New Polymer Syntheses XXVIII. Synthesis and Thermal Behavior of New Organometallic Polyketones and Copolyketones Based on Diferrocenylidenecyclohexanone

Kamal I. Aly

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

ABSTRACT: A new interesting category of organometallic polyketones and copolyketones were synthesized via the Friedel–Crafts reaction through the polymerization of 2,6-[bis (2-ferrocenyl)methylene] cyclohexanone (II) with different diacid chlorides. The model compound was synthesized by reacting the monomer (II) with benzoyl chloride and characterized by ^{1}H-NMR, IR, and elemental analyses. The polyketones and copolyketones were insoluble in most organic solvents but easily soluble in protic solvents. The thermal properties of these polyketones and copolyketones were evaluated and correlated to their structural units by thermogravimetric analysis and DSC measurements, and they had inherent viscosity of 0.29–0.52 dI g^{-1}. Moreover, the electrical conductivity of one of the polyketones, as a selected example, namely poly [carbonyl-terephthaloyloxy-(2-oxo-1,3-cyclohexanediylidene)methylidyne-ferrocenyl], **Va,** and copolyketone, **VI,** was investigated above the temperature range (300–500 K) and it followed an Arrhenius equation with activation energy 2.09 eV. The morphological properties of selected example of polyketones were determined by scanning electron microscopy. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1440–1448, 2004

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

INTRODUCTION

Polyketones represent a new class of potential engineering thermoplastics. Their property set is positioned in the area of polyamides and polyacetales. They are characterized by their stiffness, high melting temperature, and resistance against water and moisture. In particular, one should also mention chemical resistance, stability under hydrolysis conditions, impact toughness, flame resistance without additives containing halides or red phosphor, and short cycle times in injection molding.[1–3] Friedel–Crafts polymers, formed by polycondensation of 4,4'-dichloromethyl-diphenyl ether with benzene, toluene, isomeric chlorotoluenes and xylenes, phenol, and isomeric cresols, have been reported.[4–6] Recently, a considerable amount of research effort has concentrated on the synthesis of polyketones via the Friedel–Crafts reaction.[7–12]

To our knowledge, no work has been reported concerning the synthesis of polyketones and copolyketones containing ferrocenylidene cyclohexanone in the main chain. The work reported in this paper outlines the synthesis and properties of some new polyketones and copolyketones based on 2,6-[bis(2-ferrocenyl)methylene] cyclohexanone. The major aim of this work was to investigate the effect of inclusion of a ferrocene moiety in the polymer backbone on the polymer properties. In addition, other characteristics of these new polymers, such as thermal stability, solubility, electrical conductivity, and crystallinity, were also examined and are discussed.

EXPERIMENTAL PROCEDURES

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}H-NMR spectra were recorded on a GNM-LA 400-MHz NMR spectrophotometer at room temperature, in DMSO or CHCl$_3$, using TMS as the internal reference. Viscosity measurements were made with 0.5% (w/v) solution of polymers in sulfuric acid (9 M) 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 radiation. Thermogravimetric analysis (TGA) and DTG measurements

Correspondence to: K. I. Aly (Kamal_61@Yahoo.com).

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_{Inh} (dI/g)	Yield (%)	Appearance of polymer
		Calcd	Found	Calcd	Found	Calcd	Found			
Va	$C_{36}H_{28}O_3Fe_2$	69.68	68.82	4.52	4.23	18.06	17.29	0.38	67	Powder, brownish
Vb	$C_{36}H_{28}O_3Fe_2$	69.68	68.88	4.52	4.12	18.06	17.67	0.29	75	Powder, brown
Vc	$C_{34}H_{32}O_3Fe_2$	68.00	67.12	5.33	5.07	18.67	18.19	0.37	65	Powder, brown
Vd	$C_{38}H_{40}O_3Fe_2$	69.51	69.02	6.10	5.94	17.07	16.39	0.47	72	Powder, brown
VI	$C_{64}H_{48}O_6Fe_2$	75.00	73.14	4.69	4.11	10.94	10.78	0.52	69	Powder, brown
VII	$C_{68}H_{56}O_6Fe_2$	75.55	74.54	5.14	5.28	10.37	10.93	0.36	62	Powder, deep brown

Note. Inherent viscosity measured in H_2SO_4 at 25°C.

were performed on V 5.1 A Du Pont 2000 thermal analyzer at a heating rate of 10°C/min in air. DSC was carried out in a nitrogen atmosphere using a Shimadzu DSC-50 thermal analyzer. 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 Joel JSM-5400 LV-ESM. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 Psi. IR die-silver paste was used to make contacts between the polymer pellets and two graphite electrodes. Conductivities were measured at room temperature under air using a 610 Keithley electrometer.

