

New Polymer Synthesis. XXX. Synthesis and Thermal Behavior of New Organometallic Polyketones and Copolyketones Based on Diferrocenyldenecycloheptanone

Kamal I. Aly, Maisa I. Abdel Monem

Polymer Lab. 507, Chemistry Department, Faculty of Science, Assiut University, 71516 Assiut, Egypt

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ABSTRACT: A new interesting category of organometallic polyketones and copolyketones was synthesized via Friedel–Crafts reactions through the polymerization of 2,7-bis[(2-ferrocenyl)methylene] cycloheptanone (**II**) with different diacid chlorides. The model compound was synthesized by reacting monomer **II** with benzoyl chloride and characterized by $^1\text{H-NMR}$, IR, and elemental analyses. The polyketones and copolyketones were insoluble in most organic solvents but easily soluble in concentrated H_2SO_4 . The thermal properties of these polyketones and copolyketones were evaluated and correlated to their structural units by TGA

and DTG measurements and had inherent viscosity of 0.32–0.65 dl g^{-1} . Moreover, the electrical conductivity of polyketone **Va** and copolyketone **VI** was investigated above the temperature range (300–500 K) and followed an Arrhenius equation with activation energy 2.09 eV. Also, the morphological properties of selected example of polyketones were detected by scanning electron microscopy. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2394–2401, 2005

Key words: polyketones; ferrocene; Friedel–Crafts; synthesis; characterization; conductivity; thermal behavior

INTRODUCTION

Aromatic polyketones are an emerging family of materials that are currently attracting technical interest on account of their impressive thermal and mechanical properties and their chemical resistance.^{1,2} At present, several aromatic polyketones have been commercialized. The commercial utility of these polymers is based on a combination of properties, among which toughness and crystallinity are crucial.³ The synthesis of these polymers is usually performed by Friedel–Crafts acylation or nucleophilic aromatic displacement, which has been a subject of research for a number of years.^{4–7} As a result, the preparation of various aromatic polyketones and investigations of their properties have been reported by many workers.^{8–11}

To our knowledge, no work has been reported concerning the synthesis of polyketones and copolyketones containing ferrocenyldiene cycloheptanone in the main chain. The work reported in this paper outlines the synthesis and properties of some new polyketones and copolyketones based on 2,7-bis[(2-ferrocenyl)methylene] cycloheptanone. The major aim of this work has been to investigate the effect of inclusion of ferrocene moiety in the polymer backbone on polymer properties. In addition, other characteristics of these

new polymers such as thermal stability, solubility, electrical conductivity, and crystallinity were also examined and discussed.

EXPERIMENTAL

Instrumentation

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 $^1\text{H-NMR}$ 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 a 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 $K\alpha$ 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. Pellets for electrical conductivity measurements

Correspondence to: K. I. Aly (kamal_61@yahoo.com).

were pressed at constant pressure, 1000 Psi, using IR die-silver paste to make contact between the polymer pellets and two graphite electrodes. Conductivities were measured at room temperature in air using a 610 Keithley electrometer.

Reagents and solvents

Ferrocene carboxaldehyde (Fluka AG) (mp 118–120°C) was used as purchased. Benzoyl chloride (Aldrich) was used as is. Terephthaloyl chloride and isophthaloyl chloride (Aldrich) were recrystallized from *n*-hexane (mp 83–84 and 43°C, respectively). Adipoyl and sebacoyl dichlorides¹³ freshly distilled at 125°C/11 Torr and at 182°C/16 Torr, respectively, were used. Cycloheptanone (Merck) was used without purification. Anhydrous aluminum chloride (Merck) and all other solvents and reagents were of high purity and were further purified by the standard method.¹⁴

Monomer syntheses

Synthesis of 2,7-bis [(2-ferrocenyl)methylene] cycloheptanone **II**

A mixture of 0.1 mol cycloheptanone and 0.2 mol ferrocene carboxaldehyde in warm ethanol was stirred, and a few drops of KOH (20%) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 1 h, and the resulting solid was collected by filtration, washed with cold water, dried, and recrystallized from ethanol as deep violet needles; yield 70%, mp 198°C. Calculated for C₂₉H₃₂O Fe₂: C, 68.50; H, 6.30; Fe, 22.05%. Found: C, 69.34; H, 6.21; Fe, 22.08%. IR (KBr, cm⁻¹): at 1600 (s, C = C), at 1660 (s, C = O of cycloheptanone). ¹H-NMR (DMSO-*d*₆, ppm), at 2.95 (for 8H, CH₂-Fe), at 6.25–6.55 (14H, ferrocene moieties), at 1.73 (2H of 2CH = C); at 1.40–1.96 (d, 4H of 2CH₂); and at 1.23–1.29 (d, 4H of middle 2CH₂ of cycloheptanone).

