Order Number 9304734

Zwitterion polymerizations of p-[[2-(oxazolin-2-yl)propyl]phenol and m-[[2-(2-oxazolin-2-yl)propyl]thioand thermal polymerization of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride

Shi, Fang, Ph.D.

City University of New York, 1992

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Ann Arbor, MI 48106

Zwitterion Polymerizations of p-[[2-(Oxazolin-2-yl)propyl]thio]phenol and m-[[2-(2-Oxazolin-2-yl)thio]benzenethiol and Thermal Polymerization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride

by

Fang Shi

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1992

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

5/12/92
Date

George Odian
Chair of Examining Committee

5/13/92
Date

Executive Officer

Supervisory Committee

The City University of New York

Abstract

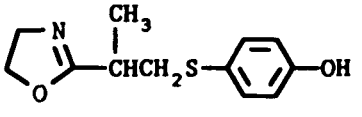
Zwitterion Polymerizations of IPOHTP and IPOBDT

by

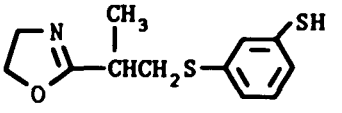
Fang Shi

Adviser: Professor George Odian

Bulk and solution polymerizations of p-[[2-(2-oxazoline-2-yl)propyl]thio]phenol (I) and m-[[2-(2-oxazoline-2-yl)propyl]thio]benzenethiol (II) were studied.



I



II

Polymerization of I occurred in the temperature range of 100-200 °C and gave polymers with two different repeat units and low molecular weight ($\bar{M}_n$ 1,000-3,000). Polymerization of II was studied over the temperature range of -27 to 150 °C and gave polymers with one repeat unit and $\bar{M}_n$ as high as 21,000. Polymerization mechanisms were proposed based on ^1H and ^{13}C NMR results on the chemical structure and end-groups of the polymers.

ACKNOWLEDGMENT

I wish to express sincere thanks to my mentor, Professor George Odian, for his generous support, guidance, patience and kindness during the course of this research.

I would also like to thank Professors Howard Haubenstock and Norman Indictor for their valuable discussions and being so generous on their time.

I gratefully acknowledge financial support of this work under grants from the Petroleum Research Foundation of the American Chemical Society and the PSC-CUNY Research Award Program of the City University of New York.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1.0 Introduction

1.1 Zwitterion Polymerization

Polymer formation via a zwitterion mechanism is a specific case of ionic polymerization in which the propagating species carry opposite charges at chain ends. Zwitterion polymerization can be classified into two categories: one is zwitterion polymerization with catalyst, the other is zwitterion polymerization with no catalyst. Both will be discussed in the following.

1.1.1 Zwitterion Polymerization with Catalyst

Initiation

$$X + M \rightleftharpoons {}^{+}XM^{-}$$
$$Y + M \rightleftharpoons {}^{-}YM^{+}$$

Propagation

$${}^{+}XM_nM^{-} + M \longrightarrow {}^{+}XM_{n+1}M^{-}$$
$${}^{+}YM_nM^{-} + M \longrightarrow {}^{+}YM_{n+1}M^{-}$$

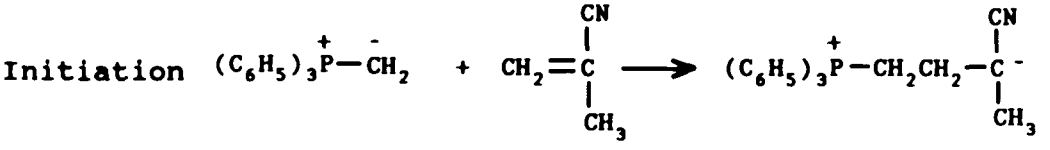
Termination (by added ion transfer agents)

$${}^{+}XM_{n+1}M^{-} + HA \longrightarrow (A^{-})({}^{+}XM_{n+1}MH)$$
$${}^{-}YM_{n+1}M^{+} + BOH \longrightarrow (B^{+})({}^{-}YM_{n+1}MOH)$$

Two types of monomers, vinyl monomers and strained ring monomers, will be discussed in this category.

1.1.1.1 Vinyl Monomers

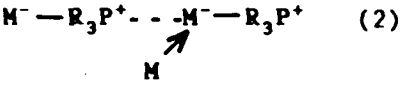
Klippert and Ringsdorf[1,2] investigated the methacrylonitrile polymerization initiated with triphenylphosphonium methylide.

Initiation 

Propagation

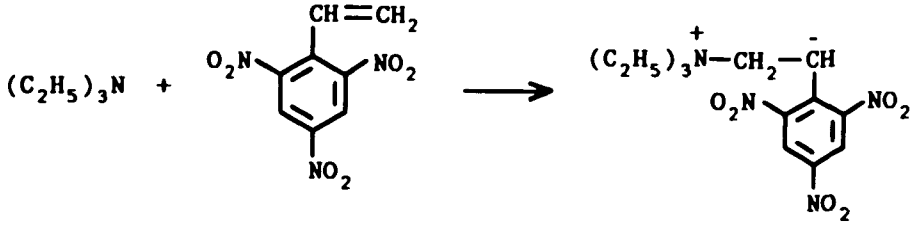
Two propagation steps are considered: insertion into the intramolecular ion pair macrocycle (1) or into the linear aggregate (2).

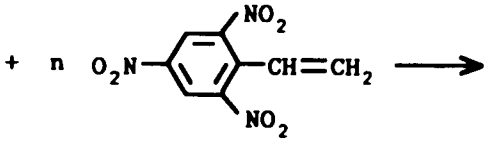
 (1)

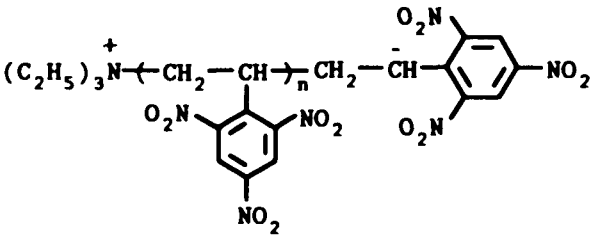
 (2)

The authors favor reaction (2), because they believe that steric hindrance would make the formation of oligomeric rings from α-methyl vinyl compounds very difficult.

Another vinyl monomer is 2,4,6,-trinitrostyrene which was polymerized with tertiary amines[3]. The following mechanism is suggested.





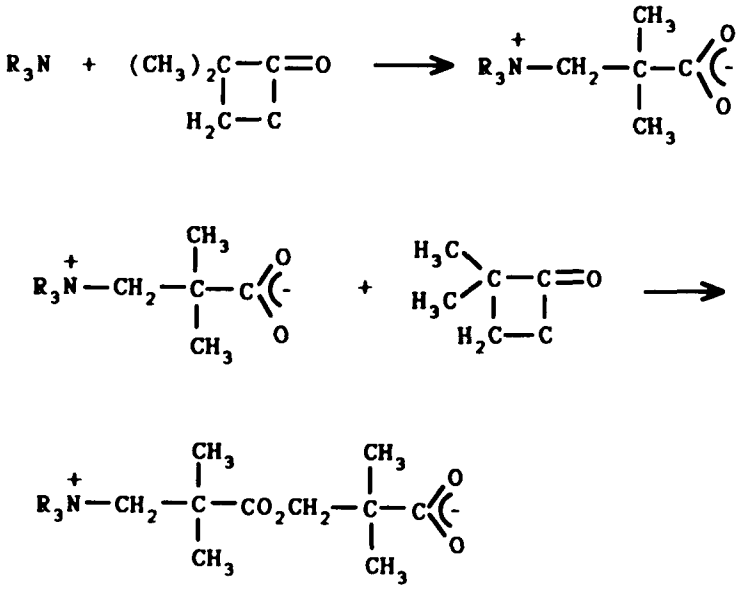


2-Vinyl- and 4-vinylpyridines and 4-dimethylaminostyrene copolymerize with 2,4,6-trinitrostyrene without added initiator. The authors concluded that zwitterion formation is the first step. These polymerizations seem to be analogous to those with strained ring monomers and will be described later.

Other vinyl monomers, such as acrylonitrile[4,5], acylic acid[6], nitroethylene[7], diethylmethylenemalonate[8,9], alkyl 2-cyanoacrylates[10-12], methylenemalononitrile[13], methyl vinyl ether[14], have been also studied and reported. Their polymerizations appear to proceed via zwitterions, similar with the one for methacrylonitrile and 2,4,6-trinitrostyrene.

1.1.1.2 Strained Ring Monomers

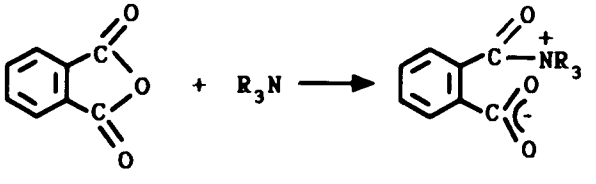
Of the cyclic monomers which polymerize via zwitterions lactones are the most studied group. Etienne and Soulas[15] studied the polymerization of α,α-disubstituted, and α,α,β-trisubstituted derivatives as well as unsubstituted derivatives. Amines like triethylenediamine with readily accessible nitrogen atoms are especially effective initiators. In the presence of such amines lactones form high molecular weight polymer.



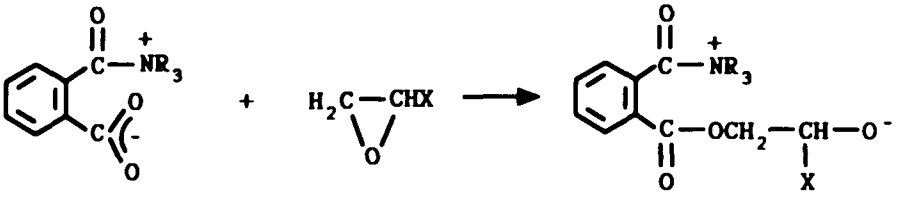
By comparison unsubstituted lactones such as propiolactone polymerize more slowly and molecular weights are lower. The authors believe that propagation is slower, the carboxylate anion formed from pivalolactone ring opening being more nucleophilic because of the inductive effect of the two methyl substituents.

An equimolar mixture of epoxide and cyclic anhydride has the stoicheometry of a polyester. Fisher[16] has shown that if a tertiary amine is added to such a mixture, maintained at 70-100 °C, epoxide and anhydride disappear at identical rates to yield polyester. The following scheme is proposed.

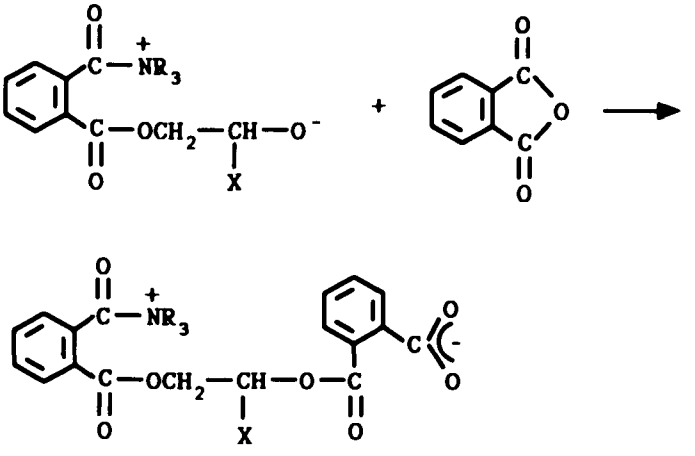
Zwitterion formation:



Reaction of carboxylate anion with epoxide:



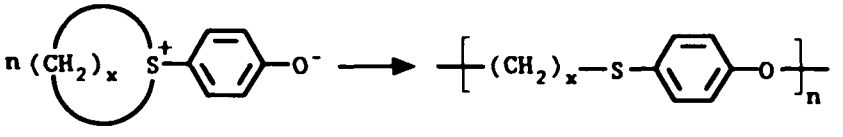
Reaction of alkoxide anion with anhydride:



1.1.2 Zwitterion Polymerization with No Catalyst

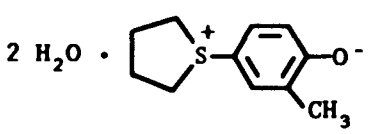
1.1.2.1 Zwitterions are isolable

Schmidt and our group[17-21] have succeeded in synthesizing isolable zwitterions which polymerize when heated.