Reagents and solvents

Ferrocenecarboxaldehyde (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 dichlorides[13] were freshly distilled at 125°C/11 Torr and at 182°C/16 Torr, respectively. Cyclohexanone (Merck) was freshly distilled at bp 155°C. Anhydrous aluminum chloride (Merck) and all other solvents and reagents were of high purity and were further purified by standard methods.[14]

Monomer syntheses

Synthesis of 2,6-[bis (2-ferrocenyl)methylene] cyclohexanone (**II**)

A mixture of 0.1 mol cyclohexanone and ferrocene carboxaldehyde (0.2 mol) in warm ethanol was stirred, and a few drops of KOH (20%) were added into 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 was 85%, mp 261°C. Calculated for $C_{28}H_{26}O Fe_2$:

C,68.57; H,5.31; Fe, 22.86%. Found: C, 68.34; H, 5.21; Fe, 22.08%. IR (KBr, cm^{-1}): at 1600 (s, C = C), at 1660 (s, C = O). ^{1}H-NMR (DMSO-d$_6$, ppm), at 7.0–8.0 (m, 18H of ferrocenyl moieties and 2H of 2CH = C); at 2.5 (s, 4H of 2CH$_2$ cyclohexanone); and at 2.0 (s, 2H of middle 2CH$_2$ of cyclohexanone).

Synthesis of 2,6-bis(benzylidene)cyclohexanone (**III**)

This monomer was prepared as described in our earlier 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 was placed a solution of 2,6-[bis(2-ferrocenyl)methylene] cyclohexanone (**II**) (1 mmol) and benzoyl chloride (2 mmol) in dry carbon disulfide (40 mL). The flask was purged with nitrogen during stirring and anhydrous aluminum chloride (20 mmol) was added portion-wise 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 a vacuum at room temperature. An analytical sample was obtained by recrystallization from benzene as deep brown crystals; yield was 75%, mp 234°C. Calculated for $C_{42}H_{34}O_3$ Fe$_2$: C, 72.21; H, 4.87; Fe, 16.05%. Found: C, 71.98, H, 4.78, Fe, 15.84%. IR (KBr, cm^{-1}): at 1665 (C = O of cyclohexanone), at 1700 (C = O of benzoyl group), at 1600 (C = C group). ^{1}H-NMR (DMSO-d$_6$, ppm), 7.1–8.5 (m, 10H, Ar-H; 8H, ferrocenyl moieties and 2H of 2CH = C), 2.5 (s,4H of 2CH$_2$ of cyclohexanone), 2.0 (s, 4H of middle 2CH$_2$ of cyclohexanone).
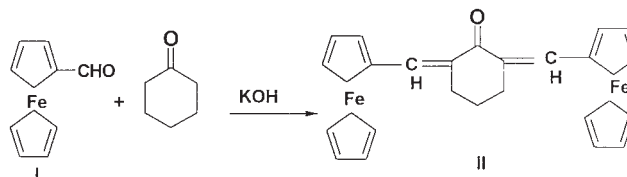
Scheme 1

Scheme 2
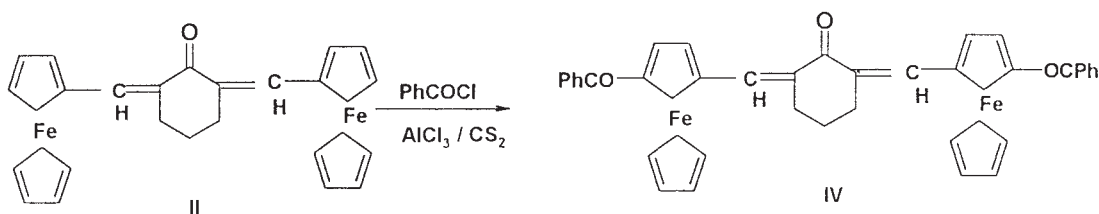
Synthesis of polyketones (Va–d)

The Friedel–Crafts method was applied for the preparation of all polymers. Typically, in a 500-mL round-bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet was placed a solution of 2,6-bis (2-ferrocenyl) methylene cyclohexanone **(II)**(2.940 g, 6 mmol) and isophthaloyl chloride (1.218 g, 6 mmol) in dry carbon disulfide (25 mL). The flask was purged with nitrogen during stirring, and aluminum chloride (2.66 g, 20 mmol) was added during the nitrogen flush. The reddish–brown reaction mixture was stirred for 24 h and then filtered, and the separated product was triturated three times with HCl (1 *N*) and 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, viscosities, and colors are listed in Table I.

