzaldehyde with isopropylpiperidone; the structure was elucidated by IR, $^1\text{H-NMR}$ spectra, and elemental analyses. The polymers, copolymers, and terpolymers were characterized by elemental analyses, IR, $^1\text{H-NMR}$ spectra, UV and visible spectra, viscometry, and X-ray analysis. The thermal behavior of the synthesized polymers was evaluated by TGA and DSC analyses and correlated with their structures. The morphology of terpolymer IV was examined by a scanning electron microscope. Electrical conductivities in the 10^{-9} – $10^{-11} \Omega^{-1} \text{cm}^{-1}$ range were observed; doping with iodine showed a small increase. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2369–2377, 1999

Key words: synthesis; conjugated polymers; piperidone; terpolymers; morphology

INTRODUCTION

The need for specialty polymers with enhanced electrical properties (conductivity) has led to extensive research in this field. It is well known that electronic mobility in conjugated organic polymers is greatly enhanced along a polymer molecule with conjugated bonds. A great variety of such materials have received attention.^{1–5} These materials are prepared by polymerization of simple monomers that are able to form a network of highly delocalized electrons. Moreover, conjugated organic polymers have gained increasing interest in recent years as electrically conducting polymers [e.g., poly(*p*-phenylene), polypyrrole, polythiophene, and others].^{6–9}

In previous work in our laboratory,¹⁰ polyconjugated arylidene polymers and copolymers were synthesized and studied. In this article we present a route for the synthesis and characterization of some new polymers, copolymers, and terpolymers containing the piperidone moiety (as a heterocyclic moiety) in the polymer backbone. A major target of this work was to study the effect of the piperidone moiety upon the properties of polyconjugated polymers, including their thermal stability, solubility, and crystallinity.

EXPERIMENTAL

Measurements

Elemental analyses were performed with a Perkin–Elmer 240C Instrument. The IR spectra were recorded on a IR-470 Shimadzu spectrophotometer using the KBr pellet technique. $^1\text{H-NMR}$ spec-

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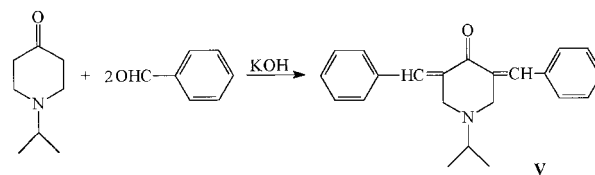
tra were run on a Varian EM-390 90-MHz NMR spectrometer at room temperature in dimethylsulfoxide (DMSO) using tetramethylsilane as the internal reference. The UV-visible spectra were scanned on a Shimadzu 2110 PC scanning spectrophotometer in dimethylformamide (DMF). The inherent viscosity of the polymer solutions (0.5 w/v) in sulfuric acid were determined at 30°C using an Ubbelohde suspended level viscometer. The solubility of the polymers was determined using 0.02 g of polymers in 3–5 mL of solvent at room temperature. X-ray diffractography was performed using an X-ray PW 1710 diffractometer with Ni-filtered Cu K α radiation. TGA and DSC were carried out in air with Du Pont models 951, 910, and 1090 thermal analyzers at a heating rate of 10°C min⁻¹. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 psi using an IR die. Silver paste was used to make the contacts that were sandwiched between two graphite electrodes. Conductivities were measured at room temperature under air using a 610 C Keithley electrometer, and Arrhenius plots were applied for calculations. Iodine doping was accomplished by the vapor-phase doping technique.⁷ The morphology of the polymers was examined by SEM using a JEOL JSM-5400 LV instrument.

Monomers and Reagents

Isopropylpiperidone, cyclopentanone, and cyclohexanone were purchased from Aldrich and Merck and distilled prior to use. Terephthalaldehyde was purchased from Aldrich and recrystallized twice from water. Potassium hydroxide was analytical grade. All other chemicals and solvents were highly pure and were purified by standard methods.¹¹

Synthesis of Model Compound: 3,5-Dibenzylideneisopropylpiperidone (V)

A mixture of 0.2 mol benzaldehyde and 0.1 mol isopropylpiperidone was dissolved in about 50 mL absolute ethanol and vigorously stirred at room temperature. Then a few drops of a 10% alcoholic solution of KOH was added and the temperature was allowed to rise to 50°C over 30 min. At the end of the reaction a bright yellow solid separated out that was filtered off, washed with water, and recrystallized from ethanol. Yellowish needles were obtained with a yield of 89% at a melting point (mp) of 231°C.



Scheme 1 Synthesis reaction of the model compound 3,5-cibenzylideneisopropylpiperidone (V).

ANAL. Calcd for C₂₂H₂₃ON: C, 83.28%; H, 7.26%; N, 4.42%. Found: C, 83.11%; H, 7.23%; N, 4.36%. IR (KBr): 1595 cm⁻¹ (S, C=C), 1665 cm⁻¹ (S, C—O). ¹H-NMR (δ /CF₃COOH): 1.4, 1.5 ppm (2s, 6H, 2CH₃); 3.9 ppm (m, 1H, CH); 4.8 ppm (s, 4H, 2CH₂); 6.9 ppm (s, 2H of CH=C); 7.3–7.8 ppm (m, 10H, Ar-H).