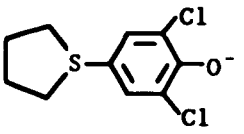


(3)

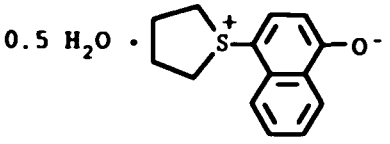
The polymerization of the following zwitterions have been studied in detail.



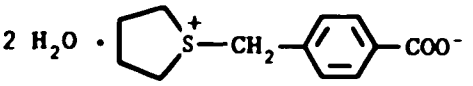
I



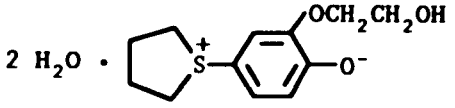
II



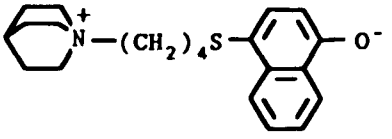
III



IV

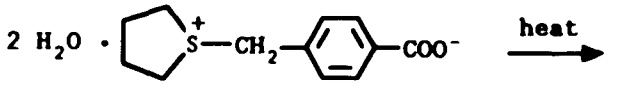


V

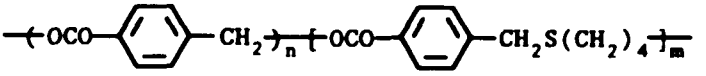


VI

Zwitterions I, III, IV and V were isolated as hydrates while zwitterions II and VI could be isolated in anhydrous form. These zwitterions polymerize through a ring opening mechanism where the anion attacks the α-carbon of the tetrahydrothiophenium ring or quinuclidinium ring to form an alternating copolymer. Odian, O'Callaghan and coworkers reported that the polymerization[20] of zwitterion V resulted in polymer with molecular weight of 67,800 which represents the highest yet to be reported for a zwitterion polymerization. Gunatillake, Odian and Schmidt reported that zwitterion IV was isolated as a hydrate and on polymerizing resulted in the formation of random copolymer VII.



IV



(4)

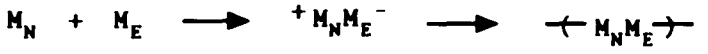
VII

The polymerization proceeds by attack of the carboxylate anion on either the benzylic carbon or α-carbon of the tetrahydrothiophenium ring. The copolymer was rich in the oxycarbonyl-1,4-phenylenemethylene unit. Molecular weight as high as 41,000 was obtained.

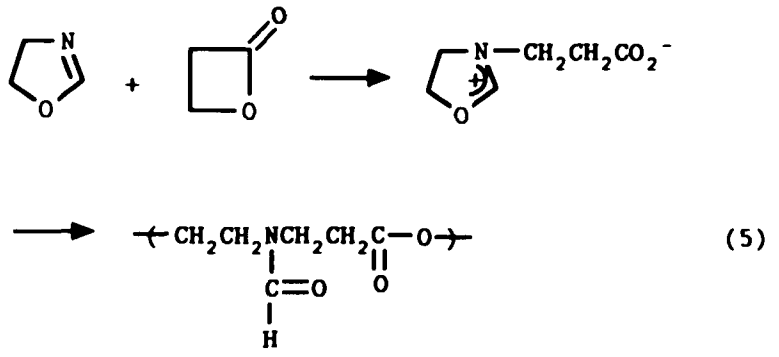
1.1.2.2 Zwitterions are not isolable

1.1.2.2.1 Spontaneous Alternating Copolymerization

An equimolar mixture of a nucleophile (M_N) and an electrophile (M_E) undergoes spontaneous alternating copolymerization.

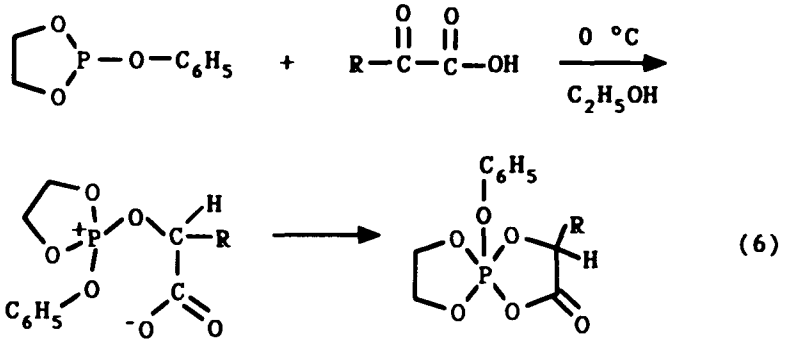


Saegusa[22-32] et al have used this method to produce a wide range of alternating copolymers. For instance a quantitative yield of alternating copolymer is obtained when equimolar amounts of 2-oxazoline and β-propiolactone are mixed in an aprotic solvent at room temperature.



(5)

Macrocycles were not detected among any of the products. However, cyclization of the initial zwitterion did occur with the two dioxaphospholane nucleophiles and several electrophiles[33], e.g.



(6)

The nucleophiles and electrophiles which have been studied for spontaneous alternating copolymerization are listed in Table 1-1 and Table 1-2, respectively.

Table 1-1

The Nucleophiles for Spontaneous Alternating Copolymerization

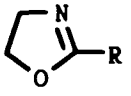
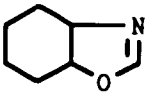
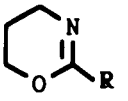
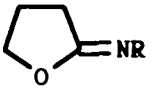
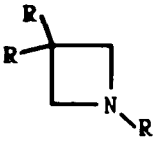
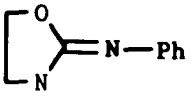
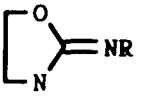
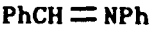
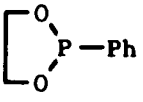
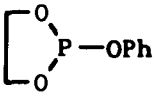
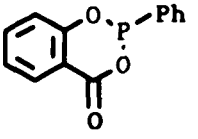
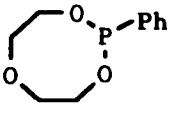
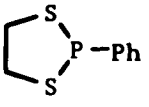
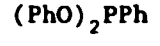
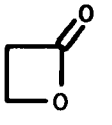
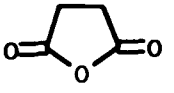
			
oxazoline	oxazoline	oxazoline	imine
			
amine	imine	imine	imine
			
dioxaphosphine	dioxaphosphine	dioxaphosphine	dioxaphosphine
			
dithiaphosphine	dioxaphosphine	trioxaphosphine	

Table 1-2

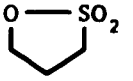
The Electrophiles for Spontaneous Alternating Copolymerization



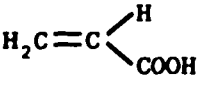
lactone



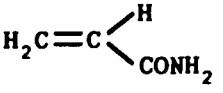
anhydride



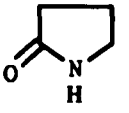
sulfonate



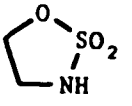
allyl acid



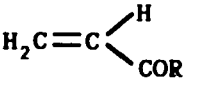
allyl amide



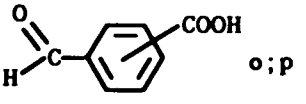
lactam



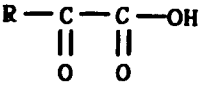
aminosulfonate



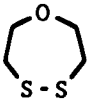
allyl ketone



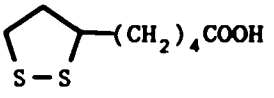
aldehyde



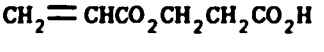
carbonyl acid



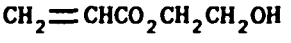
disulfide



disulfide

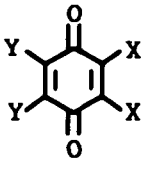


allyl ester

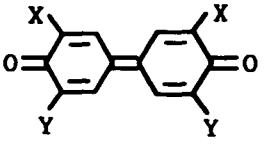


allyl ester

vinyl sulfonamide



quinone



quinone

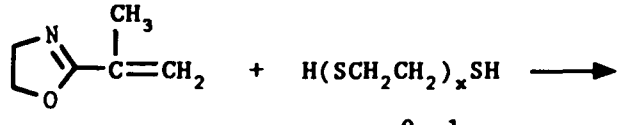
These spontaneous alternating copolymerizations give polymers with molecular weight no higher than a few thousands.

1.1.2.2.2 Nonionic Adduct of a Nucleophile and an Electrophile Is Isolable

This type of polymerization is illustrated in the following scheme.

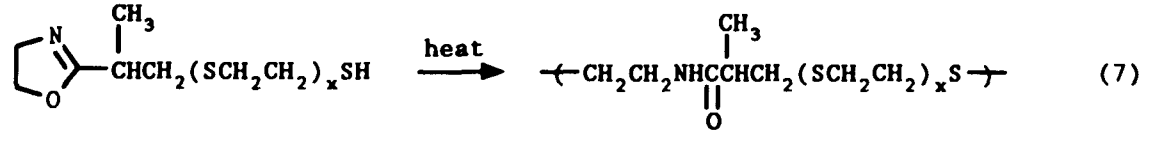
$$M_N + M_E \longrightarrow M_N M_E \text{ (adduct)} \xrightarrow{\text{heat}} [{}^{+}M_N M_E^{-}] \longrightarrow \text{-}(M_N M_E)\text{-}$$

Tomalia and our group[34-37] have studied two systems in this area. The first system was the polymerization of 2-isopropenyl-2-oxazoline and H_2S or 1,2-ethanedithiol.



$x = 0, 1$

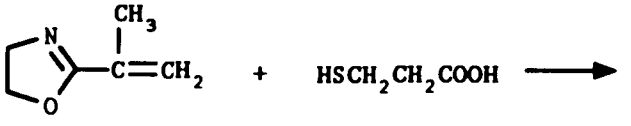
VIII IX



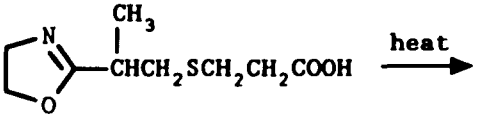
X XI (7)

The adduct (X), when x = 0, was isolated as a colorless liquid with bp 51 °C/0.01 torr, and polymerized upon heating with no catalyst. All polymerization reactions proceeded with near quantitative conversion (ca. 98%) of adduct to polymer. The

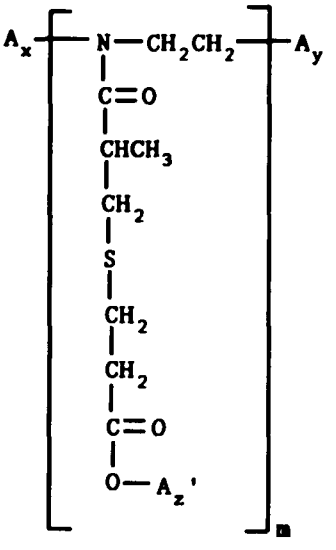
molecular weights as high as 42,900 were reported which is the highest reported under this type of polymerization. The second system was the polymerization of 2-isopropenyl-2-oxazoline and 3-mercaptopropionic acid.