Synthesis of 2,7-bis(benzylidene)cycloheptanone **III**

This monomer was prepared as described previously in our paper.¹⁵

Synthesis of model compound IV

In a 100-mL round-bottom flask equipped with a magnetic stirrer and a nitrogen inlet and outlet we placed a solution of 1 mmol 2,7-[bis(2-ferrocenyl)methylene] cycloheptanone **II** (1 mmol) and benzoyl chloride (2 mmol) chloride in dry carbon disulfide (40 mL). The flask was purged with nitrogen under stirring and anhydrous aluminum chloride (20 mmol) was added portionwise to the solution. The solution was stirred for 24 h at 25°C, and the separated solid product was filtered off, washed with water, and dried in vacuum at room temperature. An analytical sample was obtained by recrystallization from benzene in yellow needles, yield 75%, mp 134°C. Calculated for C₄₃H₄₀O₃ Fe₂: C, 72.06; H, 5.59; Fe, 15.64%. Found: C, 70.98, H, 4.88, Fe, 15.83%. IR (KBr, cm⁻¹): at 1665 (C = O of cycloheptanone), at 1700 (C = O of benzoyl group), at 1600 (C = C group). ¹H-NMR (DMSO-*d*₆, ppm), at 7.1–7.85 (m, 10H, Ar-H); at 2.95 (for 8H, CH₂-Fe), at 6.75–6.95 (12H, ferrocene moieties), at 1.78 (2H of 2CH = C); at 1.44–1.98 (d, 4H of 2CH₂); and at 1.28–1.34 (d, 4H of middle 2CH₂ of cycloheptanone).

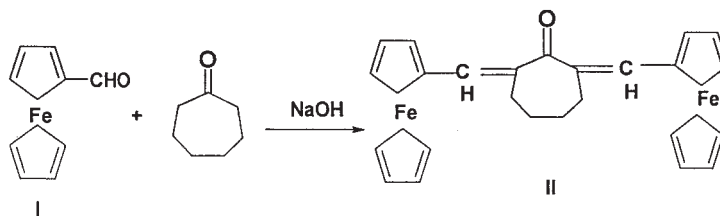
Synthesis of polyketones Va–d

The Friedel–Crafts method was applied for synthesis of all polymers. Typically, in a 100-mL round-bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet we placed a solution of 3.024 g (6 mmol) 2,7-bis[(2-ferrocenyl)methylene] cycloheptanone **II** and 1.218 g (6 mmol) of isophthaloyl chloride in 25 mL of dry carbon disulfide. The flask was purged with nitrogen under stirring, and 2.66 g (20 mmol) of aluminum chloride was added during the nitrogen flash. The reddish–brown reaction mixture was stirred for 24 h, and then it was filtered off and the separated product was triturated three times with a large excess of methanol. The powdery material was again filtered off, washed with water, methanol, and acetone, and dried under reduced pressure (1 mm Hg) at 70°C for 2 days. This method was applied for the preparation of other polyketones; whose yields, elemental analyses, viscosity, and colors are listed in Table I.

TABLE I
Elemental Analysis, Inherent Viscosity, Yield, and Color of Polyketones Va–d and Copolyketones VI and VII

Polymer code	Repeating unit	C%		H%		Fe%		η^a Inh (dI/g)	Yield (%)	Appearance of polymer
		Calcd	Found	Calcd.	Found	Calcd.	Found			
Va	C ₃₇ H ₃₄ O ₃ Fe ₂	69.59	68.21	5.33	5.06	17.67	17.33	0.65	85	Powder, yellowish
Vb	C ₃₇ H ₃₄ O ₃ Fe ₂	69.59	71.15	5.33	4.98	17.67	17.52	0.61	78	Powder, yellowish
Vc	C ₃₅ H ₃₄ O ₃ Fe ₂	68.40	67.89	5.54	5.17	18.24	17.67	0.44	65	Powder, brown
Vd	C ₃₉ H ₄₆ O ₃ Fe ₂	69.44	67.82	6.82	6.11	16.72	16.32	0.39	72	Powder, brown
VI	C ₆₆ H ₅₆ O ₆ Fe ₂	75.00	76.72	5.30	4.76	10.65	10.43	0.45	63	Powder, brown
VII	C ₇₀ H ₆₄ O ₆ Fe ₂	75.54	74.02	5.76	5.05	10.11	10.89	0.32	71	Powder, yellowish

^a η , Inherent viscosity measured in H₂SO₄ at 25°C.



