

Synthesis and characterization of a new chelating polymer and its metal complexes

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Abstract

The monomer *exo*-7-isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic-acidanhydride (I) [J.H. Day, Chem. Revs., 53 (1953) 167] undergoes smooth homopolymerization using the $WCl_6/(CH_3)_4Sn$ or $MoCl_5/(CH_3)_4Sn$ based ring opening metathesis polymerisation initiators to give a polymer (PI). Aiming to synthesize a chelating polymer, the monomer (I) was treated with the potential complexing agent *S*-methylhydrazinecarbodithioate to give monomer (II) which was subjected to metathesis polymerization using WCl_6 and $MoCl_5$ based catalysts. Unfortunately, the formation of complexes between (II) and these initiators completely inhibits ring opening polymerization. However, the synthesis of polymer containing chelating group (PII) was achieved by treating (PI) with $NH_2NHCSSCH_3$ in DMF as solvent. The chelating polymer (PII) reacts with metal(II) acetates in a 2:1 repeating unit: metal molar ratio giving neutral complexes of the general formula (PIII) which are insoluble in common organic solvents. The isolated polymers and their metal complexes were characterized by elemental analysis, IR, NMR, TG and DTA measurements.

Keywords: Chelating polymers; Metal complexes

1. Introduction

At present time many laboratories are attempting to synthesize new chelating polymers which possess high thermal stability and good mechanical properties [2]. In addition, there has been an increasing interest in chelating polymers that are selective towards some toxic metals [3–5]. In order to synthesize such materials it is necessary to solve important problems such as: (a) the appropriate choice of the chelating group and (b) the direct or indirect introduction of the chelating functionality into the polymeric matrix. Recently we [6–10] and other workers

[11–13] have examined several kinds of substituted bicyclic[2,2,1]hept-2-enes or bicyclo[2,2,1]hepta-2,5-dienes as potential monomers for the preparation of high molecular weight polymers via ring opening metathesis polymerization (ROMP) using $WCl_6/(CH_3)_4Sn$ as the initiator system. This paper outlines our attempt to incorporate an excellent chelating group namely *S*-methylhydrazinecarbodithioate, into an established ROMP monomer, namely *exo*-7-isopropylidenebicyclo-[2,2,1]hept-2-ene-5,6-dicarboxylicacidanhydride (I) (Scheme 1) to form (II) which can be polymerized by the same technique. Unfortunately the complex formation between the monomer (II) and the WCl_6 initiator completely inhibited the ROMP process.

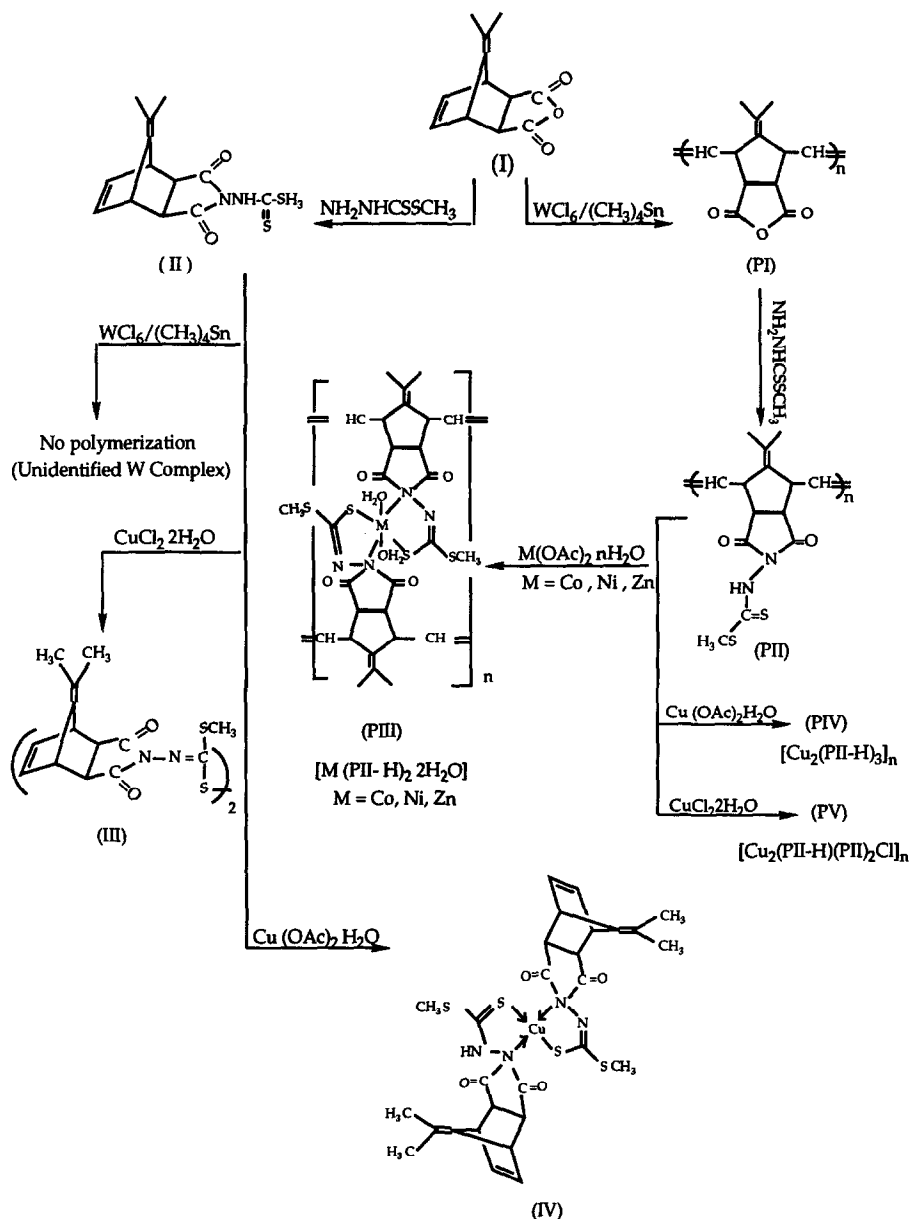
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However, the synthesis of the desired chelating polymer (PII) was carried out by the condensation of S-methylhydrazinecarbodithioate with the anhydride precursor polymer (PI). The current work also presents the synthesis and characterization of Ni(II), Co(II), Zn(II), Cu(II) and Cu(I) complexes derive from the chelating group containing compound monomer (II) and polymer (PII).