VIII XII



XIII



XIV (8)

where A = $-OCOCH_2CH_2SCH_2CH(CH_3)CONHCH_2CH_2-$, and A′ = $-CH_2CH_2NHCOCH(CH_3)CH_2SCH_2CH_2COO-$. A and A′ have the same structure, but their directions in the polymer structure are opposite of each other. The polymer was broken down by

hydrolysis and found no homosequences of branched sites (i.e., m = 1). The percent branching, defined as the number of branch units multiplied by 100% and divided by the total number of repeat units, vary from 3% to 34% depending on polymerization condition. The molecular weights reported on this system were low ranging from 1,050 to 3,370.

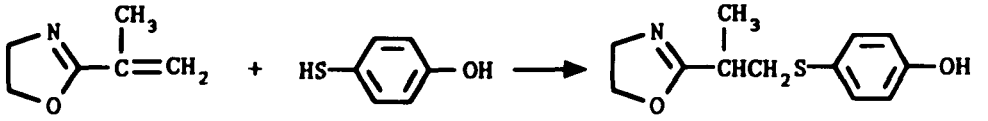
1.2 Scope of Present Work

1.2.1 Zwitterion Polymerizations of p-[[2-(2-oxazolin-2-yl)propyl]thio]phenol (System I) and m-[[2-(2-oxazolin-2-yl)propyl]thio]benzenethiol (System II)

This work is a continuation of the previous work[34-37] on no catalyst zwitterion polymerization with isolable adduct (Section 1.1.2.2.2). Of the two studied systems the first gave high molecular weight polymer, and the second gave low molecular weight polymer. This work is aimed at studying the polymerization mechanism and preparing high molecular weight polymers. Two systems will be studied. System I is the polymerization of 2-isopropenyl-2-oxazoline (IPO) and 4-hydroxythiophenol (HTP); System II is the polymerization of 2-isopropenyl-2-oxazoline (IPO) and 1,3-benzenedithiol (BDT). In System I, the adduct of IPO and HTP will be referred to as IPOHTP, and the zwitterion and the polymer derived from IPOHTP as IPOHTP zwitterion and IPOHTP polymer, respectively. In System II, the adduct of IPO and BDT will be referred to as IPOBDT, and the zwitterion and the polymer as IPOBDT zwitterion

and IPOBDT polymer, respectively.

System I:

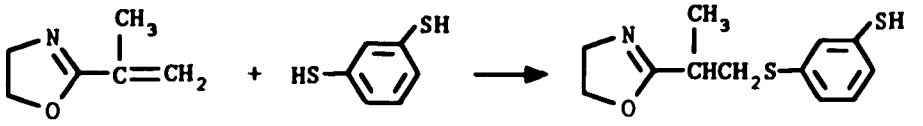


(9)

VIII XV XVI

→ IPOHTP polymers

System II:



(10)

VIII XVII XVIII

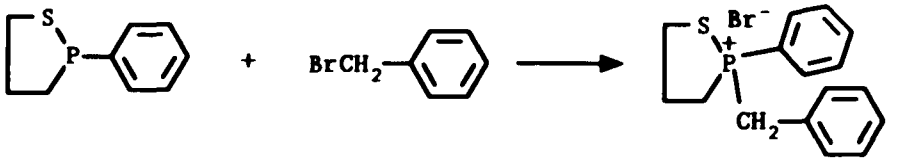
→ IPOBDT polymers

The two adducts are aromatic analogues of the previously studied adducts. The two adducts have very similar chemical structures -- the difference between the two is the nucleophilic centers, one is —OH, the other —SH. We were interested to see the difference of the two adducts in polymerization behavior.

1.2.2 Thermal Polymerization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride

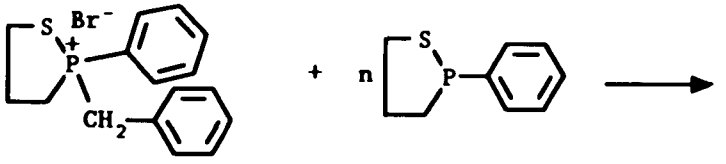
This work proposed to develop further our study of no catalyst zwitterion polymerization with isolable zwitterions (Section 1.1.2.1). In the previously studied isolable zwitterions, nitrogen and sulfur served as electrophilic centers. The objective of this work was to synthesize an

isolable zwitterion with phosphorus as an electrophilic center. Based on the cationic polymerization (11 and 12) of 2-phenyl-1,2-thiaphospholane (XIX) with benzyl bromide (XX) and the reaction (13) of tetrahydrothiophene (XXIII) and 4-chloromethyl benzoic acid (XXIV),

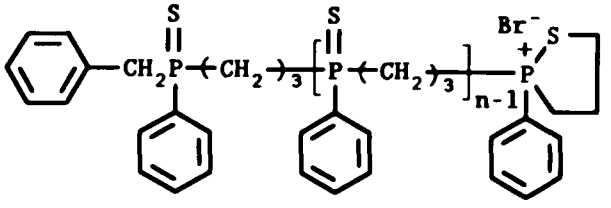


(11)

XIX XX XXI

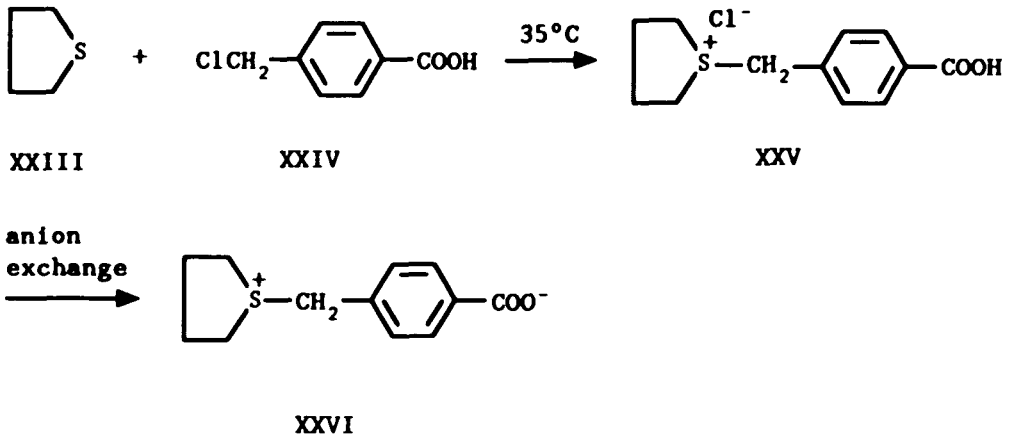


XXI XIX



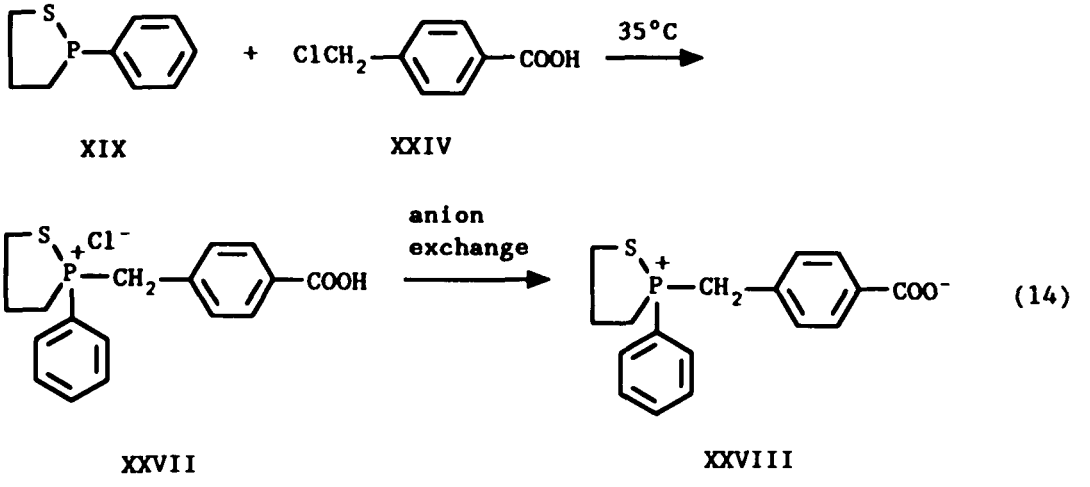
(12)

XXII



XXIII XXIV XXV XXVI (13)

the following reaction route (14) was designed to prepare the isolable zwitterion with phosphorus as an electrophilic center.



XIX XXIV XXVII XXVIII (14)

2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride (XXVII) was successfully made but not stable enough to make the speculated zwitterion XXVIII. The thermal polymerizations of XXVII were carried out and reported in this work.

2.0 Experimental

2.1 Purification of Solvents and Reagents

2-Isopropenyl-2-oxazoline (Dow) was dried over activated 3 Å molecular sieves for 4 days at room temperature with a small amount of 3,5-di-t-butyl-4-hydroxyanisole added and then distilled under reduced nitrogen atmosphere (40 torr). The distillate at 67 °C was collected and stored under nitrogen in a freezer. 4-Hydroxythiophenol and 1,3-benzenedithiol (Aldrich) were used as received. Triethylamine and pyridine (Aldrich, A.C.S. reagent) were dried over CaH_2 and then distilled. Acetic anhydride (Aldrich, A.C.S. reagent) and bromine (Fisher, reagent A.C.S.) were used as received. Tetrahydrofuran (THF) and ether were refluxed and then distilled over calcium hydride and sodium, respectively. Acetonitrile and N,N'-dimethylformamide (DMF) were dried over activated 3 Å molecular sieves for a week and distilled under reduced nitrogen atmosphere. Thiolacetic acid, allyl chloride, dichlorophenyl phosphine, 4-chloromethyl benzoic acid and lithium rod were used as received from Aldrich.

2.2 Synthesis of IPOHTP

4-Hydroxythiophenol and 2-isopropenyl-2-oxazoline were separately dissolved in acetonitrile to make 30 vol-% solutions, respectively. To 4-hydroxythiophenol solution cooled in ice-water bath was added 2-isopropenyl-2-oxazoline

solution dropwise with stirring under dry nitrogen atmosphere. After the addition the reaction mixture was allowed to stand at room temperature for another 30 min and then left in a refrigerator overnight. The precipitate was filtered and washed with ice-cold acetonitrile once and then ether twice to give IPOHTP as a white powder. The crude IPOHTP was purified by recrystallization in acetonitrile and dried in vacuum at room temperature for 2 h. The overall yield was 85%.

2.3 Bulk Polymerization of IPOHTP

The polymerizations were carried out at 100, 150 and 200 °C. In the typical run, 0.5 g of IPOHTP was heated in a polymerization tube under vacuum (0.1 torr) at 70 °C for 2 h, the tube sealed and heated at 100 °C for 96 h, 150 °C for 24 h or 200 °C for 2 h. The polymer prepared at 100 °C was a colorless transparent solid and became a white powder after purification by dissolving in the minimum amount of N,N'-dimethylformamide, precipitation by adding to a 15-fold excess of ether and drying in vacuum at 60 °C overnight. The polymers made at 150 and 200 °C were yellowish powders after the purification. The overall yield was 100%, 90% and 70%, respectively, for the polymerizations at 100, 150 and 200 °C.