Scheme 1

Synthesis of copolyketones VI and VII

The same method, which was applied in the synthesis of the polyketones, was also applied in the synthesis of the copolyketones.

Typically, in a 100-mL round-bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet we placed a solution of 1.512 g (3 mmol) 2,7-bis[(2-ferrocenyl)methylene]cycloheptanone (**II**), 0.864 g (3 mmol) 2,7-bis(benzylidene)cycloheptanone **III**, and 1.218 g (6 mmol) of terephthaloyl chloride in 50 mL of dry carbon disulfide. The flask was purged with nitrogen under stirring, and 2.66 g (20 mmol) of aluminum chloride was added during the nitrogen flash. The reddish-brown reaction mixture was stirred for 24 h, and then it was filtered off and the separated product was triturated three times with a large excess of methanol. The powdery material was again filtered off, washed with water, methanol, and acetone, and dried under reduced pressure (1 mm Hg) at 70 °C for 2 days. This method was applied for the preparation of copolyketone **VII**, whose yields, elemental analyses, viscosity, and colors are listed in Table I (thermo-gravimetric analyses, 10% weight loss, for polyketones **Va–d** and copolyketones **VI**, **VII** are 305, 310, 290, 255, 260, and 235°C, respectively).

RESULTS AND DISCUSSION

Synthesis of monomer II

2,7-bis[(2-Ferrocenyl)methylene]cycloheptanone **II** monomer was synthesized in good yields by the base catalyzed condensation of 2 mol ferrocene carboxaldehyde with 1 mol cycloheptanone, as shown in Scheme 1.

Synthesis of model compound IV

Before polymerization was attempted, model compound was synthesized by the reaction of monomer **II**

with two equivalents of benzoyl chloride. A typical reaction is depicted in Scheme 2.

Synthesis of polyketones Va–d

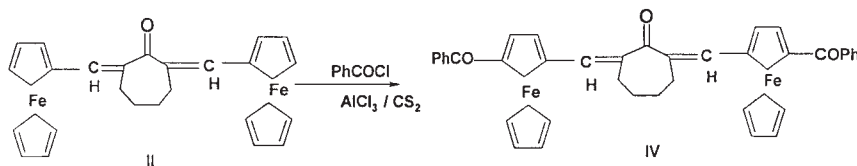
To determine an adequate catalyst for the synthesis of polyketones based on bis-ferrocenyl methylene cycloheptanone in the main chain, Friedel–Crafts polycondensation of 2,7-bis[(2-ferrocenyl)methylene]cycloheptanone (**II**) with terephthaloyl chloride (as an example) (polymer **Vb**) was carried out in the presence of various Lewis acids such as FeCl_3 , SbCl_5 , and AlCl_3 . It appeared that anhydrous AlCl_3 gave the best result with respect to yield and degree of polymerization. The favorable mole ratio of catalyst to each reactant was ~ 2.0 .

As shown in Figure 1, the preferred reaction time was around 24 h. No appreciable increase in yield or extent of polymerization was observed with longer reaction time.

On the basis of these results, Friedel–Crafts polycondensation of dicarbonyl chlorides including isophthaloyl, terephthaloyl, adipoyl, and sebacoyl dichlorides with 2,7-bis[(2-ferrocenyl)methylene]cycloheptanone **II** was carried out at room temperature for 24 h. These reactions are shown in Scheme 3.

The inherent viscosities of the resulting polymers were in the range 0.32–0.65 dl g^{-1} . The structures of the obtained polyketones were identified by IR and $^1\text{H-NMR}$ spectroscopy as well as elemental analyses (Table I).

The microanalysis of all polymers reflected the characteristic repeating unit of each polymer. The data are listed in Table I. The analysis of the polyketones and copolyketones deviated up to 1.72% from the theoretical values (Table I). However, it is not uncommon for polymers, especially those of high molecular weight, to trap solvent molecules within the polymer matrix,



Scheme 2

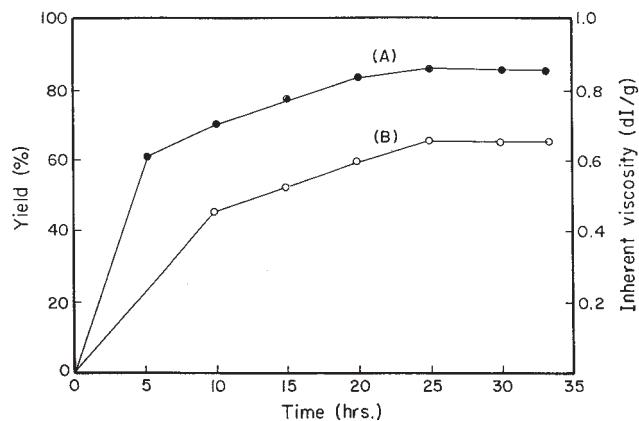


Figure 1 Effect of reaction time on polymerization yield and extent of polymerization: (A) yield; (B) inherent viscosity. Friedel-Crafts polycondensation was carried out with 6.0 mmol I and 6.0 mmol isophthaloyl dichloride in 60 mL dichloromethane at 25°C in the presence of 20 mmol AlCl_3 .