There was good agreement between the calculated and found analytical data, IR, and ¹H-NMR; this reaction is depicted in Scheme 1.

Polymerization

In a three-necked flask equipped with a condenser, a magnetic stirrer, and a dry nitrogen inlet and outlet, a mixture of 3.5 mmol (0.4693 g) terephthalaldehyde and 3.5 mmol (0.4935 g) isopropylpiperidone was dissolved in 50 mL of absolute ethanol and vigorously stirred at room temperature. Then a few drops of a 15% alcoholic solution of KOH was added, the temperature was allowed to rise to 80°C over 30 min, and reflux was continued for 3 h. At the end of that time a colored polymer had precipitated. The formed polymer was filtered off, washed with water, hot alcohol, and hot acetone, and dried under reduced pressure (1 mmHg) at 70°C for 2 days.

Copolymerization and Terpolymerization

A similar procedure was applied as described above. The copolymers were synthesized by polycondensation of 3.5 mmol (0.4693 g) terephthalaldehyde with a mixture of 1.75 mmol (0.2468 g) isopropylpiperidone and 1.75 mmol (0.1472 g) cyclopentanone or 1.75 mmol (0.1715 g) cyclohexanone. The terpolymer was synthesized by polymerization of 5.25 mmol (0.70413 g) terephthalaldehyde with a mixture of 1.75 mmol (0.2468 g) isopropylpiperidone, 1.75 mmol (0.1472 g) cyclopentanone, and 1.75 mmol (0.1715 g) cyclohexanone. The synthesized polymer, copolymers, and terpolymer, their yields, and some of their physical properties are listed in Table I.

Table I Results of Elemental Analyses and Physical Properties of Polymers I-IV

Polymer	Analysis						Yield (%)	η_{inh}^a (dL g ⁻¹)	Polymer Appearance
	C%		H%		N%				
	Calcd	Found	Calcd	Found	Calcd	Found			
I	80.33	79.85	7.11	7.05	5.86	5.12	86	0.37	Yellow powder
II	79.00	78.12	6.58	6.12	4.39	4.09	91	0.51	Yellow powder
III	79.28	78.73	6.91	6.54	4.20	4.28	89	0.59	Yellow powder
IV	81.55	80.61	6.41	6.07	2.72	2.61	83	0.33	Yellow powder

^a The inherent viscosity in concn H₂SO₄ (0.5 g/100 mL) at 30°C.

RESULTS AND DISCUSSION

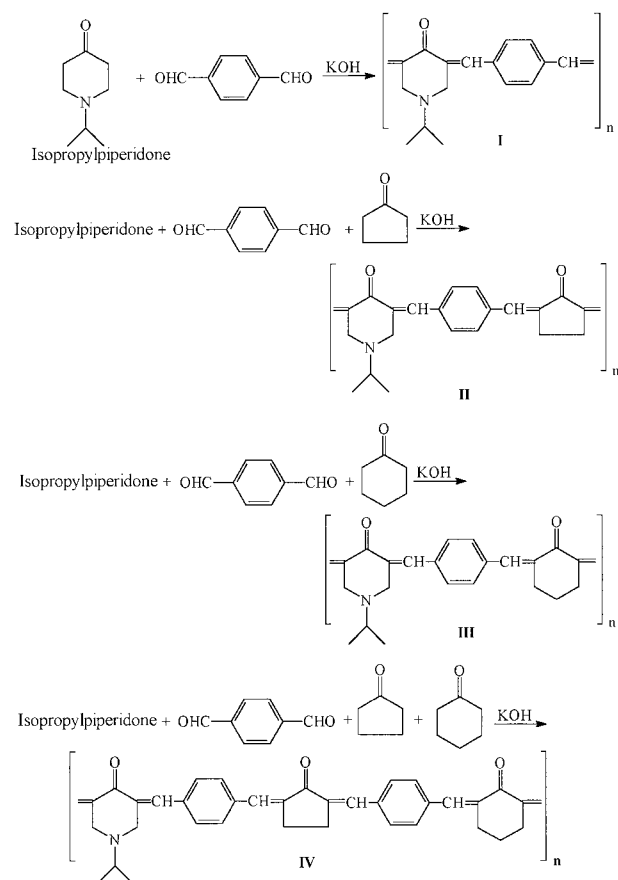
A new and unreported class of polyconjugated polymers, copolymers, and terpolymers, which were based on isopropylpiperidone as a heterocyclic moiety, were synthesized via solution polymerization of terephthalaldehyde with isopropylpiperidone to give polyconjugated polymers. A literature survey revealed that the interaction of dialdehyde (e.g., terephthalaldehyde) and diamines leads to polyimines as typically conjugated polymers by the step growth polycondensation reaction.¹² Thus, condensation of terephthalaldehyde with isopropylpiperidone in alcoholic potassium hydroxide gave the polyconjugated polymer poly(3,5-benzylidene)isopropylpiperidone I. Copolycondensation of equimolar quantities of terephthalaldehyde with a mixture of piperidone and/or cyclopentanone and cyclohexanone gave copolymers II and III, respectively. Terpolymerization of terephthalaldehyde with piperidone, cyclopentanone, and cyclohexanone yielded terpolymer IV (Scheme 2).