Synthesis of copolyketones VI and VII

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

Typically, in a 500-mL round-bottom flask equipped with a magnetic stirrer and nitrogen inlet and outlet was placed a solution of 2,6-[bis (2-ferrocenyl) methylene] cyclohexanone **(II)**(1.470 g, 3 mmol); 2,6-bis (benzylidene)cyclohexanone **(III)** (0.822 g ,3 mmol) and terephthaloyl chloride (1.218 g, 6 mmol) in dry carbon disulfide (50 mL). The flask was purged with nitrogen during stirring, and aluminum chloride (2.66 g, 20 mmol) was added during the nitrogen flush. The reddish–brown reaction mixture was stirred for 24 h and then filtered, and the separated product was triturated three times with HCl (1 *N*) and methanol. The powdery material was again filtered off, washing 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**. For both copolymers yields, elemental analyses, viscosities, and colors are listed in Table I.

RESULTS AND DISCUSSION

Synthesis of monomer II

2,6-[Bis (2-ferrocenyl)methylene] cyclohexanone monomer **(II)** was synthesized in good yield by the basic
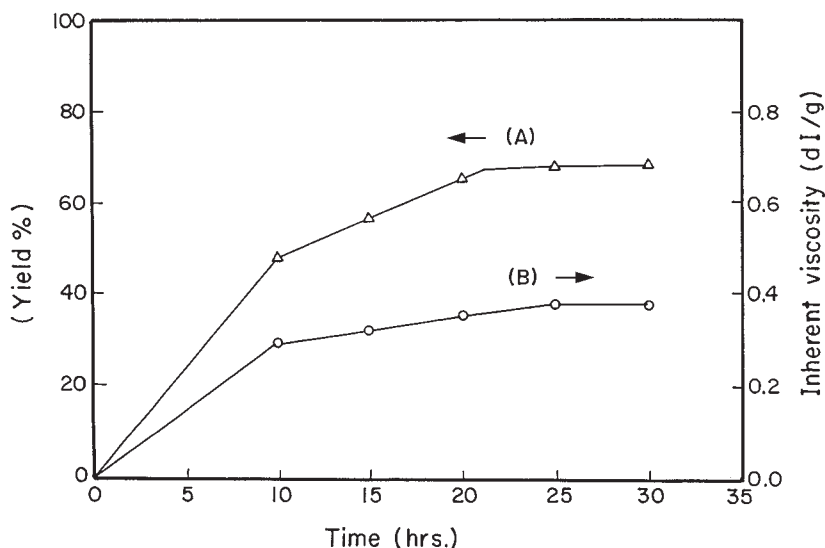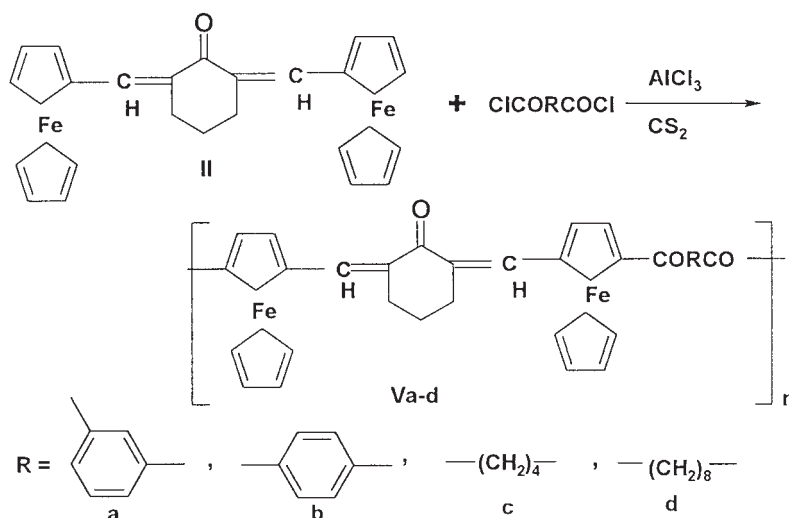

Figure 1 Effect of reaction time on polymerization yield and extent of polymerization: (A) yield; (B) inherent viscosity. Friedel–Crafts polycondensation was carried out with 6.0 mmol II and 6.0 mmol isophthaloyl dichloride in 60 mL dichloromethane at 25°C in the presence of 20 mmol AlCl₃.

Scheme 3

catalyzed condensation of 2 mol ferrocene carboxalde-hyde with 1 mol cyclohexanone, as shown in Scheme 1.

Synthesis of model compound IV

Before the polymerization was attempted, a model compound was prepared by the reaction of monomer (**II**) with two equivalents of benzoyl chloride. The reaction is depicted in Scheme 2.