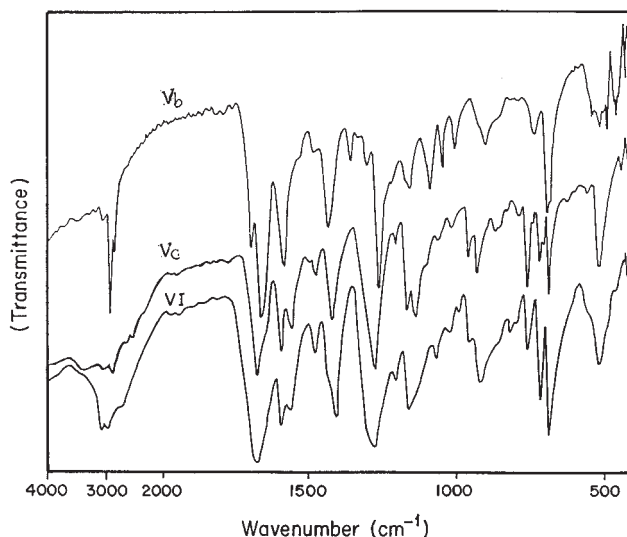


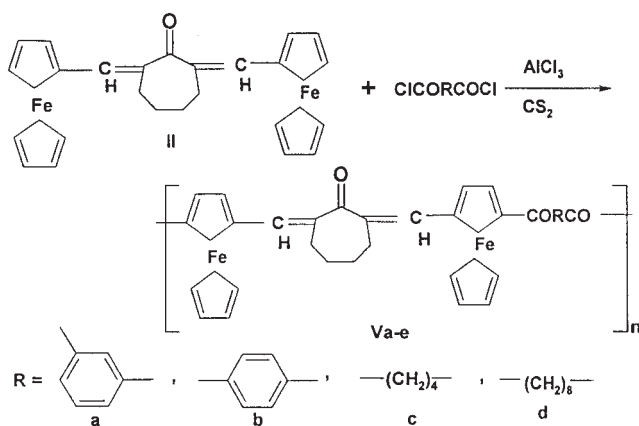
Figure 2 IR spectra of polyketones Vb, c and copolyketone VI.

and these polymers contain polar groups that are capable of hydrogen bonding with solvent molecules.¹⁶

Spectral data reveal that the presence of strong absorption bands at 1690–1710 cm^{-1} ($\nu \text{C}=\text{O}$ stretching of ketone), at 1640–1660 cm^{-1} , ($\nu \text{C}=\text{O}$ stretching of carbonyl group of cycloheptanone), and at 1590–1610 cm^{-1} for ($\nu \text{C}=\text{C}$ stretching) appeared in the IR spectra. No detectable carbonyl chloride absorption bands were observed (Fig. 2).

Synthesis of copolyketones VI and VII

Unreported copolyketones VI and VII contained two different moieties, e.g., bis-ferrocenylidene cycloheptanone as organometallic moiety and bis-benzylidene cycloheptanone in the polymer main chain. These two copolymers were synthesized from the copolymerization of monomer II and monomer III with two different diacid chlorides, e.g., terephthaloyl or adipoyl, as shown in Schemes 4.