2. Experimental

2.1. Materials

Hydrazine hydrate (100%), carbon disulphide, ammonia solution, methyl iodide (Aldrich) were used as received to synthesise the S-methylhydrazine-carbodithioate, $\text{NH}_2\text{NHCS-SCH}_3$, following literature procedures [14,15].



Scheme 1.

Exo-7-iso-propylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic anhydride, (I), was obtained from the Diels–Alder reaction between dimethyl fulvene and maleic anhydride following the literature procedure [1]. The exo adduct of monomer (I) was polymerized to (PI) using an activated catalyst system $WCl_6/(CH_3)_4Sn$ in chlorobenzene at 70°C [16]. Methylene chloride was distilled from phosphorus pentoxide and stored over 4 Å molecular sieves. Absolute ethanol, methanol, diethyl ether (BDH) and the metal(II) salts (Alfa) were used as received, benzene, acetone and dicyclopentadiene were purchased from (BDH). Cyclopentadiene was prepared by thermal cracking of dicyclopentadiene [17]. The dimer was distilled at atmospheric pressure through a Vigreux column (40 cm) and the diene collected slowly in the range 40–45°C, it was used without further purification, when necessary it was stored in the deep freeze (–20°C) and under these conditions it could be kept for several days.

2.2. Preparation of monomeric exo-7-isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acidamido-S-methylhydrazinecarbodithioate, (II); its dimeric disulphide (III); and its polymeric form (IV)

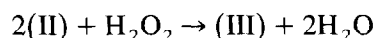
2.2.1. Preparation of monomer (II)

A solution of S-methylhydrazinecarbodithioate (0.1 mol) in dry benzene (50 ml) was added dropwise to a solution of (I) (0.1 mol) in dry benzene (50 ml) and the solution refluxed for 1 h. The resulting reaction mixture was evaporated to half of its original volume and left to cool. The colourless precipitate which separated out was recovered by filtration, recrystallized from dry diethyl ether and stored in a vacuum desiccator (m.p. = 195°C, yield = 95%).

2.2.2. Preparation of the dimeric disulphide (III)

A clear hot solution of copper (II) chloride dihydrate (0.01 mol) in ethanol (30 ml) was added to a hot solution of (II) (0.02 mol) in

ethanol (30 ml). The resulting olive green solution was refluxed for 1 h. During this time a white microcrystalline material was deposited, which was recovered by filtration, washed with hot ethanol, recrystallized from chloroform and dried under vacuum. (m.p. > 240°C (decomp.), yield = 80%). An authentic sample of disulphide (III) was obtained as a white solid on treatment of a solution of (II) with the stoichiometric amount of H_2O_2 in acetone at 0°C.



2.2.3. Preparation of polymer (PII)

A clear solution of the anhydride polymer (PI) (0.1 mol) in dry DMF (30 ml) was treated with S-methylhydrazinecarbodithioate (0.1 mol) in dry DMF (30 ml). The reaction mixture was heated in an oil bath at 75°C for 12 h and left to cool. The DMF solvent was removed by vacuum distillation. The resulting viscous solution gave a creamy precipitate on treatment with chloroform (150 ml). The desired polymer (PII) was purified by three successive reprecipitations into chloroform from a methanolic solution, then recovered by filtration and finally stored under vacuum (yield = 90%).