2.4 Solution Polymerization of IPOHTP

About 0.4 g of IPOHTP was dissolved in 0.4 g of dry DMF, bubbled with dry nitrogen, degassed by freeze-pump-thaw

cycles. The tube was then sealed under vacuum and kept in a hot oil bath over a period of 96 h. The polymer was isolated by pouring the reaction mixture into 15-fold excess of ether, washing the precipitate with ether three times and drying under vacuum at 60 °C overnight to give a paste-like solid. The overall yield was 60%.

2.5 Acetylation of IPOHTP Polymers

About 0.5 g of IPOHTP polymer was dissolved in a minimum amount of DMF. To the resultant solution 3 ml of triethylamine was added dropwise at room temperature with stirring followed by 2 ml of acetic anhydride. The solution was heated up to 90 °C for 5 min, then cooled down to room temperature. The acetylated polymer was precipitated out in 20 ml of water. After washing with water and drying under vacuum at 60 °C overnight, the polymer was again dissolved in a minimum amount of DMF, precipitated out in water and dried under vacuum at 60 °C overnight.

2.6 Bromination of IPOHTP Polymers

About 0.05 g of IPOHTP was dissolved in 0.3 ml of DMSO-d_6 in a NMR tube to make a 17% (w/v) solution. To this solution 4 drops of bromine was added and the solution became dark red. After shaking for 2 min, the solution was checked by ^{1}H NMR spectroscopy.

2.7 Synthesis of IPOBDT

Equimolar amounts of IPO and BDT were separately

dissolved in acetonitrile to make 60 vol-% solutions. To the BDT solution the IPO solution was added dropwise at 0 °C. The reaction was complete immediately after the addition with a small portion of IPOBDT polymerized. The product was not isolated from its solution due to difficulties to do so. The effort was made to isolate IPOBDT by (i) cooling its solution in a freezer, nothing crystallizing out; (ii) evaporating the solvent, resulting in about 60% of IPOBDT polymerized.

2.8 Solution Polymerization of IPOBDT

Equimolar amounts of IPO and BDT were separately dissolved in acetonitrile. To the BDT solution the IPO solution was added dropwise at 0 °C under dry nitrogen. Without isolating the adduct the solution was kept at the desired temperature for 96 h under nitrogen. The precipitated polymer was washed three times with ether and dried under vacuum overnight at room temperature, and a white foam-like polymer was obtained in an overall yield of above 98%. With this procedure, the polymers were prepared at temperatures of -27, 0, ambient (ca. 25) and 70 °C.

The polymerization was also conducted in tetrahydrofuran at -27, 0, ambient (ca. 25) and 70 °C. IPO and BDT in a 1:1 molar ratio were separately dissolved in tetrahydrofuran (60 vol-%). To the BDT solution IPO solution was added dropwise at 0 °C under nitrogen. 5 min after the addition, aliquots of the mixture were allowed to stand at -27, 0 and ambient (ca. 25) and refluxed at 70 °C

under nitrogen for 96 h. The polymer stayed in solution during the polymerization. The polymer was purified by pouring into a 15-fold excess of ether, washing with ether three times and drying at room temperature overnight to give a pure white solid. The overall yield was around 95%.

N,N'-dimethylformamide was used as a solvent for solution polymerization at -27, 0, ambient (ca. 25), 70 and 150 °C. Equimolar amounts of IPO and BDT in a concentration of 60 vol-% were mixed together at 0 °C under dry nitrogen with stirring. For the polymerization at -27, 0, ambient (ca. 25) and 70 °C the resultant mixture was kept at the desired temperature under nitrogen for 96 h; for the polymerization at 150 °C, the resulting mixture was transferred to a polymerization tube, bubbled with nitrogen, cooled in a dry ice-acetone bath, sealed in vacuum (0.1 torr) and sit in a hot oil bath for 96 h. The polymer was purified by pouring to 15-fold excess of ether, washing with ether three times and drying under vacuum oven at 50 °C overnight. All the polymers were pure white after purification. The polymerization was a homogeneous reaction with a yield of above 95%.

2.9 Bulk Polymerization of IPOBDT

2-Isopropenyl-2-oxazoline and 1,3-benzenedithiol in a 1:1 molar ratio were separately dissolved in ether (20 vol-%). The solution of 2-isopropenyl-2-oxazoline was added to 1,3-benzenedithiol solution dropwise at 0 °C under dry nitrogen. About 5 min after the addition was complete, the

ether was evaporated by rotavapor at room temperature and the residue was transferred to a polymerization tube, sealed under vacuum at -78 °C and heated at -27, 0, ambient (ca. 25), 70, 150 °C for 96 h. All the polymers were purified by dissolving in tetrahydrofuran, precipitation by ether, washing three times with ether and drying under vacuum at room temperature overnight to yield a white foam-like polymer. The overall yield was around 95%.

2.10 Acetylation of IPOBDT Polymers

About 0.2 g of IPOBDT polymer was dissolved in 4 ml of dry THF, and to it 0.2 ml of pyridine (distilled over CaH_2) was added. To this mixture 0.4 ml of acetyl chloride in 2 ml of THF was added dropwise at 0 °C. The polymer gradually precipitated out during the addition. The reaction mixture was stirred for another 30 min after the addition. After decanting the solution, the polymer was washed with distilled water once, 1M HCl twice, 1M NaOH twice and water again twice and then dried in a vacuum oven at 50 °C overnight. This crude product was dissolved in THF and added to a large amount of water to precipitate the polymer. After washing with water three times and drying in a vacuum oven at 50 °C overnight, a white solid was obtained.

2.11 Bromination of IPOBDT Polymers

About 0.10 g of IPOBDT polymer was dissolved in 0.3 ml of DMSO-d_6 in a NMR tube to make a 34% (w/v) solution. To this solution 4 drops of bromine was added and the solution

became dark red. After shaking for 2 min, the solution was checked by ^1H NMR spectroscopy.

2.12 Synthesis of 3-Chloropropyl Thiolacetate

25.4 g (1/3 mole) of thiolacetic acid was added to 25.5 g (1/3 mole) of allyl chloride dropwise at 0 °C with stirring. The mixture was refluxed at 60 °C under a UV light. The reaction was monitored by thin layer chromatography and found the reaction complete after refluxing for 1 h. The product contained a small amount of impurities which could not be removed by fractional distillation. This crude product was used for the preparation of 3-chloropropanethiol without further purification. The yield was 100%.

2.13 Synthesis of 3-Chloropropanethiol

Methanol (25 ml) was mixed with 12.3 g of 3-chloropropyl thiolacetate and 5 drops of concentrated sulfuric acid at room temperature with vigorous stirring. The mixture was heated at 60 °C under dry nitrogen for 6 h, then concentrated and distilled under vacuum to give 7.0 g of crude 3-chloropropanethiol with bp 81-82 °C/7 torr. This crude 3-chloropropanethiol was further purified by silica gel chromatography. The overall yield was 38%.

2.14 Synthesis of 2-Phenyl-1,2-thiaphospholane

Under dry nitrogen, to a mixture of dichlorophenyl phosphine (24 ml), pyridine (15 ml) and tetrahydrofuran (100

ml) was slowly added 17.3 ml of 3-chloropropanethiol in 60 ml of tetrahydrofuran at 0 °C with vigorous stirring. After refluxing for 1 h, the precipitate of pyridinium hydrochloride was removed by filtration. The filtrate was cooled to -78 °C and to it 2.47 g of lithium metal pieces were added. This mixture was stirred at -78 °C overnight and then allowed gradually to warm up to room temperature. The solution was filtered through a piece of glass wool and concentrated on rotavapor at room temperature. To this residue about 300 ml of ether was added slowly to extract the product. The mixture was stirred at 0 °C until a clear solution separated from the precipitate (LiCl and polymeric product). After sitting for 12 h, the solution was decanted to another flask and concentrated to 30 ml and then vacuum distilled (0.1 torr). The distillate from 105-106 °C was collected to give 5.6 g of 2-phenyl-1,2-thiaphospholane in a yield of 17%.

2.15 Synthesis of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride

4-Chloromethyl benzoic acid (1.0 g, 0.0059 mole) was dissolved in 4.5 g of tetrahydrofuran. To the resultant mixture 6.4 g (0.0354 mole) of 2-phenyl-1,2-thiaphospholane was added dropwise at room temperature to yield a clear solution. Sealed under nitrogen, the mixture was kept at 35 °C for 48 h. The resulting light green solid was filtered, washed with tetrahydrofuran and then ether, and dried under vacuum at room temperature to yield the first crop of

product (1.5 g). The filtrate was concentrated and to it 1.0 g of 4-chloromethyl benzoic acid was added. The resulted solution was sealed under nitrogen and kept at 35 °C for 48 h. The solid was filtered out, washed and dried to give the second crop of product (1.0 g). The filtrate was concentrated again and to it 1.0 g of 4-chloromethyl benzoic acid was added. The solution was kept under nitrogen at 35 °C for 72 h to form the third crop of product (0.8 g). The overall yield was 37%. The crude product was dissolved in the minimum amount of methanol at room temperature, followed by adding ether to slight cloudiness, and then kept in a freezer (ca. -27 °C) to crystallize out 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride as a light green powder.

2.16 Thermal Polymerization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride

Thermal polymerizations of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride were carried out under continuous vacuum and in vacuum-sealed tubes, respectively. In the typical run, 0.5 g of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride was heated under continuous vacuum (0.1 torr) or sealed under vacuum (0.1 torr) and heated at 70, 100, or 150 °C for 6 or 24 h.

2.17 ^{1}H and ^{13}C NMR spectroscopy

All the ^{1}H and ^{13}C NMR spectra were recorded on an IBM WP 200SY FT-NMR spectrometer with a 5 mm dual $^{13}C/^{1}H$ probe. The magnetic field was 200.1 Hz for ^{1}H and 50.3 Hz for ^{13}C. ^{1}H and ^{13}C spectra were obtained at 27 °C with 10-20% (w/v) solution in DMSO-d_6 and 1,1,2,2-tetrachloroethane-d_2. Me_4Si was used as an internal reference for both ^{1}H and ^{13}C NMR. The acquisition parameters for ^{1}H NMR were 30° pulse angle, 4.1 second relaxation delay and 128 scans. The acquisition parameters for ^{13}C NMR were 30° pulse angle, 2.6 second relaxation delay and 5000-20,000 scans. Data were acquired and Fourier transformed in 16K.

2.18 Distortionless Enhancement by Polarization Transfer Spectroscopy (DEPT)

The pulse sequence of DEPT was the following:

^{1}H: D1 -- 90 -- D2 -- 180 -- D2 -- P0 -- D2 -- BB

^{13}C: ---------- 90 --------- 180 ------- FID

where D1 is ^{1}H relaxation delay, 1-5 T_1 for ^{1}H; D2 is J(C-H) evolve, 0.5/J(C-H) for optimum polarization; P0 is variable depending on desired multiplicity selection. In this experiment, a D1 of 5 second and D2 of 0.0033 second were used; P0 was 135° ^{1}H pulse, so methyl and methine groups gave positive peaks, methylene groups gave negative peaks and quaternary carbons were absent; Decoupling power was 10H; 90° pulse width of ^{1}H and ^{13}C were 16 μs and 15 μs in DMSO-d_6, respectively. The spectrum was taken at room

temperature in a concentration of 20% (w/v) in DMSO-d_6.