The early precipitation of polymers within 20 min after mixing the monomers indicated that the polymers were insoluble in ethanol. The time of polymerization ranged from 2 to 3 h. All the polymers were yellow and intense yellow solids. Polymers were immediately isolated (see the Experimental section) at the end of the reaction period.

The resulting polymers were characterized by elemental analysis, IR spectra, ¹H-NMR, solubility, viscometry, TGA, DSC, X-ray analysis, conductivity measurements, and morphology.

The elemental analysis of all the different polymers coincided with the characteristic repeating units of each polymer. These data are included in Table I. The spectral data support the structural assignments for the polymers and are in agree-

ment with spectral data obtained for the model compound. IR data obtained in KBr disks for all polymers indicated the appearance of characteristic absorption bands at 1660–1690 cm⁻¹ (broad, C=O of piperidone interference with C=O of cyclopentanone or cyclohexanone), 1595–1600 cm⁻¹



Scheme 2 Polymerization reactions of terephthalaldehyde with piperidone, cyclopentanone, and cyclohexanone that yields polymers I-IV.

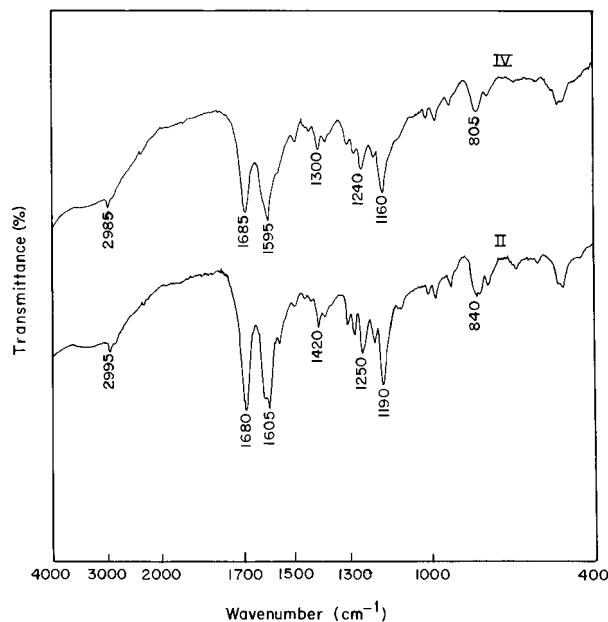


Figure 1 IR spectra of copolymer II and terpolymer IV.

for C=C groups, 2980–2995 cm^{-1} for C—H aliphatic, and other characteristic absorption bands for the rest of the molecule (Fig. 1).

The UV and visible spectra of polymer I and copolymers II and III were measured in DMF (1×10^{-3} w/v). The UV spectrum of polymer I showed an absorption band at 266 nm due to a π – π^* transition (benzenoid system). Copolymer II showed three bands at 265, 361, and 377 nm due to a π – π^* transition (benzenoid system and α,β -unsaturated ketone). Copolymer III showed two bands at 266.5 and 343 nm (benzenoid and α,β unsaturation). The spectra of the polymers showed broadened absorption bands and small bathochromic shifting of both bands, indicating high conjugation in these polymers (Fig. 2).

The $^1\text{H-NMR}$ spectra (δ/DMSO) for copolymer III showed peaks at 1.3–1.5 ppm (m, 6H, 2CH_3), 1.7–2.0 ppm (pent, 2H, CH_2 of cyclohexanone), 2.6–3.0 ppm (m, 4H, 2CH_2 of cyclohexanone, 4H, 2CH_2 of piperidone), 3.8 ppm (m, H of $\text{CH}<$), 7.3