Synthesis of polyketones Va–d

To determine an adequate catalyst for the synthesis of polyketones based on ferrocenylidene cyclohexanone in the main chain, Friedel–Crafts polycondensation of 2,6-[bis (2-ferrocenyl)methylene] cyclohexanone (**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 molar 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 poly-condensation of dicarbonyl chlorides, including isoph-thaloyl, terephthaloyl, adipoyl, and sebacoyl dichlo-rides with 2,6-bis [(2-ferrocenyl) methylene] cyclohex-anone (**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 0.29–0.52 dI g^{-1}. The structures of the obtained polyketones were identified by IR and ^{1}H-NMR spectroscopy as well as elemental analyses (Table I).

The microanalysis of all the polymers reflected the characteristic repeating unit of each polymer; the data are listed in Table I. It should be noted that the anal-ysis of the polyketones and copolyketones deviated up to 1.86% from the theoretical values. However, it is not uncommon for polymers, especially those of high molecular weight, to trap solvent molecules within the polymer matrix, and these polymers contain polar groups that are capable of hydrogen bonding with solvent molecules.[16]

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

Polymer code	DMSO	DMF	NMP	Chloroform + acetone (1:1)	THF	Trifluoroacetic acid	H_2SO_4
Va	±	±	−	−	−	±	+
Vb	+	±	±	±	±	±	+
Vc	±	±	±	±	±	+	+
Vd	+	+	±	+	±	+	+
VI	±	±	±	±	±	+	+
VII	+	±	±	+	±	+	+

Note. +, Soluble at room temperature (RT); ±, partially soluble at RT; −, insoluble.
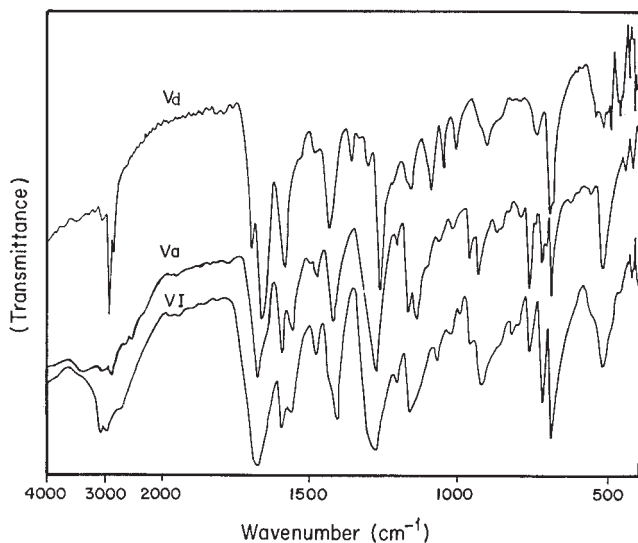
Figure 2 IR spectra of polyketones **Va,d** and copolyketone **VI**.

Characteristic peaks, resulting from (2-ferrocenyl)-methylidene cyclohexanone protons (for polymer **Vb**), could be found at δ 6.9–8.2 (m, 8H, ferrocenyl rings; 4H Ar-H and 2H of 2CH = C); at 2.5 (s, 4H of 2CH$_2$ of cyclohexanone); and at 2.0 (s, 4H of middle 2CH$_2$ of cyclohexanone) ppm in ^{1}H-NMR spectra. Also strong absorption bands at 1690–1710 cm^{-1} (ν C = O stretching of ketone), at 1640–1660 cm^{-1}, (ν C = O stretching of carbonyl group of cyclohexanone), and at 1590–1610 cm^{-1} for (ν C = 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,** containing two different moieties, e.g., bis-ferrocenylidene cyclohex-anone as organometallic moiety and bisbenzylidene-cyclohexanone in the polymer main chain, were synthesized from the copolymerization of monomers **II** and **III** with two different diacid chlorides, e.g., terephthaloyl or adipoyl, as shown in Scheme 4.

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 (9 M), dimethylsulfoxide (DMSO), trifluoro-acetic acid, chloroform and acetone mixture(1:1), N-methylpyrrolidone (NMP), tetrahydrofuran (THF), 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 acids like acetic or formic acids (except for 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 poly-ketones with its copolyketones, we found that the latter possess better solubility than the former. This was attributed to the higher flexibility of cyclohex-anone moiety as described in our previous papers.[17,18]