2.3. Preparation of monomeric and polymeric metal complexes

2.3.1. Preparation of monomeric [Cu (II-H) (II)] complex (IV)

A hot clear solution of copper acetate monohydrate (0.01 mol) in methanol (30 ml) was added dropwise with constant stirring to a hot solution of (II) (0.02 mol) in methanol (30 ml). The bluish green solution of copper acetate disappeared instantaneously. The colourless solution was refluxed for 30 min, during this time a white precipitate was deposited, which was recovered by filtration of the hot mixture and washed with hot methanol. The title compound was recrystallized from methylene chloride and dried under vacuum (yield = 86%).

2.3.2. Preparation of polymeric metal (II) complexes (PIII) of the general formula $[M(PII-H)_2 \cdot 2H_2O]_n$ [$M = Co(II), Ni(II)$ and $Zn(II)$]

A hot clear solution of polymer (PII) (0.02 mol) in ethanol (30 ml) was treated with the appropriate hot metal(II) acetate solution (0.01 mol) in ethanol (30 ml). A coloured polymeric complex was precipitated instantaneously. The solution was refluxed for an additional 30 min. The precipitated complex was recovered by filtration, washed thoroughly with hot ethanol and ether then dried under vacuum for 6 h.

2.3.3. Preparation of polymeric P(IV) of the general formula $Cu_2(PII-H)_3$ complex

This complex was prepared using the same procedure described above except using copper(II) acetate monohydrate.

2.3.4. Preparation of P(V) of the general formula $[Cu_2(PII-H)(PII)_2Cl]_n$

This complex was prepared using the same procedure described above except using copper(II) chloride dehydrate.

2.4. Analytical procedures

All elemental analyses were performed by Desert Analytics, Tucson, AZ 85717. The ana-

lytical data for the above compounds are collected in Table 1.

2.5. Physical measurements

Solution electronic spectral measurements were recorded using a Perkin-Elmer 552 spectrophotometer in matched quartz cells at room temperature in methylene chloride. Infrared spectra (KBr disks) were obtained using a Perkin-Elmer Model 567 spectrometer calibrated with respect to the 906.5 or 3026.3 cm^{-1} absorptions of polystyrene. 1H - and ^{13}C -NMR spectra were recorded using a Varian-400 MHz FTNMR spectrometer using TMS as internal standard. Approximately 10–30% (wt/v) solutions were used. A 90° pulse width with a pulse delay of 1 s was used. Merck deuterio chloroform and/or d^6 -DMSO were used as solvents.

3. Result and discussion

Exo-7-isopropylidenebicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid anhydride (I) was prepared by Diels–Alder reaction between dimethyl fulvene and maleic anhydride. The m.p. (135–136°C), IR spectrum, 1H - and ^{13}C -NMR spectroscopy, mass spectrometry and elemental

Table 1
Analytical data for polymer (II) and its metal complexes

| Compound | Colour | Yield (%) | C (%) | H (%) | N (%) | M (%) | X (%) |
|---|------------|-----------|------------------|----------------|----------------|------------------|-------------------------------|
| P(II) | cream | – | 52.13 (51.53) | 5.46 (5.52) | 9.16 (8.59) | | 18.99 ^a (19.63) |
| P(II) + Ni(OAc) ₂ | dark-brown | 95 | 45.63 (45.10) | 5.54 (5.10) | 6.46 (7.51) | 8.73 (7.92) | |
| P(II) + Co(OAc) ₂ | dark-brown | 93 | 46.87 (45.10) | 5.38 (5.10) | 7.08 (7.51) | 6.59 (7.92) | |
| P(II) + Zn(OAc) ₂ | brown | 87.5 | 44.22 (44.72) | 4.99 (5.05) | 6.63 (7.45) | 10.03 (8.91) | |
| P(II) + Cu(OAc) ₂ | dark-green | 94 | 45.52 (45.86) | 4.81 (4.40) | 7.11 (7.63) | 11.39 (11.56) | |
| Cu ₂ (PII)–H ₃ | | | | | | | |
| P(II) + CuCl ₂ | gray | 89 | 44.54 (43.02) | 4.36 (4.52) | 6.60 (7.17) | 10.35 (10.85) | 2.17 ^b (3.03) |
| Cu ₂ (PII) ₂ (PII)–H Cl | | | | | | | |

^a Sulphur.

^b Chlorine.

analysis were consistent with the proposed structure, and in general agreement with the literature [1]. Exo-7-isopropylidene-bicyclo[2,2,1]hept-2-ene-5,6-dicarboxylic acid-amido-S-methylhydrazine-carbodithioate, (II), was prepared by reaction of monomer (I) with S-methylhydrazine-carbodithioate in dry DMF. The reaction of monomer (II) with copper (II) chloride dihydrate in 1:2 molar ratio gave the

dimeric disulphide compound with the general formula (III), whereas a complex of the formula [Cu (II-H) (II)], i.e. monomer (IV) was obtained from reaction of monomer (II) and copper acetate monohydrate. These syntheses are summarised in Scheme 1. The structure of compounds (II–IV) follow in straight forward manner from the mode of preparation and were confirmed in a routine manner by elemental