2.19 ^1H-^1H Correlated Spectroscopy (COSY)

The COSY spectrum was obtained with 10% (w/v) solution of DMSO-d_6 at 27 °C by using the following pulse sequence:

^1H: D1 -- 90° -- D0 -- 90° -- FID

A total of 256 experiments of 1K data points were collected. 16 scans were obtained for each experiment with sweep width of 1590 Hz for IPOHTP. D1, a relaxation delay between scans was 1 second. The data were processed on a Sun work station. The FIDs were treated by phased shifted sine apodization with a phase of 0.5, end point of 1 and an integer exponent of 2 for both Fourier transformations. The spectrum was plotted as a contour map.

2.20 Infrared Spectroscopy (IR)

Fourier Transfer Infrared (FT-IR) spectra were recorded on a Bio-Rad Digilab Division FT Infrared Spectrometer, Model FTS-40, using 16 scans and resolution of 8 cm^{-1}. The samples were mixed with dry KBr at a concentration of 3 wt-% and pressed to form pellets.

2.21 Elemental Analysis

The samples of IPOHTP, IPOHTP polymer and IPOBDT polymer were sent to Desert Analytics for elemental analysis.

2.22 Molecular Weight Measurements

2.22.1 Gel Permeation Chromatography (GPC)

The molecular weight of the various polymer samples was measured at 100 °C on a Waters 150C instrument with 840 workstation using dry N,N'-dimethylformamide containing 0.05M LiBr as the mobile phase at a flow rate of 1.0 ml/min. LiBr was used to prevent polymer samples from stuck on the columns. A set of four ultrastyragel columns of 10^5, 10^4, 10^3 and 5×10^2 Å sizes constituted the stationary phase. The calibration was done with polystyrene standards with molecular weight ranging from 1,800 to 3,000,000.

2.22.2 Vapor Pressure Osmometry (VPO)

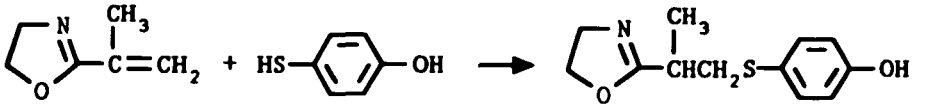
The number-average molecular weights of all IPOHTP polymers and some IPOBDT polymers were determined on a UIC 070 Vapor Pressure Osmometer coupled with UIC Semi-Automatic Osmometer Control Unit. The instrument was calibrated with benzil (dried at 50 °C under vacuum for 10 h) in a concentration range of 0.009-0.03 mol/Kg. The solvent was DMF and the temperature was 90 °C for IPOHTP polymers and the polymers of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride. The solvent was tetrahydrofuran and the temperature was 45 °C for IPOBDT polymers. The concentration of the samples ranges from 60-120 g/Kg.

2.23 Thermal Gravimetric Analysis (TGA)

TGA was obtained on a Du Pont 990 Thermal Analyzer and 950 Thermogravimetric Analyzer at a heating rate of 10 °C/min and nitrogen flow rate of 60 ml/min.

3.0 Results and Discussion on Zwitterion Polymerization of IPOHTP (System I)

3.1 Synthesis of IPOHTP (XVI)



(9)

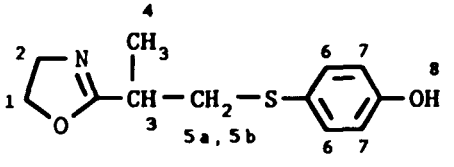
VIII XV XVI

Adduct IPOHTP (XVI) was prepared from IPO (VIII) and HTP (XV) in acetonitrile at a concentration of 30 vol-% at 0 °C under nitrogen atmosphere. IPOHTP was a white powder with mp of 91 °C after recrytallization from acetonitrile.

3.2 Characterization of IPOHTP

The chemical structure of IPOHTP was determined by ^{1}H and ^{13}C NMR spectroscopy, 2D-COSY and elemental analysis.

The ^{1}H NMR spectrum in DMSO-d_6 (Figure 3-1) supports structure XVI.



XVI

The singlet at 9.7 ppm is assigned to proton 8. The two doublets at 7.28 ppm and 6.73 ppm are aromatic protons 6 and 7,

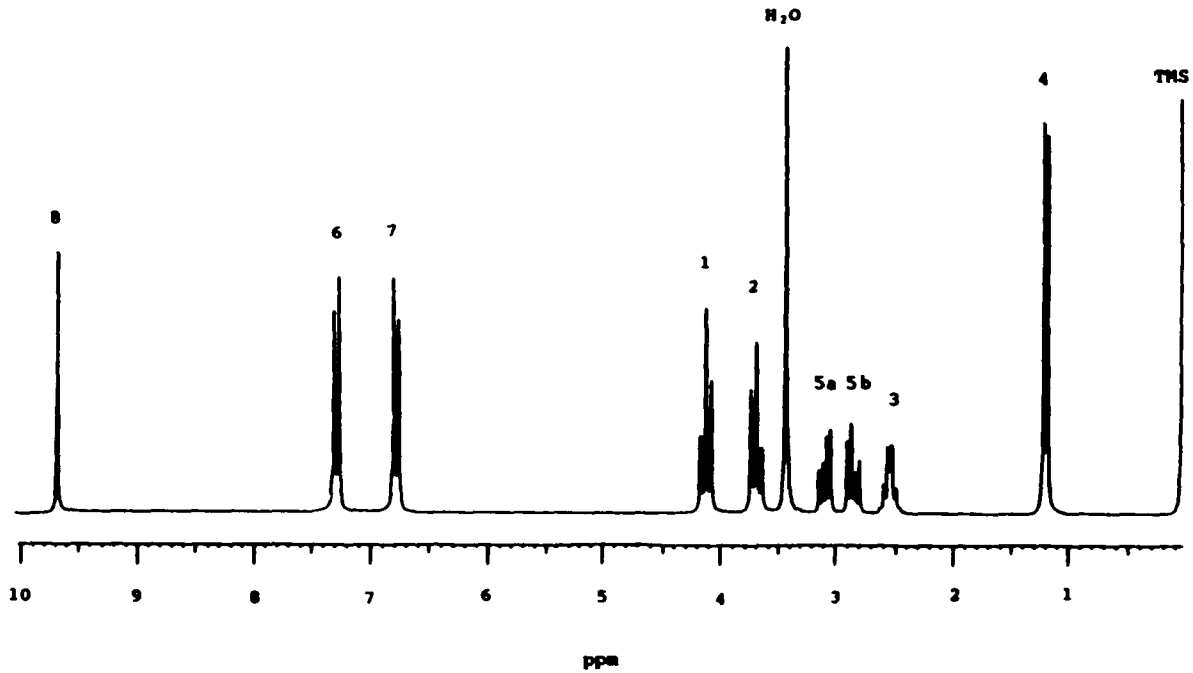
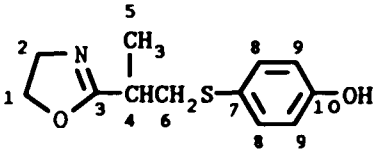


Figure 3-1 200.1 MHz ^{1}H NMR spectrum of IPOHTP in DMSO-d_6 at 27 °C

respectively. The triplets at 4.12 ppm and 3.69 ppm are protons 1 and 2, respectively. The multiplet at 2.54 ppm is proton 3. The two quartets centered around 2.95 ppm are due to the methylene protons numbered 5a and 5b. The complex splitting patterns of protons 3, 5a and 5b result from an ABX system due to the chiral carbon center that proton 3 is attached to. The doublet at 1.19 ppm is proton 4. The assignment of protons 3, 5a and 5b was confirmed by the homonuclear decoupling NMR spectrum (Figure 3-2). As proton 3 was decoupled, protons 5a and 5b became an AB system showing two doublets at 3.06 ppm and 2.82 ppm, respectively, and proton 4 became a singlet at 1.15 ppm. Protons 2, 3, 5a and 5b gave different splitting patterns in $CDCl_3$ (Figure 3-3) compared to DMSO-d_6. Proton 2 was a complex multiplet in $CDCl_3$ instead of a triplet in DMSO-d_6. Protons 3, 5a and 5b in $CDCl_3$ became an ABC system showing a multiplet located at 3.08 ppm and another multiplet at 2.81 ppm. The multiplet at 3.08 ppm is due to 5a, and the multiplet at 2.81 ppm is protons 5b and 3 overlapped together.

The ^{13}C NMR spectrum (Figure 3-4) supports the structure XVI as shown in Table 3-1.