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 polyk-etones **Va,d** and copolyketones **VI** and **VII** in Figure 4 showed few sharp peaks with an amorphous back-ground, indicating that there is a large range of struc-
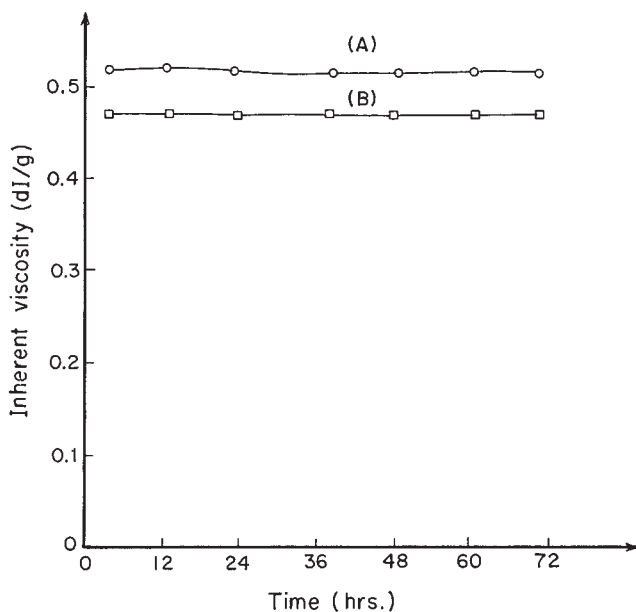

Copolyketone VI: R = —⟨benzene⟩— ; VII R = (CH$_2$)$_4$
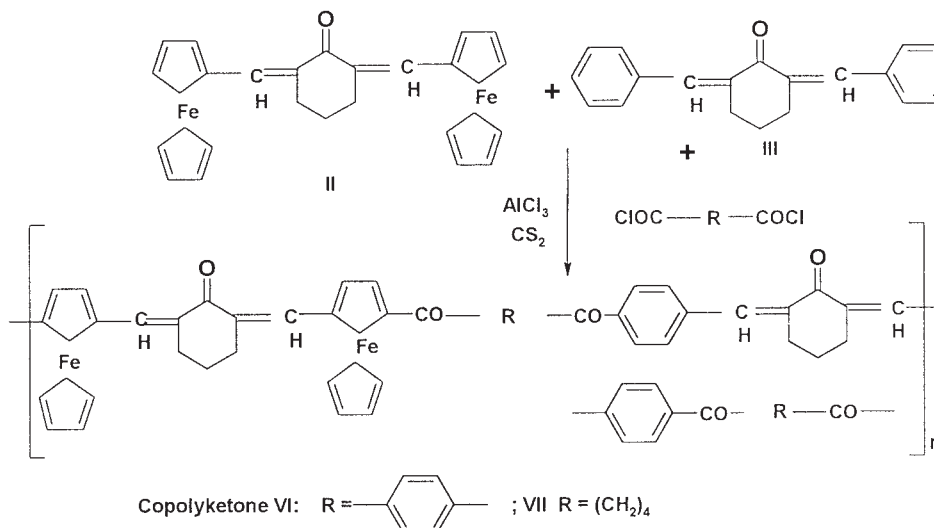
Scheme 4

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

tures in the region $2\theta = 5$–$65°$ or (d in A°). The diffractogram indicated that polyketone **Va** is amorphous and the others have some degree of crystallin-
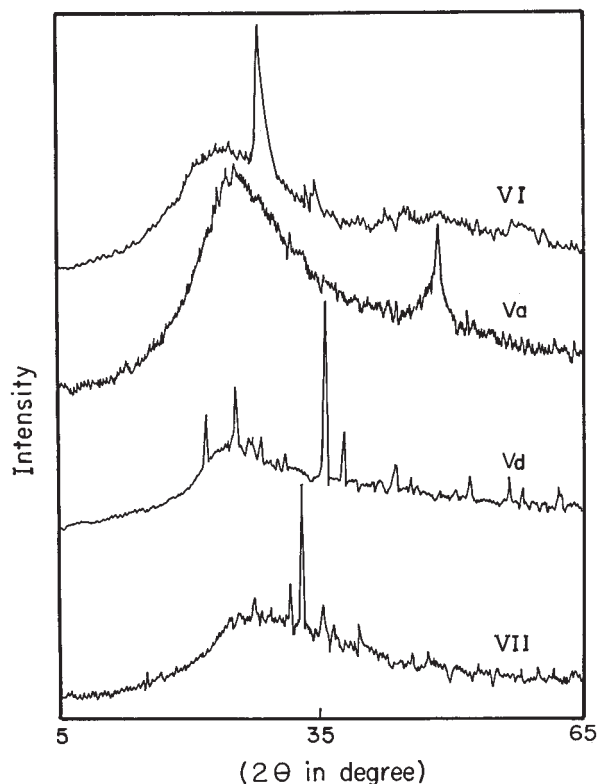