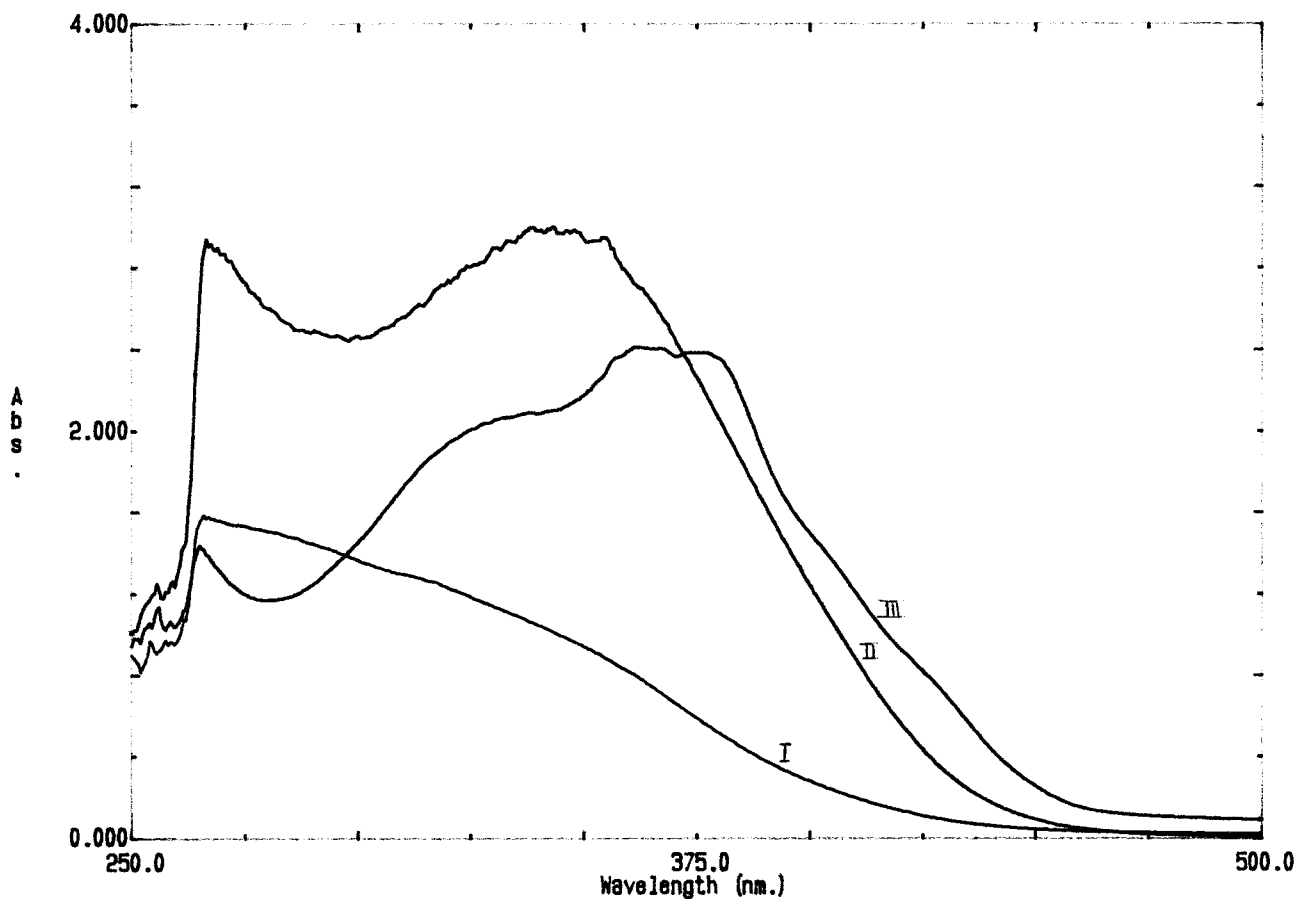


Figure 2 UV-visible spectra of polymers I–III.