Table 2
¹H NMR Shifts for compounds (I–IV) measured at 100 MHz relative to internal T.M.S. in CDCl₃

| Compound | shift (multiplicity) | integral | assignment |
|--------------|---|--|--|
| <p>(I)</p> | 1.55 (s) 3.05 (s) 3.90 (t) 6.45 (t) | 6 2 2 2 | H(a) H(d) H(c) H(b) |
| <p>(II)</p> | 1.51 (s) 2.65 (s) 2.85 (s) 3.80 (t) 6.45 (qu) 9.50 (s) | 6 3 2 2 2 1 | H(a) H(f) H(d) H(c) H(b) H(e) |
| <p>(III)</p> | 1.50 (d) 2.55 (s) 2.85 (s) 3.80 (t) 6.45 (t) | 8 3 2 2 1.8 | H(a) H(e) H(d) H(c) H(b) |
| <p>(IV)</p> | 1.52 1.70 (qu) 1.60 1.65 2.55 2.80 (d) 2.60 2.70 (d) 3.77 (qu) 6.40 (qu) | 6 6 6 6 6 6 6 6 6 6 | H(a) H(a) H(a) H(a) H(e) H(e) H(d) H(c) H(b) |

analysis, IR, MS, ^1H - and ^{13}C -NMR spectroscopy. The IR spectra of monomers (I–IV) were recorded as KBr discs; the IR spectrum of monomer (I) was identical with that of an authentic sample, showing vinylic C–H stretches at 3100 cm^{-1} , allylic C–H stretches at 2982 and 2963 cm^{-1} and anhydride carbonyl stretches at 1850 and 1770 cm^{-1} [1,6]. The IR spectrum of monomer (II) exhibited ν (N–H) absorption bands at ca. 3200 and 3050 cm^{-1} and strong absorption bands at ca. 1738 and 1709 cm^{-1} due to the amide ν (C=O), bands visible at 1269 and 802 cm^{-1} may be assigned to

thioamide ν (C=S) vibrations. The IR spectra of compounds (III) and (IV) are reasonably similar, both show the expected frequencies consistent with the proposed structure. NMR spectral data was the most structurally informative for these compounds which have not been reported previously. The ^1H -NMR chemical shifts of monomers (I–IV) are recorded in Table 2. It is clear that all these four spectra are similar in basic structure. The ^1H -NMR spectrum of monomer (I) showed resonances at δ 1.55 ppm due to the methyl protons, at δ 3.05 ppm due to the two methine protons adjacent to

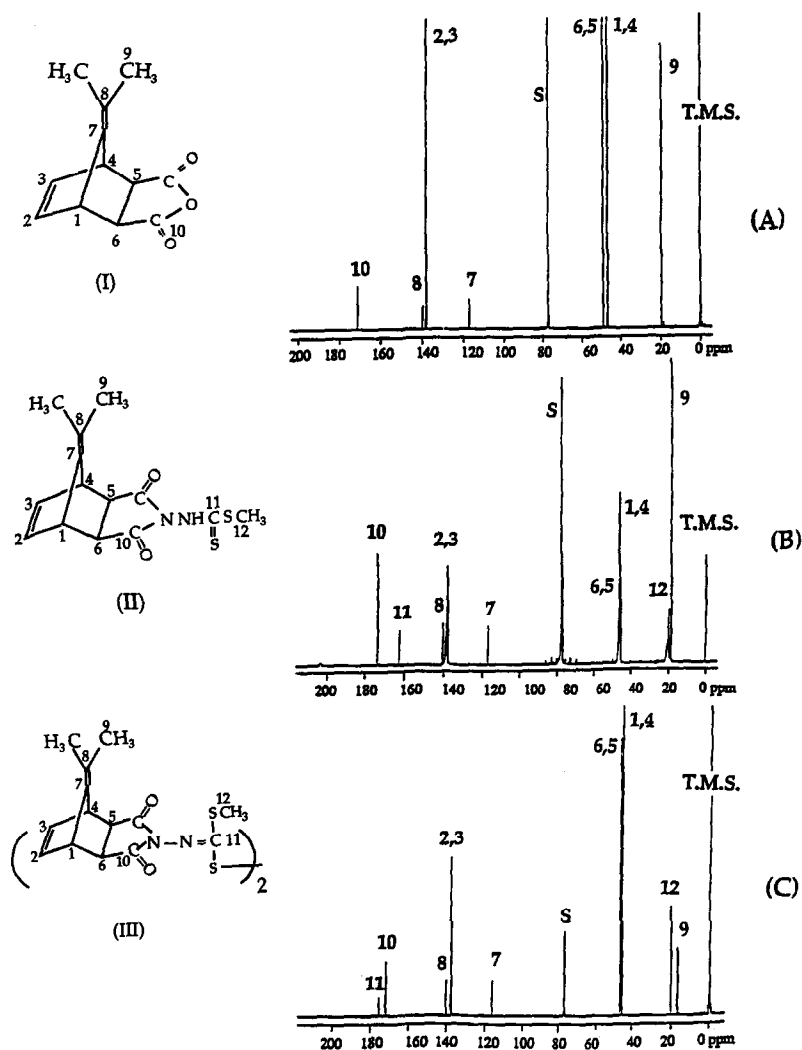


Fig. 1. The ^{13}C -NMR spectra of monomers (I), (II) and (III) recorded at 100 MHz in CDCl_3 with internal TMS as reference.