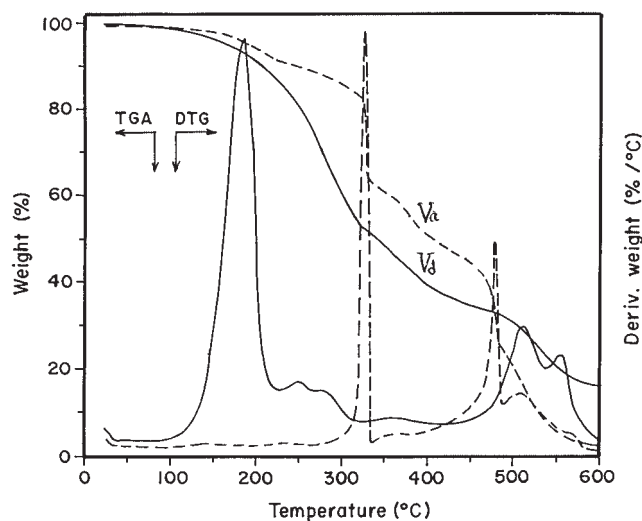**Figure 4** X-ray diffractograms of polyketones **Va,d** and copolyketones **VI** and **VII**.

Figure 5 TGA and DTG curves of polyketones **Va,d**.

ity. Moreover, the presence of C = O as a polar group, in addition to high C = C band levels chains in the polymer, led to some extent of crystallinity.[19] Also, the diffractogram indicated that polyketone **Vd** has a high degree of crystallinity in comparison with polyketone **Va.**

The thermal behavior of polyketones **Va,d** and copolyketones **VI,VII,** as selected examples, were evaluated by TGA in air at a heating rate of 10°C/min. The thermograms of polyketones **Va,d** are given in Figure 5, while Figure 6 shows the thermograms for copolyketones **VI** and **VII**. Also, Table III gives the temperatures for various percentages of weight loss for both types. In Figure 5, TGA curves show a small weight loss in the range 2–4%, starting at 160 until 200°C, which may be attributed to loss of absorbed moisture and entrapped solvents. The thermographs also indicate that the polyketones decompose in two stages.
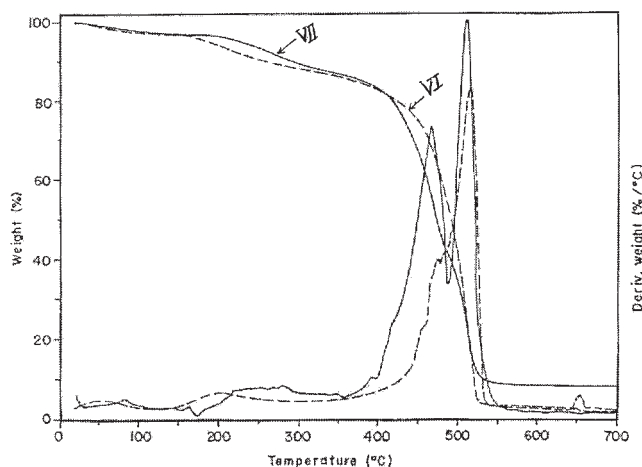

Figure 6 TGA and DTG curves of copolyketones **VI** and **VII**.

TABLE III
Thermal Properties of Polyketones Va–d and Copolyketones VI and VII

Polymer	Temperature (°C) for various decomposition levels (%)				
	10	20	30	40	50
Va	320	350	385	445	470
Vb	315	335	360	373	410
Vc	295	305	325	360	390
Vd	250	285	320	350	410
VI	235	245	260	285	305
VII	215	250	290	325	365

Note. Heating rate, 10°C min^{-1}.

The first stage between 230 and 320°C depends upon the nature of the polyketones. This result is in good agreement with decomposition of ketone linkage observed by Swedo and Marvel.[20] The second stage of degradation of polyketones occurred between 330 and 560°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 polyketone **Va** containing aromatic moiety showed better thermal stability than others based on aliphatic groups (polyketone **Vd**).

For the copolyketones **VI** and **VII** TGA curves in Figure 6 show a small weight loss in the range 2–4% starting at 170 until 210°C, which also may be attributed to loss of observed moisture and entrapped solvents. The thermograms again indicate that the copolyketones decompose in two stages. The first stage between 200 and 310°C also depends upon the nature of the copolyketones. The second stage of degradation of copolyketones occurred between 320 and 580°C. The rate of degradation in the first stage is again 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**).