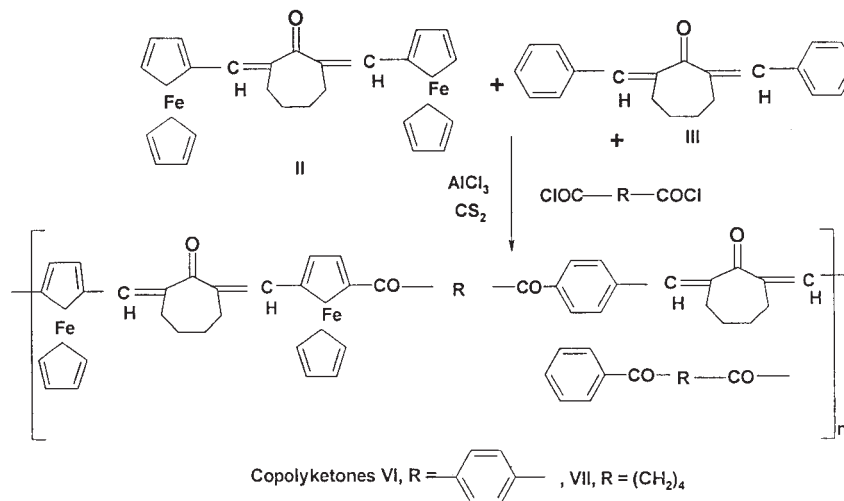
Scheme 3

Properties of the polyketones Va–d and copolyketones VI, VII

Solubility of the polyketones and copolyketones synthesized in this study was determined for powdery samples in excess solvent including concentrated sulfuric acid (9M), trifluoroacetic acid, methylene chloride, chloroform, *N*-methylpyrrolidone (NMP), nitrobenzene, *m*-cresol, and dimethylformamide (DMF). All polymers were soluble in strong acids such as concentrated sulfuric acid and trifluoroacetic acid. However, most of the polymers were insoluble in common organic solvents and weak acid like acetic or formic acids (except polymer Vd (with $n = 8$), which showed good solubility in most organic solvents, due to the flexibility of polymethylene spacers present in these polymers). On the other hand, comparing the solubility of polyketones with its copolyketones, we found that the later possess better solubility than the former. This may be attributed to the presence of cycloheptanone moiety in the polymer main chain; this increases the flexibility and improves the solubility.¹⁷

Although these polyketones were soluble in strong acids, they showed enough stability in strong acids and alkaline solutions that significant decreases in molecular weights were not observed, as shown in Figure 3.

X-ray diffractograms of selected examples of polyketones Vb, c and copolyketone VI in Figure 4 showed few sharp peaks with an amorphous background, indicating that there is a large class of structures in the region $2\theta = 10\text{--}60^\circ$. The diffractogram indicated that polyketone Vb is amorphous and the others have a degree of crystallinity (Table II). Moreover, the presence of $\text{C}=\text{O}$ as a polar group in addition to high C



Scheme 4

= C band levels chains in the polymer, led to some extent of crystallinity.¹⁸ Also, the diffractogram indicated that polyketone **Vc** has a high degree of crystallinity in comparison with polyketone **Vb**.

The thermal behavior of polyketones **Va-d** and copolyketones **VI, VII** was evaluated by thermogravimetric analysis (TGA) in air at a heating rate of 10°C/min. The thermographs of polyketones **Vb, c** are given in Figure 5, while Figure 6 shows the thermographs for copolyketones **VI, VII**. In Figure 5, TGA curves show a small weight loss in the range 2–4% starting at 155 until 180°C, which may be attributed to the loss of absorbed moisture and entrapped solvents. The thermographs also indicate that the polyketones decompose in two stages. The first stage between 220 and

330°C depends upon the nature of the polyketones. This result is in good agreement with the decomposition of ketone linkage observed by Swedo and Marvel.¹⁹ The second stage of degradation of the polyketones occurred between 335 and 520°C. The rate of degradation in the first stage is somewhat faster than in the second stage. A comparison of the T_{10} values of polymer **Va** containing aromatic moiety showed better thermal stability than others based on aliphatic groups.

For copolyketones **VI** and **VII**, the TGA curves in Figure 6 show a small weight loss in the range 2–4%

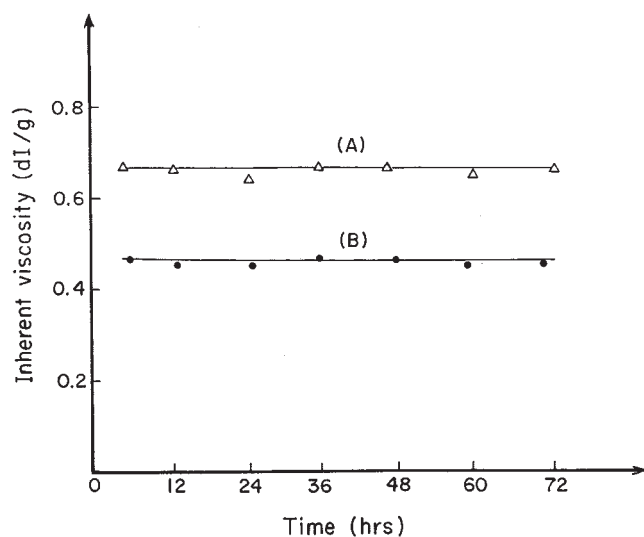


Figure 3 Stability of polyketones: (A) polyketone (**Va**) in concentrated sulfuric acid; (B) polyketone (**Vd**) in 0.5N sodium hydroxide/methanol solution.