C=O, two methine protons adjacent to the olefinic group at δ 3.90 ppm and the vinylic signal at δ 6.45 ppm. An examination of the $^1\text{H-NMR}$ spectra of monomers (I), (II) and (III) shows them to be very similar, monomer (II) has two extra bands due to the S-methyl protons at δ 2.65 ppm and at δ 9.5 ppm due to the N–H proton. This signal disappears in the spectrum of monomer (III) confirming its dimeric structure, although in this case theoretically ideal integrated intensities were not obtained. These conclusions are as expected and in agreement with the $^{13}\text{C-NMR}$ data discussed. The proton decoupled $^{13}\text{C-NMR}$ spectra for compounds (I–IV) are presented in Figs. 1 and 2, and their assignments recorded in Table 3. The assignments follow in a straight forward way from the spectrum of the previously assigned monomer I. The spectra of compounds II, III and IV consist of a group of methyl resonances (15–20 ppm), a

group of methine resonances (40–60 ppm), a group of vinyl resonances (134–140 ppm), a single or group of carbonyl carbon resonances (173–175 ppm), lower intensity signals in the low field region due to the quaternary carbons including the thiocarbonyl (C=S) and azomethine (C=N) carbons. The increasing complexity of the spectra on going from I to IV is clearly shown in Figs. 1 and 2 and all the data are collected in Table 3. If we look at the spectrum of the monomeric complex (IV) (Fig. 2) we see multiple resonances for each carbon atom, although these multiplets are not clear to the naked eye, the expanded spectrum shows that the methyl signals between 16–21 ppm split into five lines, corresponding to the S-methyl and the fulvene methyl protons. There are two distinct resonances attributed to two different kinds of methine carbon signals (C1,4 and C1',4'). The vinylic and the carbonyl car-

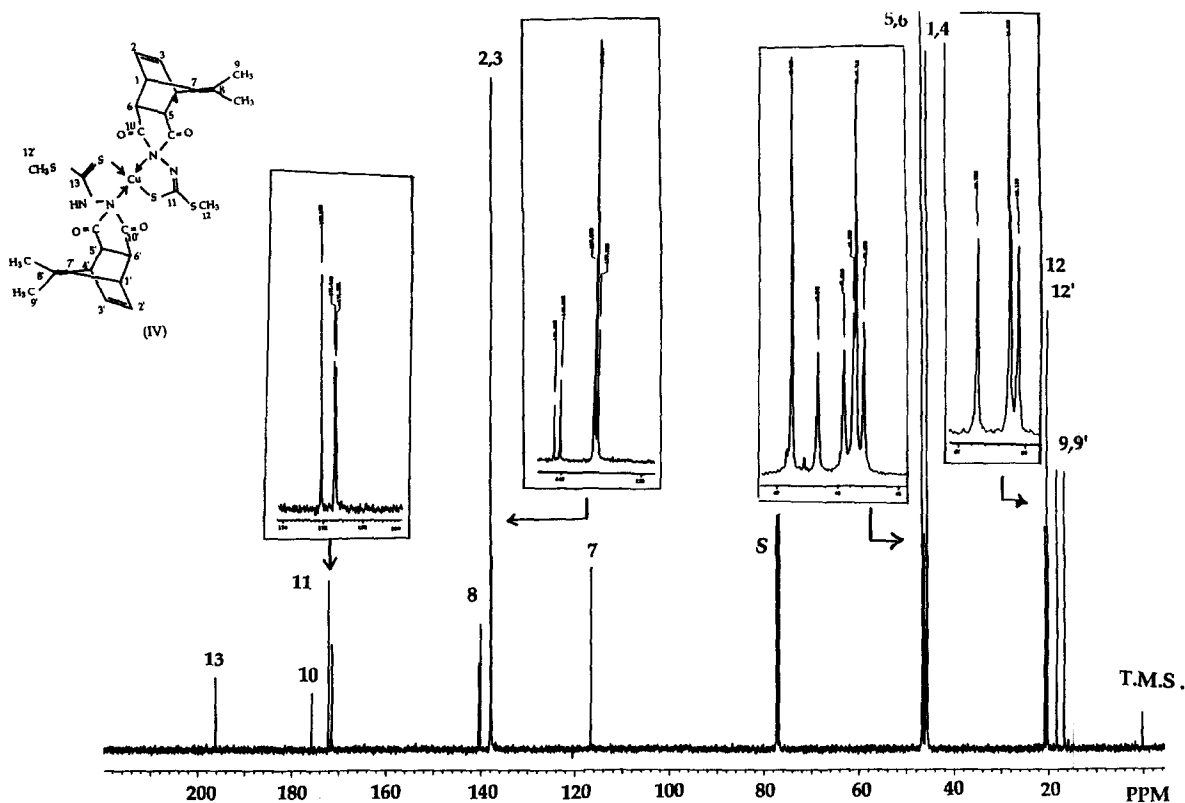


Fig. 2. The $^{13}\text{C-NMR}$ spectrum of monomer (IV) recorded at 100 MHz in CDCl_3 with internal TMS as reference.