XVI

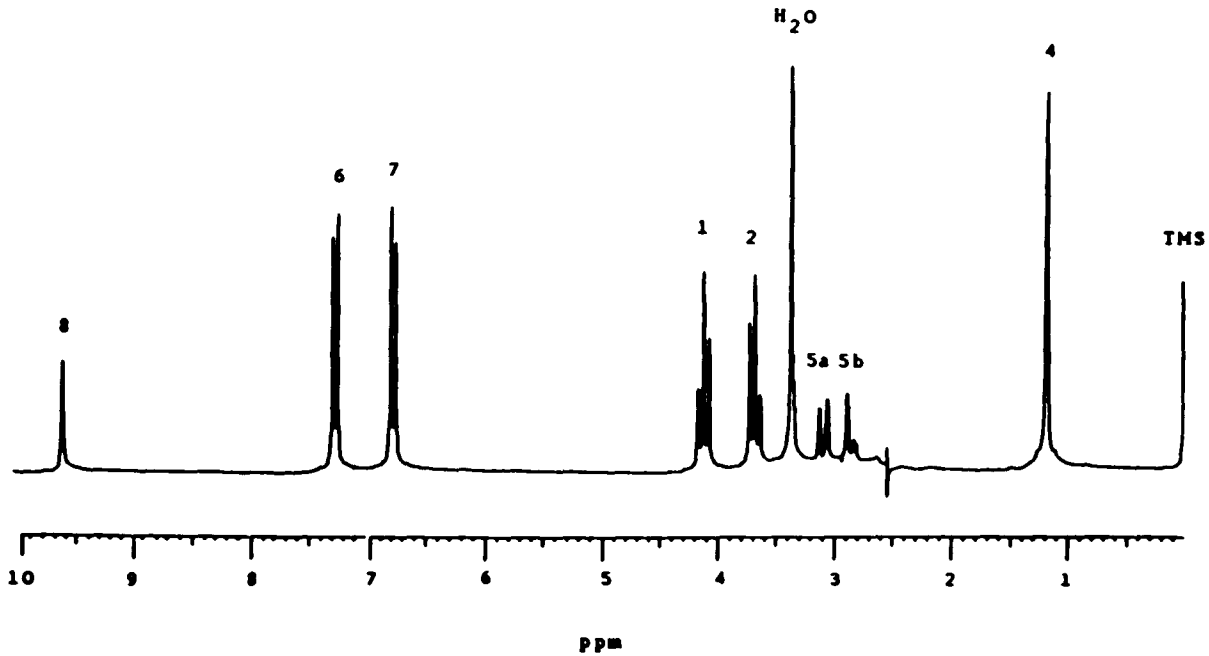


Figure 3-2 Homonuclear decoupling NMR spectrum of IPOHTP in DMSO-d_6 at 27 °C

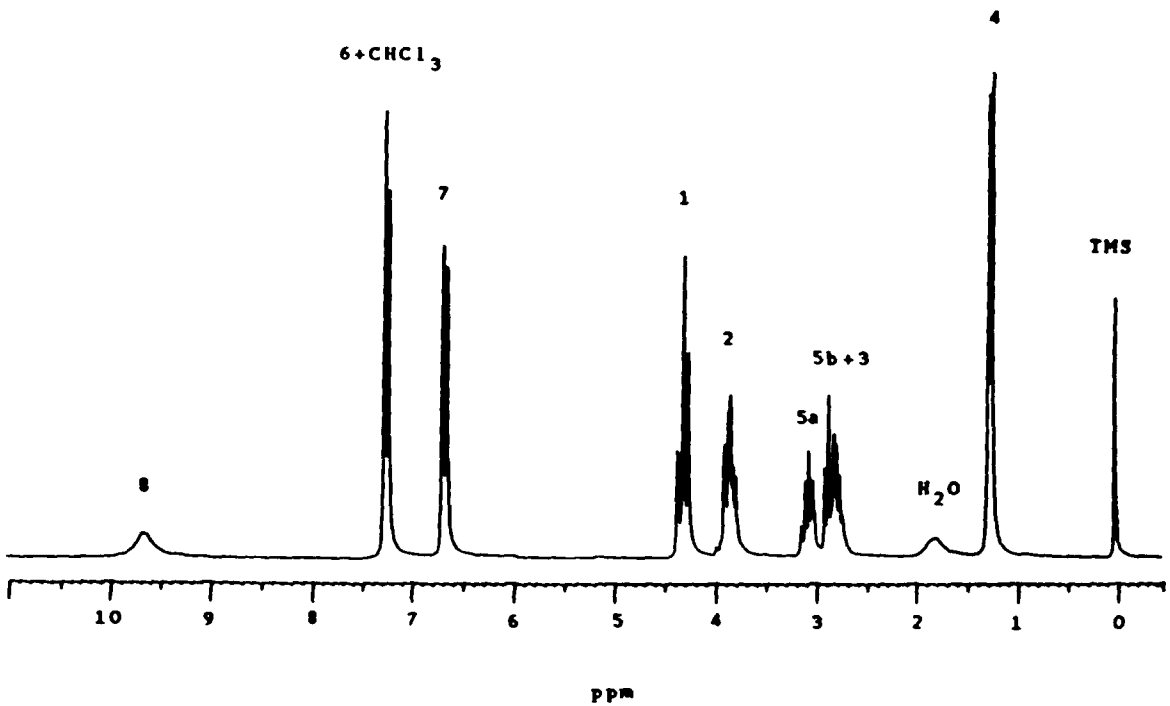


Figure 3-3 200.1 MHz ^{1}H NMR spectrum of IPOHTP in $CDCl_3$ at 27 °C

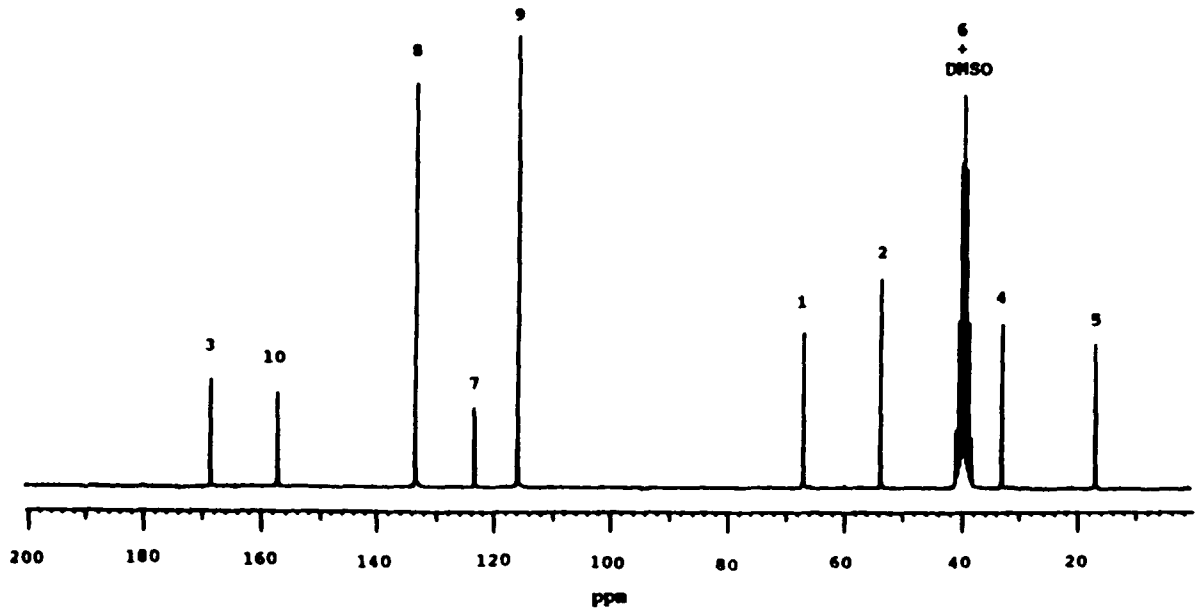


Figure 3-4 50.3 MHz ^{13}C NMR spectrum of IPOHTP in DMSO-d_6 at 27 °C

Table 3-1

The Assignment of Carbon Signals in IPOHTP

# of Carbon	Chemical Shift (ppm)
C1	66.4
C2	53.8
C3	168.0
C4	32.8
C5	16.4
C7	123.3
C8	133.4
C9	116.0
C10	157.5

The assignment of peak 4 and peak 6 was assisted by DEPT (Distortionless Enhancement Polarization Transfer) (Figure 3-5). In the DEPT spectrum, methylene group shows a downward peak, methyl and methine groups show upward peaks and quaternary carbons are not present. In Figure 3-5, the peak at 40.2 ppm is a downward peak and the peak at 32.8 ppm is an upward peak. By comparing Figure 3-4 to Figure 3-5, we know that the peak at 40.2 ppm is carbon 6 which is underneath the DMSO-d_6 peak in Figure 3-4, and that the peak at 32.8 ppm is carbon 4. The aromatic carbons were assigned by the assistance of calculation[38]. The calculated and observed chemical shifts of aromatic carbons are shown in Table 3-2.

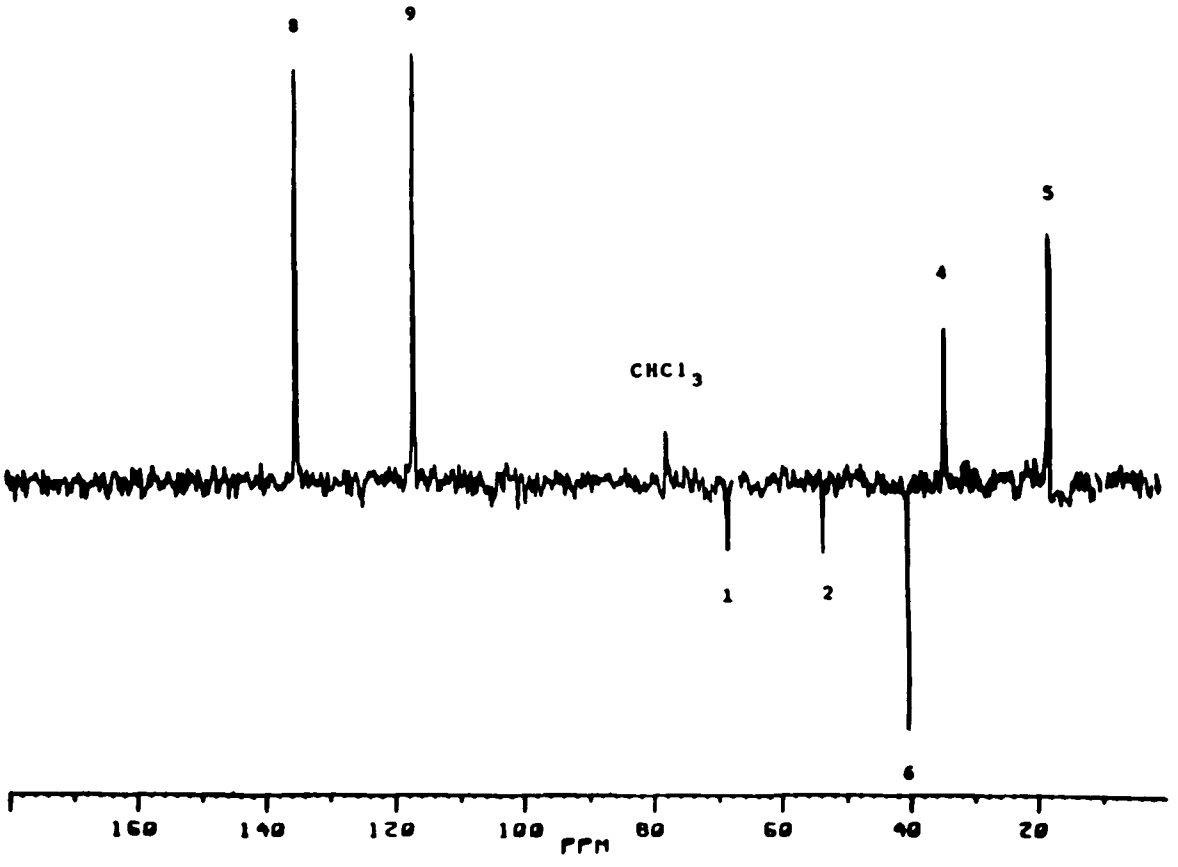


Figure 3-5 DEPT spectrum of IPOHTP in $CDCl_3$ at 27 °C

Table 3-2

Comparison of the Calculated and Observed Chemical Shifts of Aromatic Carbons in IPOHTP

# of Carbons	Calculated (ppm)	Observed (ppm)
C7	123.4	123.3
C8	130.6	133.4
C9	116.2	116.0
C10	152.3	157.5

A 2D-COSY experiment (Figure 3-6) was also run to confirm structure XVI. In the 2D-COSY spectrum, diagonal peaks correspond to the 1D spectrum, and off-diagonal peaks (cross-peaks), which are symmetrical about the diagonal, show the spin-spin coupling of two adjacent protons. To assist analyzing Figure 3-6 shows the 1D ^{1}H NMR spectrum on both axes (F1 and F2). The cross-peaks (6.7 ppm, 7.3 ppm) show the coupling of proton 6 and proton 7. The cross-peaks (3.9 ppm, 4.3 ppm) show the coupling of proton 1 and proton 2. The cross-peaks (2.8 ppm, 3.1 ppm) indicate the coupling of proton 5a and proton 5b. The weak cross-peaks (2.5 ppm, 2.8 ppm) show the coupling of proton 5b and proton 3. The weak cross-peaks (2.5 ppm, 3.1 ppm) show the coupling of proton 5a and proton 3. The cross-peaks (1.2 ppm, 2.5 ppm) show the coupling of proton 3 and proton 4.

The elemental analysis was in good agreement with that calculated from XVI:

	C	H	N	S
Found:	60.63	6.38	5.95	13.51
Theory:	60.73	6.37	5.90	13.51

3.3 Bulk and Solution Polymerizations of IPOHTP

The thermal polymerizations of IPOHTP were carried out in bulk in a temperature range of 100-200 °C. The polymer prepared at 100 °C was a colorless solid and became a white powder after dissolution in DMF and precipitation in ether.