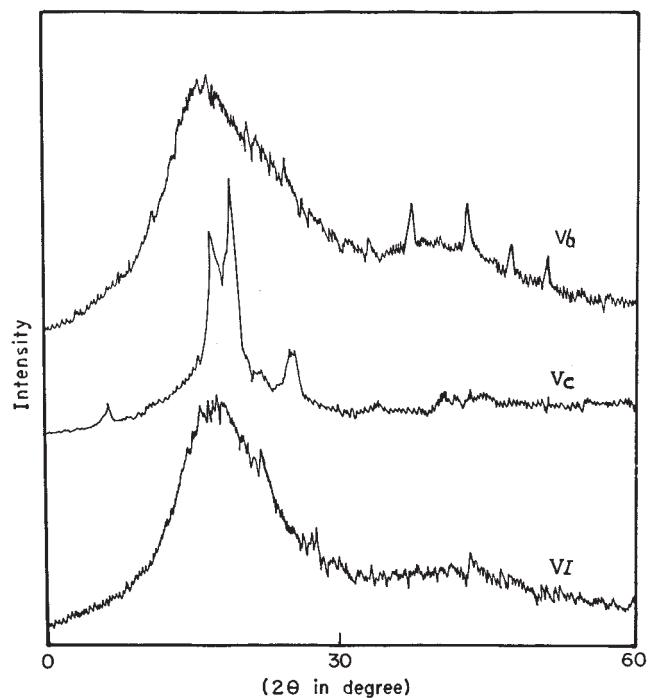


Figure 4 X-ray diffractograms of polyketones **Vb, c** and copolyketone **VI**.

TABLE II
Solubility Characteristics of Polyketones Va–d and Copolyketones VI and VII

Polymer code	DMSO	DMF	NMP	Chloroform acetone	THF	Methylene chloride	H ₂ SO ₄
Va	±	±	±	±	±	±	+
Vb	±	±	±	±	±	–	+
Vc	±	±	±	±	±	–	+
Vd	+	+	±	+	±	±	+
VI	±	±	±	±	±	±	+
VII	+	±	±	±	±	±	+

+, Soluble at room temperature (RT); ±, partially soluble at RT; –, insoluble.

starting at 150 until 180°C, which may be attributed to the loss of absorbed moisture and entrapped solvents. The thermographs also indicate that the copolyketones decompose in two stages. The first stage between 250 and 360°C depends upon the nature of the copolyketones. The second stage of degradation of copolyketones occurred between 370 and 580 °C. The rate of degradation in the first stage is somewhat faster than in the second stage. A comparison of the T_{10} values of copolyketone VI containing aromatic moiety showed better thermal stability than others based on aliphatic groups (copolyketone VII).

Studies of temperature dependence of the electrical conductivity of polyketone over the range 300–500K show that conductivity behavior follows a one-term Arrhenius-type equation (straight line) and that conductivity increases with increasing temperature and has a value of 2.8×10^{-4} at 470K with activation energy 2.09 eV (Fig. 7).

The selected sample possesses a conjugated structure (through the aromatic moieties) and the iron in the ferrocene exists in Fe²⁺ status, in addition to the low value of activation energy calculated for this sample. Therefore, the mechanism of conductivity has the

nature of *n*-conduction, with electrons participating as charge carriers for conduction as *n*-type semiconductors.²⁰

The electrical conductivity of a selected polyketone Va and copolyketone VI was measured according to the Arrhenius relation at room temperature, 300K. The results indicated that the virgin sample of organometallic polyketone Va and copolyketone VI possesses an electrical conductivity value of 2.2×10^{-10} and $3.1 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$, respectively. This reflects the onset of semiconductor behavior.

The electronic spectra of selected examples of polyketones Vb, c and copolyketones VI, VII were measured in DMSO solution. The UV spectra of polyketones in Figure 8 showed a broad absorption band at λ_{max} 375 nm for polymer Vb, at λ_{max} 422 nm for polymer Vc, at λ_{max} 385 nm for copolyketone VI, and at λ_{max} 392 nm for copolyketone VII. The appearance of a broad absorption band in the UV spectra is attributed to the excitation of (π - π^* and *n*- π^*) for C = C and C = O groups.