bons (C2,3 and C10) are also resolved into triplets. The low intensity peaks corresponding to the quaternary carbon C8 is resolved into a doublet. In the low field region the peaks corresponding to the C=S and C=N of the five membered ring appears as singlets at 175.67 and 196.21 ppm, respectively.

An attempt to polymerize monomer (II) in chlorobenzene using $WCl_6/(CH_3)_4Sn$ as a catalyst was not successful; the non-polymerizability of monomer (II) was probably due to com-

plex formation between this monomer and the WCl_6 component of the initiator system. The synthesis of the desired chelating polymer (PII) was however carried out by the condensation of S-methylhydrazinercarbodithioate with the anhydride precursor of polymer (PI). Monomer (I) was polymerized by conventional metathesis catalyst system $WCl_6/(CH_3)_4Sn$ using the polymerization technique in which an active initiator mixture is injected into the monomer solution. The product was purified by two re-

Table 3

^{13}C NMR spectra recorded at 400 MHz FTNMR in $CDCl_3$ of monomer (I–IV)

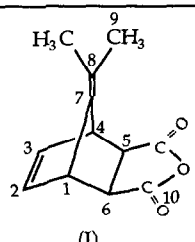
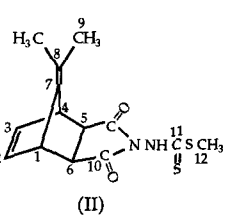
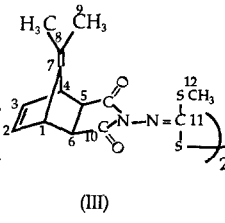
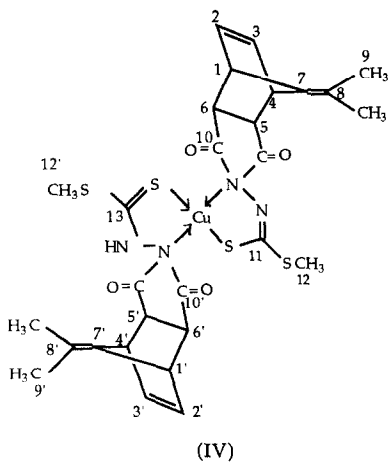
| Compound | Shift | Assignment |
|--|---|------------|
|  <p>(I)</p> | 19.58 | C9 |
| | 46.75 | C1,4 |
| | 49.17 | C5,6 |
| | 116.74 | C8 |
| | 137.93 | C2,3 |
| | 139.88 | C7 |
| | 171.29 | C10 |
| |  <p>(II)</p> | 18.17 |
| 20.26 | | C9 |
| 45.69 | | C1,4 |
| 46.24 | | C5,6 |
| 116.76 | | C8 |
| 138.03 | | C2,3 |
| 140.09 | | C7 |
| 162.36 | | C11 |
| 173.65 | | C10 |
|  <p>(III)</p> | 16.54 | C12 |
| | 20.18 | C9 |
| | 45.72 | C1,4 |
| | 46.76 | C5,6 |
| | 116.55 | C8 |
| | 137.84 | C2,3 |
| | 140.44 | C7 |
| | 172.02 | C10 |
| | 175.62 | C11 |

Table 3 (continued)

| | | |
|--|--------|--------|
|  <p>(IV)</p> | 16.60 | C12' |
| | 18.19 | C12 |
| | 20.11 | C9' |
| | 20.24 | |
| | 20.73 | C9 |
| | 45.58 | |
| | 45.91 | C1',4' |
| | 45.71 | |
| | 45.75 | C1,4 |
| | 45.91 | |
| | 46.34 | C5,6 |
| | 46.76 | |
| | 116.59 | C7 |
| | 137.74 | C2',3' |
| | 137.91 | C2,3 |
| | 137.98 | |
| | 140.07 | C8' |
| 140.45 | C8 | |
| 171.37 | C10' | |
| 171.45 | | |
| 172.10 | C10 | |
| 175.67 | C11 | |
| 196.21 | C13 | |

precipitations from acetone into methanol, it was dried under vacuum producing white solid material. Polymer (I) was identified by IR, ^1H - and ^{13}C -NMR spectroscopy [18]. Polymer (PII) was insoluble in a wide range of solvents even after prolonged refluxing, although it was freely soluble in acetone which appeared to react with the S-methylhydrazine-carbodithioate moiety. This makes it difficult for it to be used as an