Figure 7 shows typical DSC traces of polyketone **Va:** the curve shows a T_g at 167°C and T_f at 466.95°C and
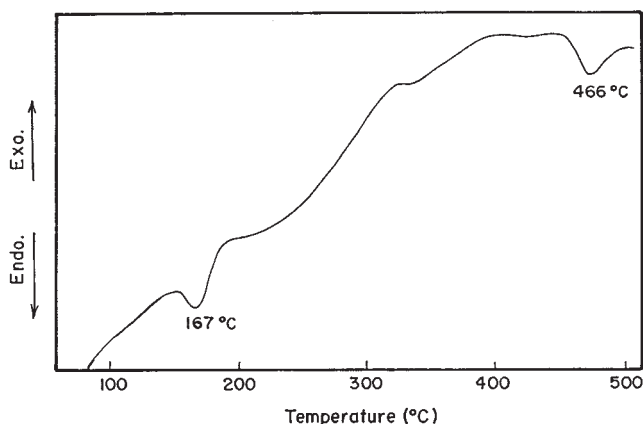

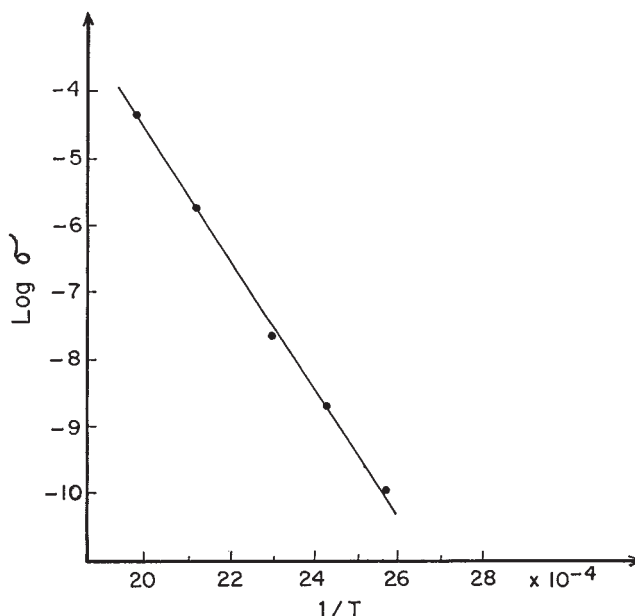**Figure 7** DSC traces of polyketone **Va**.

Figure 8 Temperature dependence of electrical conductivity of polyketone **Va**.

also a broad exothermic peak, in the range 200–320°C showing T_c character.

Studies of temperature dependence of the electrical conductivity of polyketone **Va** over the range 300–500 K show that conductivity behavior follows a single-term Arrhenius-type equation (straight line) and that conductivity increases with increasing temperature and has a value of 2.8×10^{-4} Ω^{-1} cm^{-1} at 470 K with an activation energy of 2.09 eV (Fig. 8).

The selected sample possesses conjugation (through the aromatic moieties) and the iron in the ferrocene exists in the Fe^{+2} states, 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.[21] The electrical conductivity of a selected polyketone **Va** and copolyketone **VI** was measured according to the Arrhenius relation at room temperature, 300 K. The results indicated that the virgin sample of organometallic polyketone **Va** and copolyketone **V** possess electrical conductivities values of 2.4×10^{-9} and 3.1×10^{-10} Ω^{-1} cm^{-1}, respectively. This reflects the onset of semiconductor behavior.