Polymers Va, c and copolymers VI, VII were dissolved in H₂SO₄ and the UV-vis were run in the

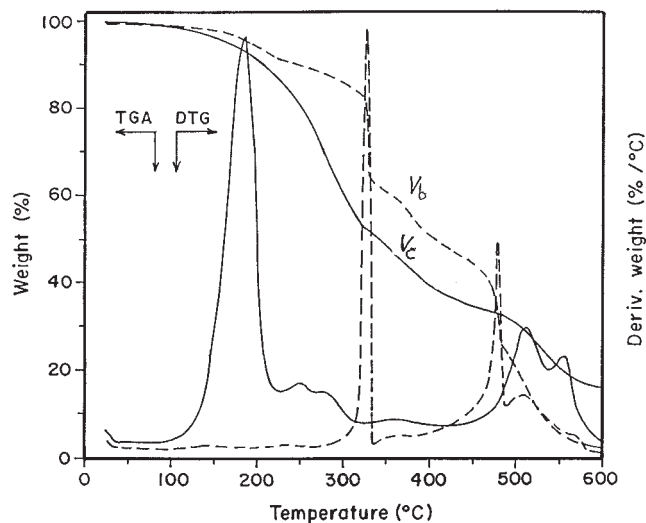


Figure 5 Thermogravimetric curves of polyketones Vb, c.

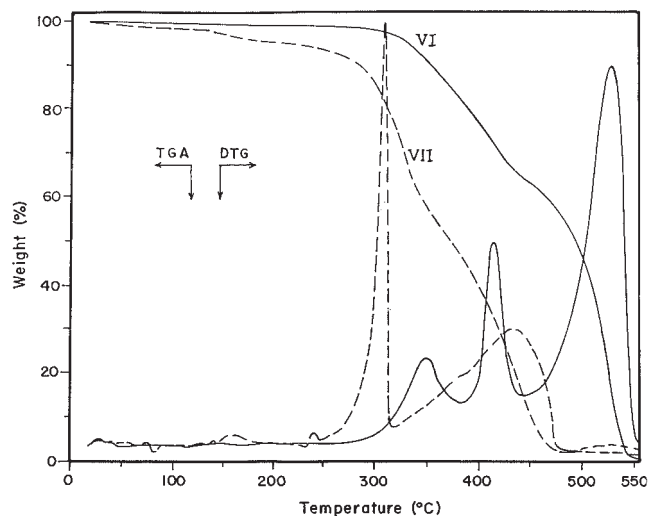


Figure 6 Thermogravimetric curves of copolyketones VI, VII.

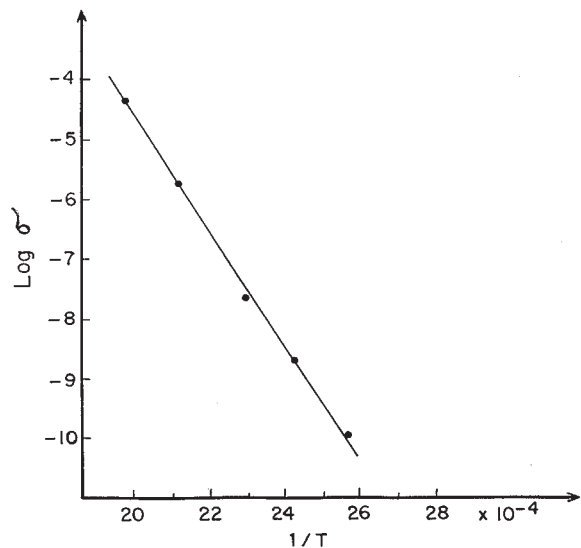


Figure 7 Temperature dependence of electrical conductivity of polyketone Vb.

region 220–700 nm and showed a peak around 500 nm (polymer Va) and also a change in color from red to deep brown. This may be attributed to the oxidation of ferrocene derivatives to the corresponding ferrocenium.

The morphology of the synthesized polyketone Vb was examined by SEM (Jeol-SM-5400 LV instrument). The SEM sample was prepared by evaporating a dilute solution of polyketone on a smooth surface of aluminum foil and coating it with gold–palladium alloy. The SEM (Camera) was performed with Ilford film at an accelerating voltage of 15 kv using a low-dose technique.²¹ The SEM study of polyketone Vb in Figure 9a and b showed that the polymer has a polymorph globular and subglobular structure, which ap-