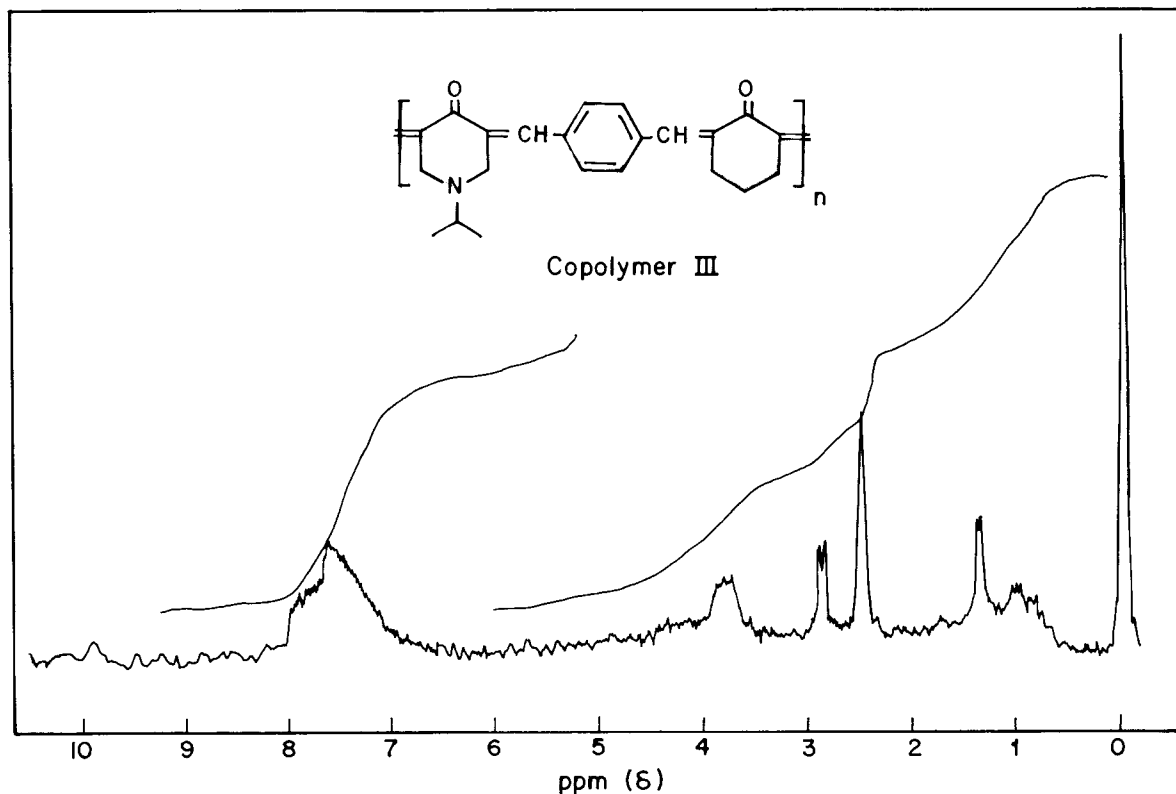


Figure 3 $^1\text{H-NMR}$ spectrum of copolymer III.

ppm (δ , 2H of $\text{CH}=\text{C}$), and 7.5–7.9 ppm (4H of Ar-H) (Fig. 3).

The solubilities of polymers I–IV were tested in various solvents including tetrahydrofuran (THF), DMF, DMSO, *N*-methylpyrrolidone (NMP), trifluoroacetic acid (TFA), *O*-cresol, concn H_2SO_4 , and methane sulfonic acid (MSA). The solubility was also tested in simple organic solvents such as acetone, CHCl_3 , CH_2Cl_2 , CCl_4 , and CH_3CN . It was found that all the polymers were insoluble in these common organic solvents. Partial solubility was observed in polar aprotic solvents (e.g., DMF, DMSO, or NMP). In polar protic acids such as

concn H_2SO_4 , TFA, and MSA, all the polymers were freely soluble, especially in concn H_2SO_4 , and were a deep violet color. Note from Table II that copolymer III, which contains a cyclohexanone moiety, was more soluble than copolymer II, which contains a cyclopentanone moiety; this is attributed to the flexibility of the cyclohexanone ring. This observation was also observed in terpolymer IV, which contains cyclohexanone and cyclopentanone moieties, but which was less soluble than copolymer III. Moreover, the inclusion of the piperidone as a heterocyclic ring slightly decreased the solubility of these conjugated poly-

Table II Solubility Characteristics of Polymers I–IV

Polymer	THF	DMF	DMSO	NMP	<i>O</i> -Cresol	CHCl_3 + Acetone (1 : 1)	Concn H_2SO_4	TFA	MSA
I	—	+	+	+	—	—	++	+	++
II	—	—	+	—	—	—	++	+	+
III	+	+	+	+	+	—	++	++	++
IV	+	—	+	—	—	—	++	++	++

(++) Soluble at room temperature (RT), (+) partially soluble at RT, and (—) insoluble at RT.