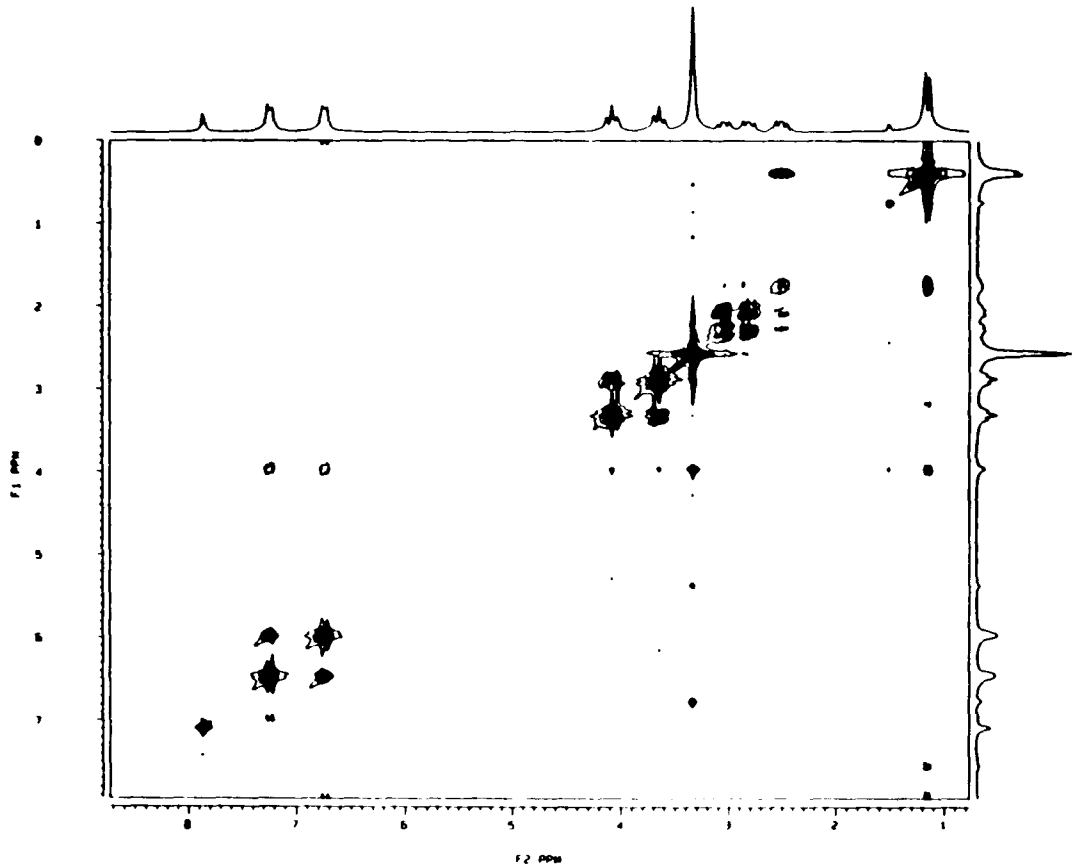


Figure 3-6 ^{1}H-^{1}H Correlated Spectroscopy (COSY) of IPOHTP in DMSO-d_6 at 27 °C

The polymers prepared at 150 and 200 °C were brown solids and became yellowish powders after purification by dissolving in DMF and precipitation by ether. The solution polymerizations of IPOHTP were conducted in dry DMF at a concentration of 50 wt-% in a temperature range of 100-200 °C. The polymers stayed in solution during polymerization and became white powders after purification. All the polymers (bulk and solution) were completely soluble in DMF and DMSO, partially soluble in TCE and insoluble in other regular solvents, such as methanol, methylene chloride, ethyl acetate, THF.

3.4 Characterization of IPOHTP Polymers

3.4.1 ^{1}H NMR Spectroscopy

Figure 3-7 shows the ^{1}H NMR spectrum of the polymer prepared in bulk at 100 °C. It was revealed that a great deal of phenolic proton (at 9.7 ppm) existed in the polymer chain while almost all the oxazoline rings had undergone ring-opening (Peak 1 in Figure 3-1 was almost gone in Figure 3-7). This resulted from self-reaction of oxazoline rings with the nitrogen atom in an oxazoline ring nucleophilically attacking another oxazoline ring (details in Section 3.6: Polymerization Mechanism of IPOHTP). Thus, the polymer chain contains two different repeat units, A (from oxygen attack) and B (from nitrogen attack). The signals were assigned to the following structure:

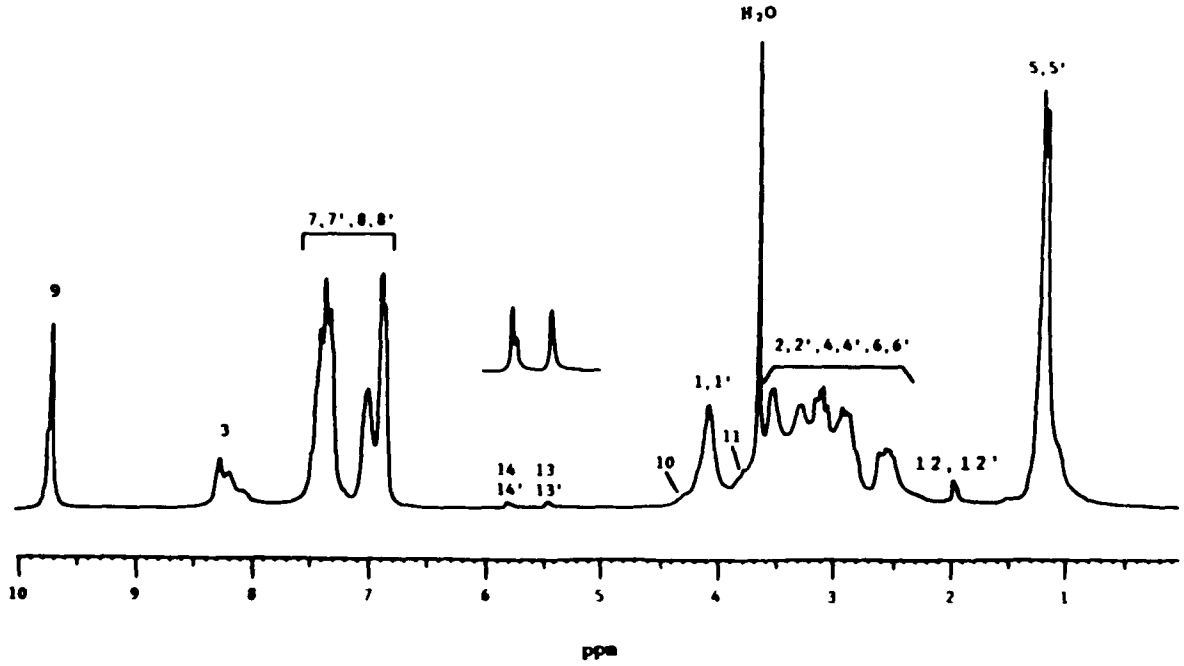
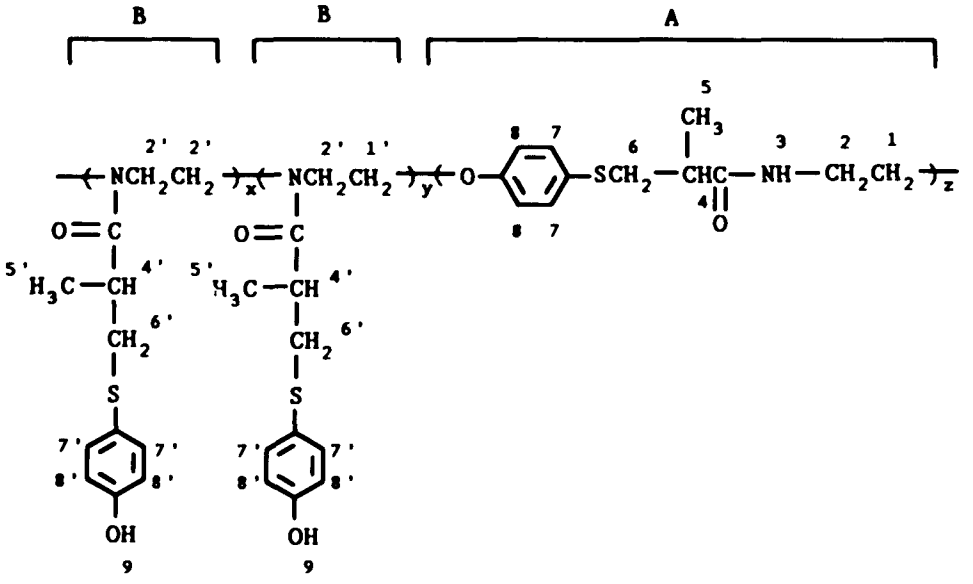


Figure 3-7 200.1 MHz ^{1}H NMR spectrum of IPOHTP polymer (bulk, 100 °C) in DMSO-d_6 at 27 °C



XXIX

The singlet at 9.70 ppm was assigned to proton 9. The broad signal from 8.01 ppm to 8.38 ppm was due to proton 3. The multiplets in the region of 6.75 ppm to 7.06 ppm were aromatic protons 7, 7′, 8 and 8′. The signal at 4.08 ppm was attributed to protons 1 and 1′, which was an unresolved multiplet containing two overlapped triplets. The complex multiplets arranged from 2.15 ppm to 3.75 ppm were assigned to protons 2, 2′, 4, 4′, 6 and 6′. The doublet at 1.17 ppm was due to protons 5 and 5′. The rest of the signals are attributed to end-groups and will be discussed in Section 3.4.6: End-group Analysis.

3.4.2 ^{13}C NMR Spectroscopy

Structure XXIX was strongly supported by ^{13}C NMR spectroscopy (Figure 3-8):

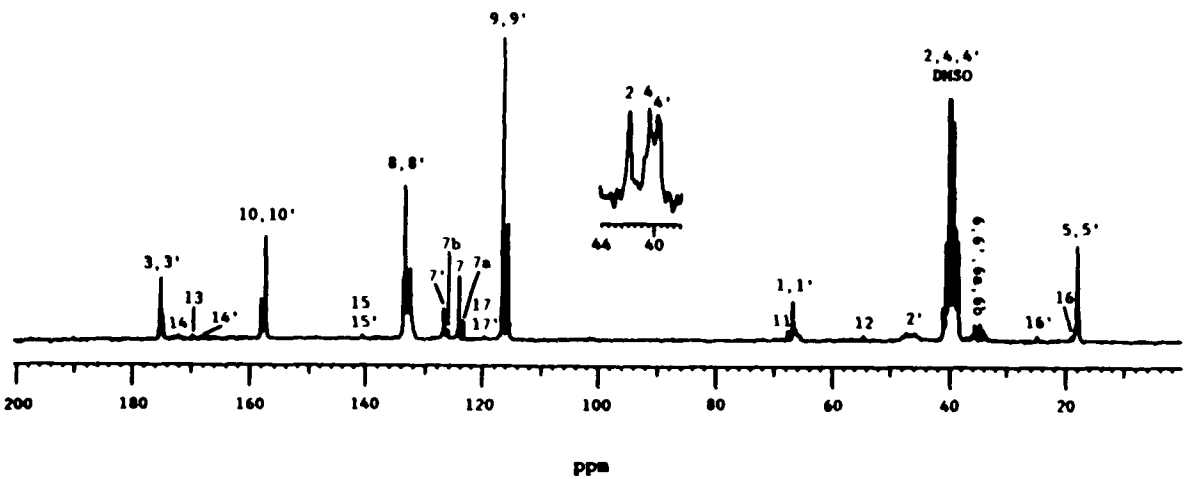
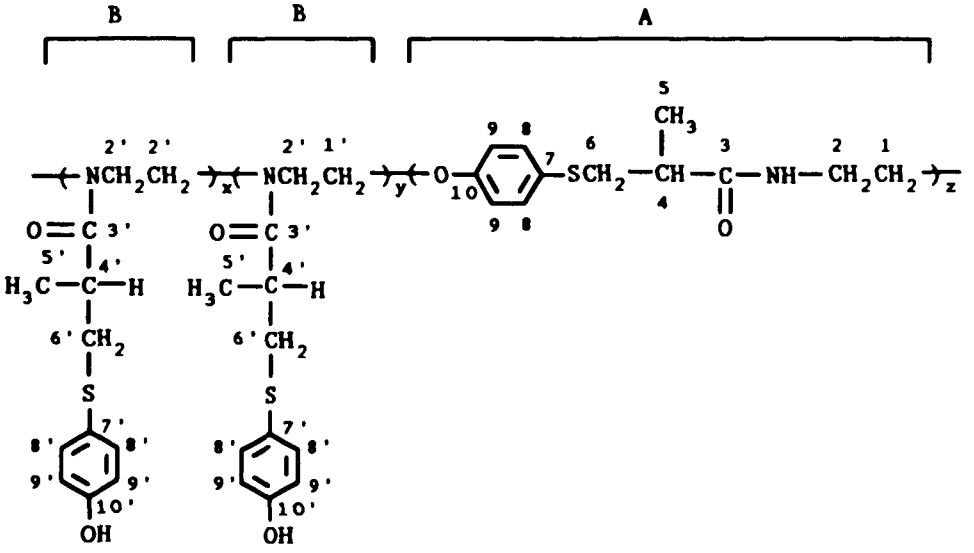