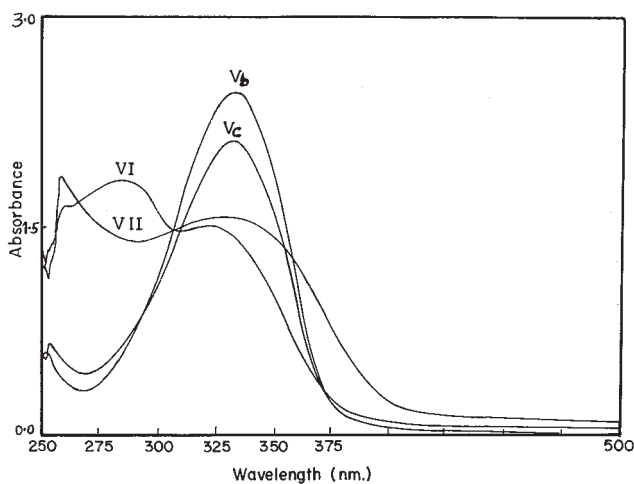
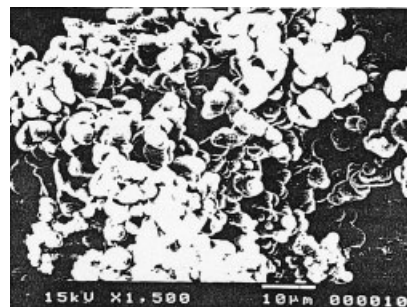
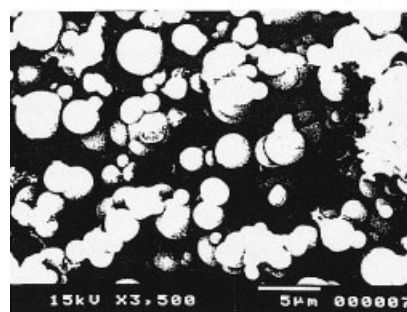


Figure 8 The UV-vis spectra of polyketones Vb, c and copolyketones VI, VII.



(a)



(b)

Figure 9 SEM image of polyketone Vb.

peared in a continuous chain with some coalescence present.

CONCLUSIONS

Two novel series of polyketones and copolyketones based on 2,7-bis [(2-ferrocenyl) methylene] cycloheptanone were synthesized via the Friedel–Crafts reaction. All polyketones and copolyketones were soluble in concentrated H₂SO₄. Thermogravimetric analyses showed that the copolyketones were somewhat less thermally stable than their polyketone counterparts. X-ray diffraction analyses indicated that most of the polymers are semicrystalline. SEM images of copolyketone VII indicated that their surfaces possess globular and aggregate structures.

References

1. Staniland, P. A. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, 1989; p 483, Vol. 5.
2. Rose, J. B. In *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Eds.; Elsevier: New York, 1986; p 187.
3. Zolotukhin, M. G.; Rueda, D. R.; Balta, F. J.; Bruix, M.; Cagliaio, M. E. *Macromol Chem Phys* 1997, 188, 1131.

4. Patel, N. Z.; Patel, J. N.; Ray, R. M.; Patel, R. M. *Angew Makromol Chem* 1991, 192, 103.
5. Patel, B. T.; Solanki, Y. K.; Patel, P. M.; Patel, R. M. *Res J Chem Environ* 1997, 1, 21.
6. Patel, B. T.; Patel, R. T.; Patel, R. M.; Patel, K. C. *Angew Makromol Chem* 1998, 263, 21.
7. Lee, J.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1983, 21, 2189.
8. Lin, S.; Kriek, G.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1970, 20, 401.
9. Lee, B.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1982, 20, 393.
10. Patel, B. T.; Patel R. M. *Intern J Polym Mater* 1998, 41, 199.
11. Patel, R. M.; Mehta, Y. N.; Patel, R. M. *Res J Chem Environ* 1998, 2, 29.
12. Patel, B. T.; Patel, R. M. *Intern J Polym Mater* 1998, 4, 199.
13. Vogel, A. In *Textbook of Practical Organic Chemistry*; Longmans & Green: London, 1967; vol. 1, p 464.
14. Perrin, D. D.; Armergo, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed; Pergamon: New York, 1980.
15. Aly, K. I.; Khalaf, A. A.; Alkskas, I. A. *Eur Polym Mater* 2003, 39, 1035.
16. Aly, K. I.; Ahmed, R. A. *Liquid Cryst* 2000, 27, 251.
17. Aly, K. I. *Polym Intern* 1998, 45, 483.
18. Mandelkern L., *Crystallization of Polymers*. McGraw-Hill: New York, 1964.
19. Swedo, R. J.; Marvel, C. S. *J Polym Sci Polym Chem Ed* 1979, 17, 2815.
20. Abd-Alla, M. A.; El-Zohary, M. F.; Aly, K. I.; Abdel-Whab, M. M. *J Appl Polym Sci* 1993, 47, 323.
21. Tager, A. *Physical Chemistry of Polymers*. Mir: Moscow: 1972.