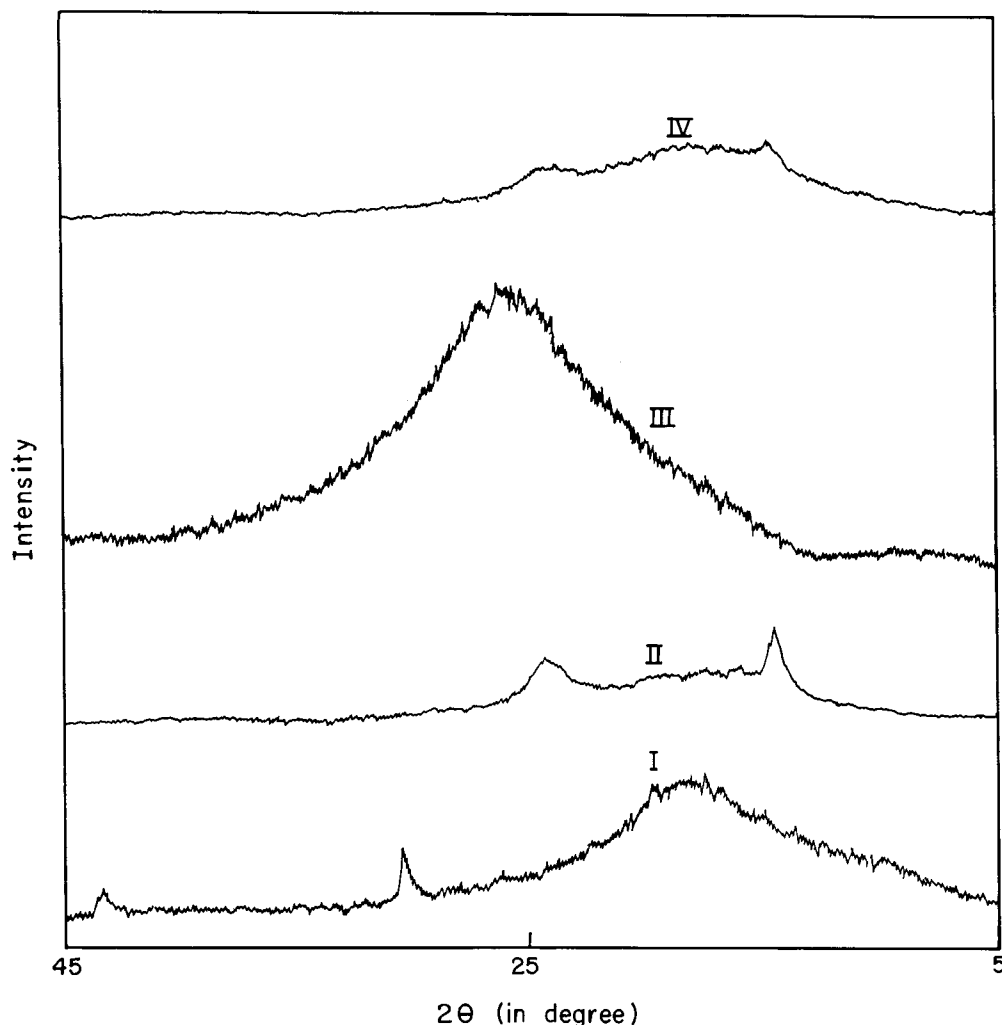


Figure 4 X-ray diffraction patterns of polymers I–IV.

mers in comparison with those that were prepared previously.¹⁰

The η_{inh} values of all polymers are listed in Table I. Note that copolymer III shows a higher degree of polymerization than polymers I, II, and IV.

The X-ray diffractographs of polymers I–IV in Figure 4 indicate an overall amorphous pattern in the region $2\theta = 5\text{--}45^\circ$. Attempts to crystallize any of the four prepared polymers from DMSO failed to produce a crystalline polymer. Comparing the crystallinity of these polymers with other polymers in the same category, it can be said that the inclusion of the piperidone moiety in the polymer chain decreases the degree of crystallinity; this is attributed to the rigidity of this ring.

The morphology of terpolymer IV was examined by SEM using a JEOL JSM-5400 LV instru-

ment. The SEM sample was prepared by evaporating a dilute solution of the polymer on a smooth surface of aluminum foil and subsequent coating with a gold-palladium alloy. SEM images were taken on a Pentax Z-50p with Ilford film at an accelerating voltage of 15 kV using a low dose technique.¹³

The scanning electron micrographs of terpolymer IV in Figure 5(b–d) show that the polymer surface has a polymorphous globular structure. In Figure 5(a) (with magnification) the globular structure has a “cauliflower” appearance.

The thermal stabilities of the polyconjugated polymers (I–IV) were evaluated by TGA and DSC. Figure 6 presents typical TGA traces of polymers in air. The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), and the maximum PDT (PDT_{max}) are

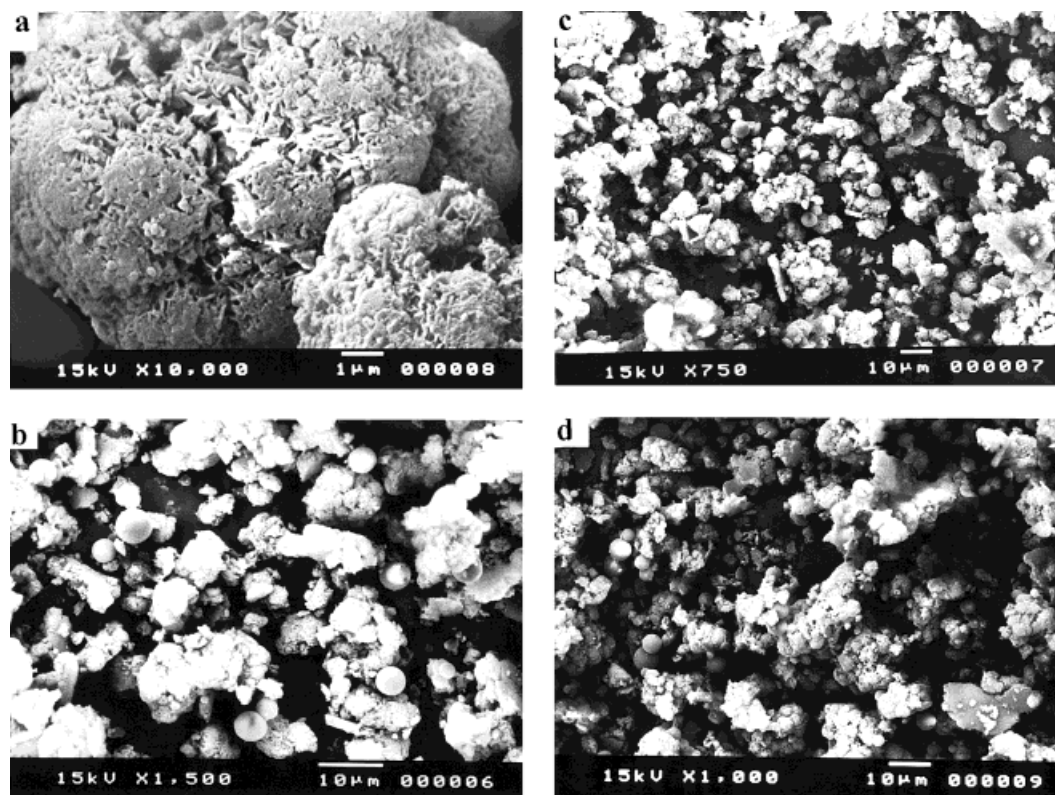


Figure 5 SEM images of polymer IV surface with (a) a globular structure with a cauliflower appearance and (b–d) polymorphous globular structures.