analytical agent. This polymer was readily swollen in excess of CD_3OD to allow ^{13}C -NMR spectrum to be recorded, however it proved difficult to record a good quality high resolution spectrum and hence to deduce the microstructure of the product although the overall features of the structure were clearly those indicated in Scheme 1. The ^{13}C -NMR spectrum kindly recorded by Sabic in Saudi Arabia, showed

signals at about 18 and 22 ppm, which can be assigned to the two kinds of methyl carbons in the repeat unit, unfortunately the spectrum in the range of 43–60 ppm was concealed by the solvent resonances which made it impossible to establish any information about the methine and allylic carbons, and to say any thing positive concerning the tacticity of the polymer. The carbonyl carbons were seen as multiplets centred at 177 and 174 ppm respectively, The carbons of the vinylic region (C5 and C6) are shown at 130 ppm (*cis*) and 134, 135 and 137 ppm (*trans*). The other low intensity signal recorded at 162 ppm is assigned to the C=S carbon atom. These resonances were also reported in the ^{13}C -NMR spectra of the related anhydride, acid and ester functionalised polymers [19–22]. The IR spectrum of polymer (P(II)) was obtained as a film cast from acetone. The principal characteristic bands for this polymer are a band at 3229 cm^{-1} due to the $\nu(\text{NH})$ absorption, CH stretches at 2978 and 2920 cm^{-1} , and bands at 1794 and 1734 cm^{-1} attributed to the C=O vibrations. The spectrum

also shows two bands at 731 and 1267 cm^{-1} assignable to $\nu(\text{C}=\text{S})$ and a combination of $\nu(\text{C}=\text{S} + \nu(\text{N}-\text{C}-\text{N}))(\text{II})$ vibrations. The other thioamide band, $[\nu(\text{C}-\text{N}) + \nu(\text{C}=\text{S})](\text{III})$, are observed at 930 cm^{-1} . The thioketo form (I) is one of the tautomeric forms of P(II) while the band at 1000 cm^{-1} assignable to $\nu(\text{N}-\text{N})$ vibration [23]. Although polymer P(II) was prepared from the precursor polymer P(I), it was not possible to examine the molecular weight of polymer (II) using gel permeation chromatography, polymer (II) was found to react with the metal of the syringe used for injection. The aim of this work is to synthesize a chelating polymer and its polymer complexes. The chelating polymer (P(II)) reacts with metal (II) acetates to give a 2:1 molar ratio of repeating unit: metal giving a neutral complex of general formula $[\text{M}(\text{P(II)-H})_2 \cdot 2\text{H}_2\text{O}]_n$ where $\text{M}=\text{Co}, \text{Ni}, \text{Zn}$, also with copper acetate and copper chloride to give $[\text{Cu}_2(\text{P(II)-H})_3]_n$ and $[\text{Cu}(\text{P(II)-H})(\text{P(II)}_2\text{Cl})_n]$ respectively. In the complexes, the ligand acts as a tetrahedral dibasic (NSSN) donor forming two five-membered rings as shown in structure P(III)

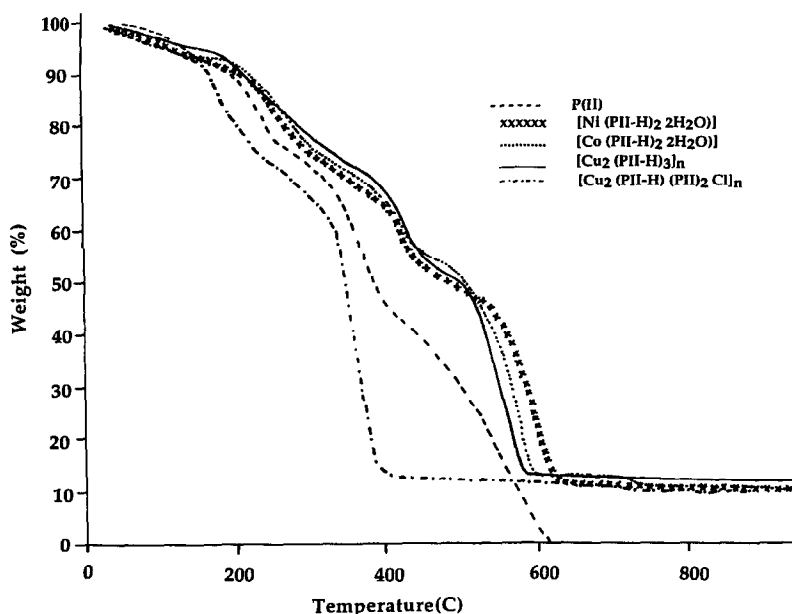


Fig. 3. The TG Thermogram of polymer P(II) and its metal complexes.