The electronic spectra of selected examples of polyketones **Va,d** and copolyketones **VI** and **VII** were measured in DMSO solution. The UV spectra of polyketones in Figure 9 showed a broad absorption band at λ_{max} 376 nm for polymer **Va**, at λ_{max} 419 nm for polymer **Vd**, at λ_{max} 387 nm for copolyketone **VI**, and at λ_{max} 389 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.
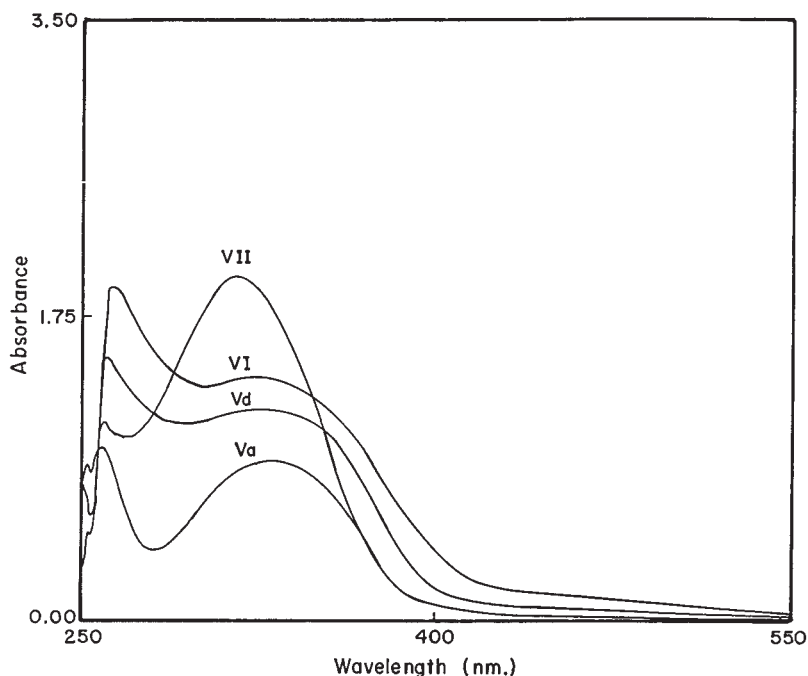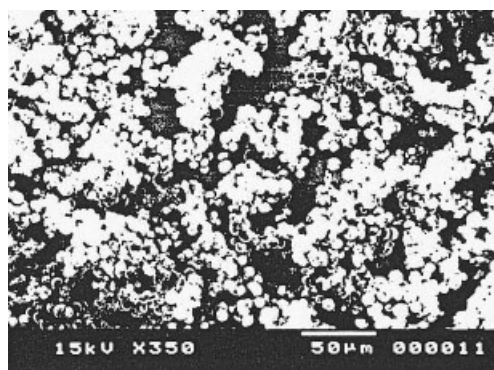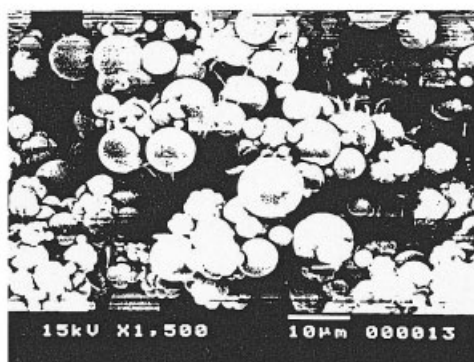
Figure 9 The UV-visible spectra of polyketones **Va,d** and copolyketones **VI** and **VII**.

The morphology of the synthesized polyketone **Vb** in Figure 10a and b 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) with Ilford film at an accelerating voltage of 15 kv was operated using a low-dose technique.[22] The SEM study showed that the polymer has polymorphic globular and subglobular structures, which appeared in a continuous chain with some coalescence present.

(a)

(b)

Figure 10 SEM image of polyketone **Vb**.

CONCLUSION

Two novel series of polyketones and copolyketones, based on 2,6-bis (2-ferrocenyl)methylene cyclohexanone, were synthesized via the Friedel–Crafts reaction. All polyketones and copolyketones were soluble in concentrated H_2SO_4. 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 polyketone **Vb** indicated that their surfaces possess globular and aggregate structures.

References

1. Cowie, J. M. G. Polymer Chemistry And Physics Of Modern Materials, 2nd ed.; Chapman & Hall: London, 1994; p. 358.
2. Seymour/Carraher's Polymer Chemistry, 5th ed.; Decker: New York, 2000; p. 263.
3. Stadlbauer, M.; Eder, G.; Janeschitz-Kriegl, H.; Polymer 2001, 42(8), 3809.

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(1), 21.

6. Patel, B. T.; Patel, R. T.; Patel, R. M.; Patel, K. C. Makromol Chem 1998, 263, 21.

7. Patel, B. V.; Patel, B. T.; Patel, R. M. Asian J Chem 1998, 10(1), 126.

8. Patel, R. T.; Mehta, Y. N.; Patel, R. M. Res J Chem Environ 1998, 2(2), 29.

9. Patel, B. T.; Patel, P. M.; Patel, R. M. Acta Cienc Indica Chem 1997, 23(2), 83.

10. Patel, D. A.; Shah, B. S.; Patel, R. M. Res J Chem Environ 1998, 2(4), 67.

11. Patel, B. T.; Patel, R. T.; Patel, R. M.; Patel, K. C. Angew Makromol Chem 1998, 263, 21.

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 Crystals 2000, 27, 251.

17. Aly, K. I. Polym Intern 1998, 45, 483.

18. Abd-Alla, M. A.; Aly, K. I.; Hammam, A.S. High Perf Polym 1989, 1, 223.

19. Mandelkern, L. Crystallization of Polymers; McGraw-Hill: New York, 1964.

20. Swedo, R. J.; Marvel, C. S. J Polym Sci Polym Chem Ed 1979,17, 2815.

21. Abd-Alla, M. A.; El-Zohary, M. F.; Aly, K. I.; Abdel-Whab, M. M. J Appl Polym Sci 1993, 47, 323.

22. Tager, A. Physical Chemistry of Polymers; Mir Publishing: Moscow, 1972.