listed in Table III. 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 Figure 6 the TGA curves show a

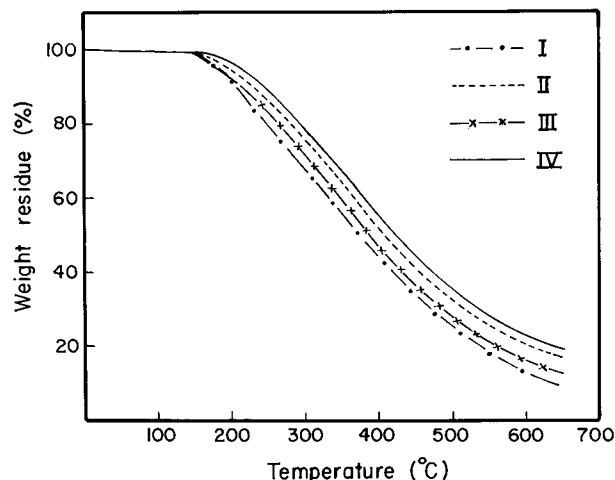


Figure 6 Thermogravimetric curves of polymers I–IV.

small weight loss in the 1.5–2% range over a temperature range of 100–160°C, which may be attributed to the loss of absorbed moisture and entrapped solvents. The expected nature of decomposition of these polymers is a pyrolytic oxidation of $-C=C-$ and scission of many bonds, in addition to the formation of char as an end product. The PDT for all polymers ranged from 308 to 335°C. Thus, the data in Table III indicate that the thermal stabilities of these polymers are in the order $IV > II > III > I$. The inclusion of a piperidone moiety into the polymer chain in-

Table III Thermal Properties of Polymers I–IV

Polymer	IDI (°C)	PDT (°C)	PDT_{max} (°C)
I	198	215	495
II	205	245	516
III	195	223	525
IV	210	250	550

IDI, the initial decomposition temperature; PDT, the polymer decomposition temperature; PDT_{max} , the maximum PDT.

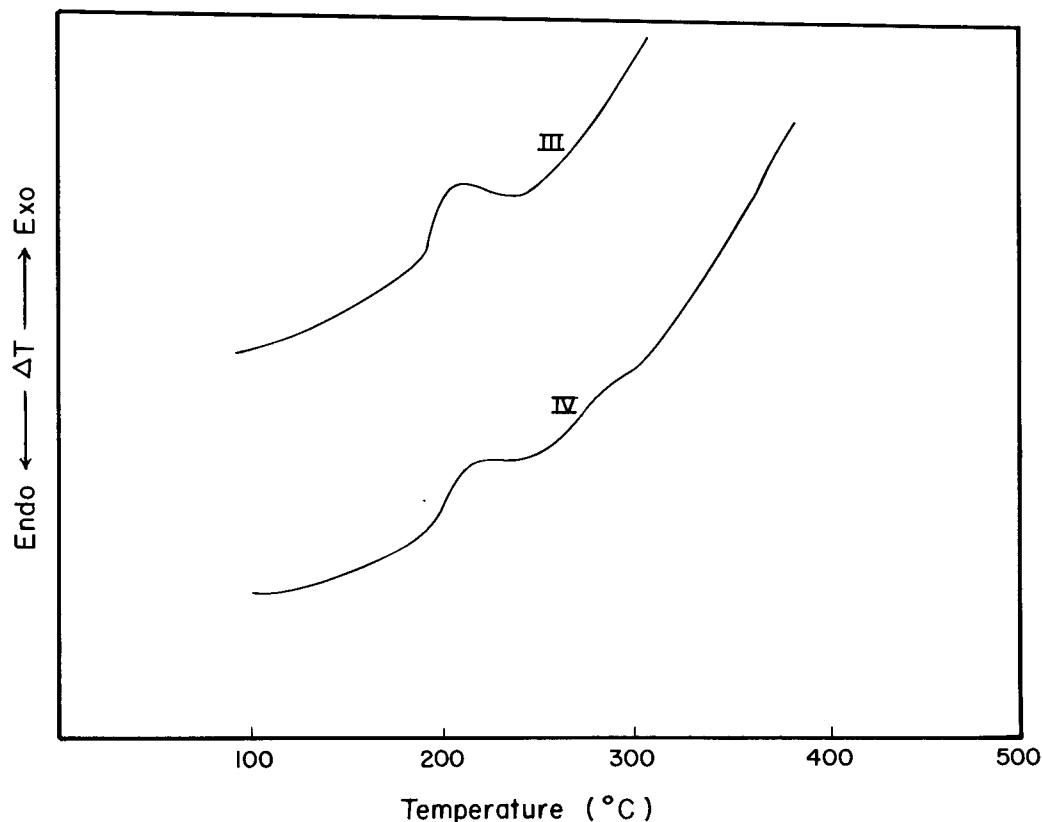


Figure 7 DSC traces of copolymer III and terpolymer IV.