for the cobalt(II), nickel(II) and zinc(II) complexes. The complexes produced are stable at room temperature and do not show any decomposition after a long period of standing. They do not possess sharp melting points but appear to decompose above 280°C. They are coloured and insoluble in most available organic solvents, the non-solubility of the isolated polymer complexes in organic solvents indicate their cross-linked natures and do not permit solution physico-chemical studies. The isolated polymer complexes were characterised by elemental analysis, IR, TG and DTA measurement. The result of elemental analysis of all metal complexes polymers are in reasonably good agreement with the calculated values and are summarised in Table 1. Information about the mode of bonding of the metal ions in the isolated complexes can be gained from infrared spectroscopic analysis. An insight into the type of bonding occurring can be achieved by a careful comparison between the IR spectra of the free ligand and their metal complexes. The IR spectra of the complexes isolated from P(II) are all fairly similar; they show a broad band around 3500 cm^{-1} attributed to $\nu(\text{OH})$ along with the disappearance of $\nu(\text{NH})$ and $\nu(\text{C}=\text{S})$. The (N–N) stretching frequency is shifted to 1030 cm^{-1} and two new bands appear at ca. 1560 cm^{-1} and 410 cm^{-1} which can be attributed to $\nu(\text{C}=\text{N})$ and $\nu(\text{M}-\text{N})$ [24]; this evidence suggests nitrogen coordination. The thioamide band I suffers a negative shift upon coordination through nitrogen. Strong evidence for enothiolization is the disappearance of thioamide II and IV bands; this indicates that the $-\text{NH}-\text{C}(\text{S})-$ moiety converts to $-\text{N}=\text{C}(\text{SH})-$ by enothiolization. This phenomenon is also confirmed by the appearance of $\nu(\text{M}-\text{S})$ vibration at 470 cm^{-1} . Finally, the existence of amid bands, which are more or less invariant, indicates that the $\text{C}=\text{O}$ group is not taking part in coordination. The thermal behaviour of Co(II), Ni(II), Zn(II) and Cu(II) complexes of P(II) were studied by TG and DTA. The TG thermograms of M(II) complexes (Fig. 3) show a weight loss at 160°C

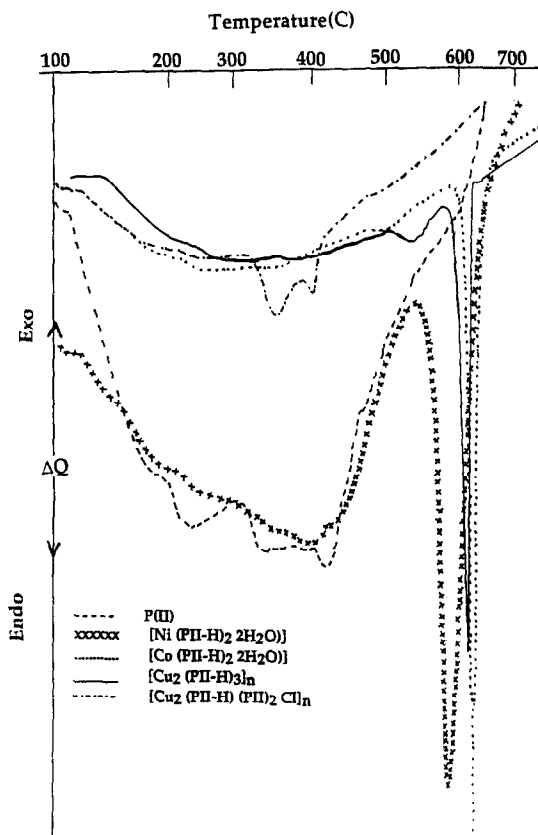


Fig. 4. The DTA Thermogram of polymer P(II) and its metal complexes.

(calc. 5.1%, found 6.0%) corresponding to loss of water from the coordination sphere of the complex. The anhydrous polymer complex begins to decompose from 160°C a process continuing up to 595°C and corresponding to the decomposition of the organic part (calc. 81.02%, found 81.9%). Above 600°C, a stable steady state is observed consequent of the formation of the metal oxides. The remaining mass of oxide is in good agreement with the calculated one. The DTA graph Fig. 4 also shows peaks at 150, 260, 400 and 540°C corresponding to the decomposition of the organic moiety and the formation of metal oxides, all the evidence gathered from IR and thermal studies suggest structure for $[\text{M}(\text{PII}-\text{H})_2 \cdot 2\text{H}_2\text{O}]$ for the polymer complex [25].

4. Conclusion

It was known that substituted polycyclic alkenes could undergo metathesis ring-opening polymerization with catalyst derived from $WCl_6/(CH_3)_4Sn$. The initial objective of this work was to extend the range of monomers which could be polymerized by this technique, in particular using monomer (II) which carries a potentially complexing group. The work reported demonstrates that this kind of monomer is difficult to polymerise via the expected ring-opening polymerization mechanism. The chelating polymer (PII) was prepared from the precursor polymer (PI), it reacts with metal(II) acetates and the isolated polymer–metal complexes were shown to have the general structure $[M(PIV-H) \cdot 2H_2O]$.

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