creases the thermal stability, which was reported previously in our laboratory.¹⁴ Moreover, terpolymer IV, which contains cyclopentanone and cyclohexanone moieties, is more stable than the others. Copolymer II, which contains cyclopentanone and piperidone (Scheme 1), is more stable than copolymer III or polymer I; this may be attributed to the rigidity of such a ring.^{15,16}

Figure 7 shows typical DSC traces of copolymer III and terpolymer IV. Large broad exotherms were observed in III and IV above 210°C, and these exotherms should be attributed to curing reactions involving the olefinic bonds.¹⁷

The electric conductivities of polymers I–IV ranged from 10^{-9} – $10^{-11} \Omega^{-1} \text{ cm}^{-1}$ at 25°C. Copolymers II and III, which contained cyclopentanone and cyclohexanone, respectively, were the most conductive among the polymers examined. The difference in the affinity (absorbed amount) toward iodine between these two copolymers and the others (polymers I and IV) was also examined; after being left overnight, copolymers II and III absorbed 82 and 67 wt % of iodine per polymer, respectively, whereas polymers I and IV took up only 8 and 12 wt % of iodine under the same

conditions. The iodine-doped polymers were dark brown to completely black in color, depending upon the iodine content, while the undoped polymers were yellow. The electrical conductivity was raised by iodine doping and reached as high as 10^{-7} – $10^{-8} \Omega^{-1} \text{ cm}^{-1}$ as shown in Table IV.

More details in the studies of electrical properties, curing, and radiation of these novel polymers

Table IV Electrical Conductivity of Polymers I–IV

Polymer	Affinity Toward I ₂ ^a (wt %)	Electrical Conductivity ^b ($\Omega^{-1} \text{ cm}^{-1}$)	
		Undoped	I ₂ Doped
I	8.0	1.5×10^{-11}	2.0×10^{-8}
II	82	2.8×10^{-9}	3.4×10^{-7}
III	67	3.1×10^{-10}	1.9×10^{-8}
IV	12.0	2.9×10^{-11}	3.0×10^{-8}

^a The iodine content was calculated from the weight increase.

^b Measured by the dielectric constant method at room temperature (25°C).

are in progress and the results will be published in the near future.

CONCLUSION

A new series of polyconjugated polymers, copolymers, and terpolymers were synthesized by a solution polymerization technique. All the polymers were soluble in concn H_2SO_4 . X-ray diffraction analysis showed that all the polymers are amorphous. The inherent viscosity was in the 0.33–0.59 dL g^{-1} range. The TGA showed that terpolymer IV is more stable than the other polymers. Electrical conductivities were in the range of semiconducting properties after doping.

REFERENCES

1. Everaerts, A.; Roberts, S.; Hall, H. K., Jr. *J Polym Sci Part A* 1986, 24, 1703.
2. Seymour, R. S. *Conductive Polymers*; Plenum Press: New York, 1981.
3. Ahmed, M. M.; Feast, W. J. *Polym Commun* 1984, 25, 231.
4. Gordon, B.; Hancock, L. F. *Polymer* 1987, 28, 585.
5. Kuzmany, H.; Mehring, M.; Roth, S. *Electronic Properties of Polymers and Related Compounds*; Springer Series in Solid State Sciences, Vol. 63; Springer-Verlag: Heidelberg, 1985.
6. Rehahn, M.; Schlüter, A. D.; Weger, G.; Feast, W. J. *Polymer* 1989, 30, 1054.
7. Rehahn, M.; Schlüter, A. D.; Weger, G.; Feast, W. J. *Polymer* 1989, 30, 1060.
8. Gagnan, D. R.; Capistran, J. D.; Karaz, F. E.; Lenz, R. W.; Antoun, S. *Polymer* 1987, 28, 567.
9. Ng, S. C.; Chan, H. S. O.; Yu, W. L. *J Mater Sci Lett* 1997, 16, 809.
10. Abd-Alla, M. A.; El-Zohry, M. F.; Osman, M. M. *Polym Bull* 1991, 25, 287.
11. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
12. Stevens, M. P. *Polymer Chemistry, An Introduction*; Addison-Wesley: Reading, MA, 1975.
13. Tager, A. *Physical Chemistry of Polymers*; Mir: Moscow, 1972.
14. Aly, K. I.; Geies, A. A. *High Perform Polym* 1992, 4, 187.
15. Abd-Alla, M. A.; Kandeel, M. M.; Aly, K. I.; Hammam, A. S. *J Macromol Sci Chem* 1990, A27, 523.
16. Aly, K. I.; Abd-Alla, M. A. *Polym J* 1992, 24, 165.
17. Mikroyannidis, J. A. *Eur Polym J* 1988, 24, 1093.