Figure 3-8 50.3 MHz ^{13}C NMR spectrum of IPOHTP polymer (bulk, 100 °C) in DMSO-d_6 at 27 °C



XXIX

The assignment of carbon signals is shown in Table 3-3. The signal of carbon 2′ from 48.1 ppm to 43.5 ppm was broad because the rigid amide bond, N–C–O and/or probable random sequence of units A and B give carbons 2′ many different chemical environments. The signals of carbons 2, 4 and 4′ were buried underneath the DMSO peaks. A separate spectrum taken in TCE-d_2 showed these signals at 39.4, 39.9 and 41.4 ppm (see insert to the left of DMSO signal in Figure 3-8. The origin of signals 6a, 6b, 7a and 7b and the signals which are not mentioned above will be discussed in Section 3.4.6: End-group Analysis.

Table 3-3

The Assignment of Carbon Signals of IPOHTP Polymers

# of Carbons	Chemical Shift (ppm)
1 and 1′	64.8-67.1
2	41.4*
2′	43.5-48.1
3	174.5
3′	174.2
4	39.9*
4′	39.4*
5 and 5′	17.6
6,6′,6a and 6b	32.4-37.3
7	123.8
7′	126.4
7a	123.1
7b	125.7
8	133.1
8′	132.2
9	116.3
9′	115.4
10	156.8
10′	157.6

* from the spectrum taken in TCE-d_2.

3.4.3 IR Spectroscopy

The IR data (Figure 3-9) is also consistent with structure XXIX: 1647.2 cm^{-1} (C=O stretch), 3286.7 cm^{-1} (N-H stretch), [illegible], 1581.6 cm^{-1}, 1597.8 cm^{-1} (mainly N-H in-plane deformation), 1172.7 cm^{-1} (aromatic C-H in plane deformation), 825.5 cm^{-1} (aromatic C-H out-of-plane deformation), 2978.4 cm^{-1}, 2951.6 cm^{-1} (C-H stretch), 1258.3 cm^{-1}, 1269.2 cm^{-1} (C-O-Ar stretch), 3298.3 cm^{-1} (O-H stretch).

3.4.4 Elemental Analysis

The elemental analysis result is in good agreement with structure XXIX:

	C	H	N	S
Found	60.47	6.27	6.00	13.26
Theory	60.73	6.37	5.90	13.51

3.4.5 Molar Ratio of Unit A to Unit B

The composition of the polymer in terms of A and B repeat units was obtained from the ^1H NMR spectrum by comparing the CH_2O signal area with the area for all methyl protons. This analysis is probably not accurate to better than 10-20 % since the CH_2O signal is far from baseline-resolved. The results for polymer composition are shown in Table 3-4.

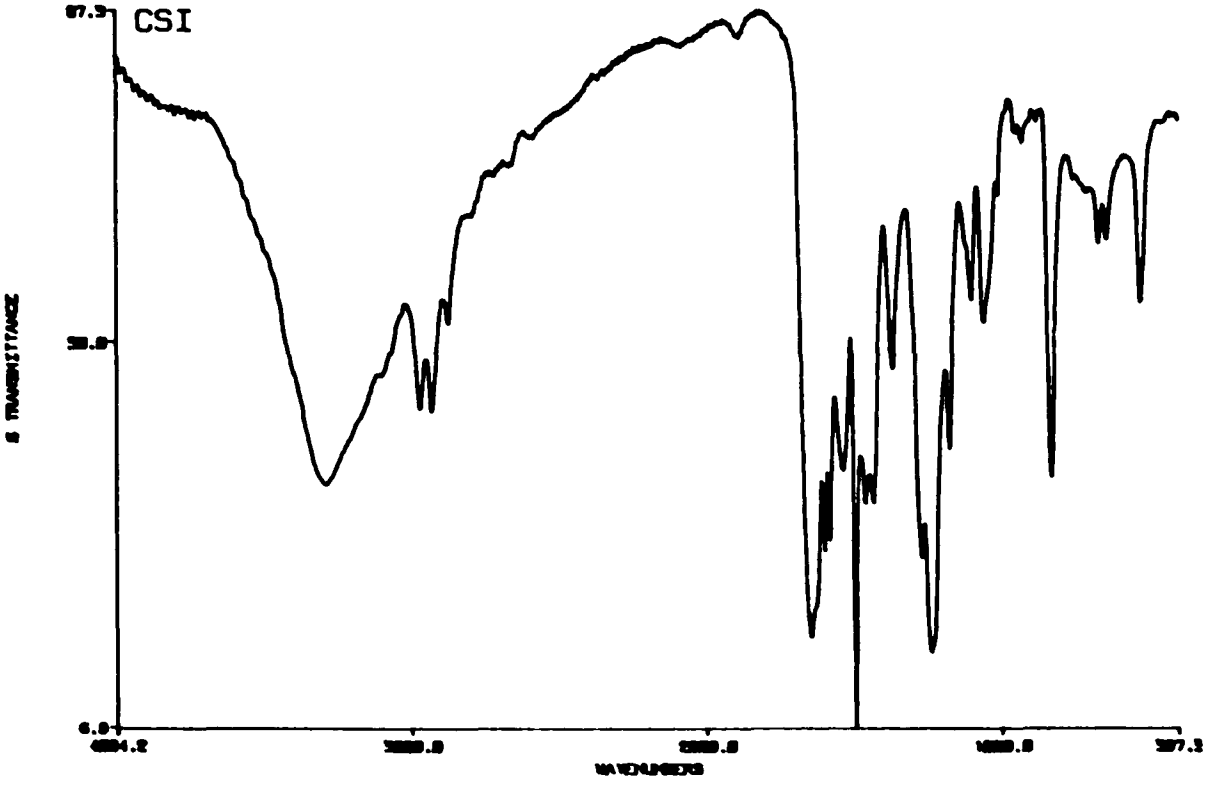


Figure 3-9 IR spectrum of IPOHTP polymer (bulk, 100 °C) in KBr

Table 3-4

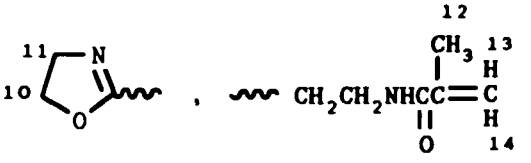
Number-Average Molecular Weight ($\bar{M}_n$) and Unit B Content of IPOHTP Polymers

Polymerization Temperature (°C)	Bulk			DMF Solution		
	$\bar{M}_n$		Unit B(%)	$\bar{M}_n$		Unit B(%)
	VPO	NMR		VPO	NMR	
100	2,920	4,606	48	1,878	4,804	61
150	2,153	1,533	47	1,666	2,703	63
200	1,547	1,343	56	1,428	2,069	67

3.4.6 End-group Analysis

3.4.6.1 ^{1}H NMR Spectroscopy

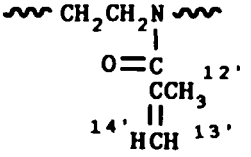
Figure 3-7 showed the following end-groups,



XXX XXXI

where ~~ stands for a polymer chain

and pendant isopropenyl group,



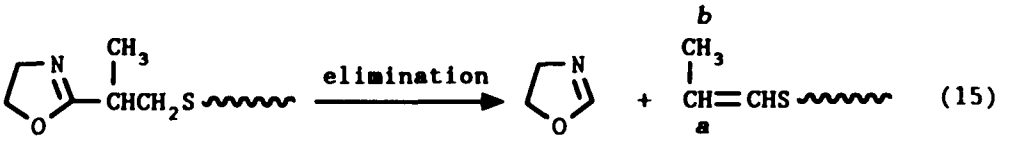
XXXII

where ~~ stands for a polymer chain

The two shoulders around 4.2 and 3.7 ppm are assigned to proton 10 and proton 11, respectively, because they are in the same position as they are in IPOHTP. The signal at 1.8 ppm is attributed to protons 12 and 12′. The two signals at 5.7 and 5.3 ppm are due to protons 14 and 14′ and protons 13 and 13′, respectively. The area ratio of the signal of protons 12 and 12′ to the signals of protons 13, 13′, 14 and 14′ is approximately 3 to 2. The intensity of the signals of protons 12, 12′, 13, 13′, 14 and 14′ grows with polymerization

temperature.

Since the signal of proton 12 and the signal of proton 12' were partially overlapped together and looked like a doublet, initially, instead of structures XXXI and XXXII, structure XXXIII was suspected:



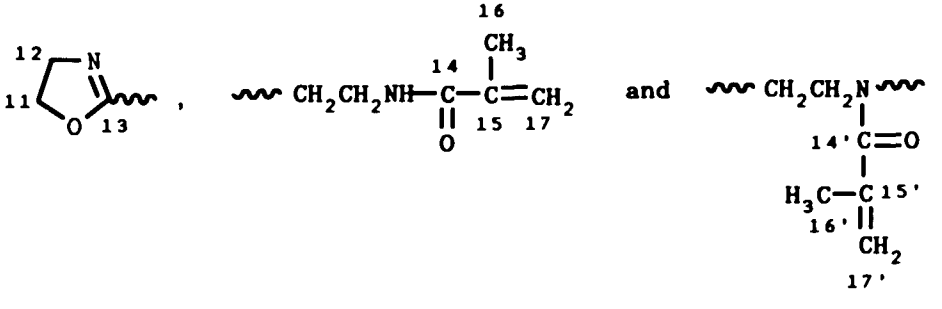
(15)

XXXIII

The decoupling of proton *a* would convert proton *b* from a doublet into a singlet. Thus the homonuclear decoupling NMR spectra (Figure 3-10a and Figure 3-10b) were obtained. In Figure 3-10a and 3-10b, the signal at 5.7 ppm and the signal at 5.3 ppm were decoupled, respectively, and no change of the signal of the methyl group at 1.8 ppm was seen, so it was concluded that the "doublet" must be two partially overlapped singlets from two different end-groups, i.e., XXXI and XXXII.

3.4.6.2 ^{13}C NMR spectroscopy

Figure 3-8 confirmed the existence of XXX, XXXI and XXXII shown as follows:



XXX XXXI XXXII

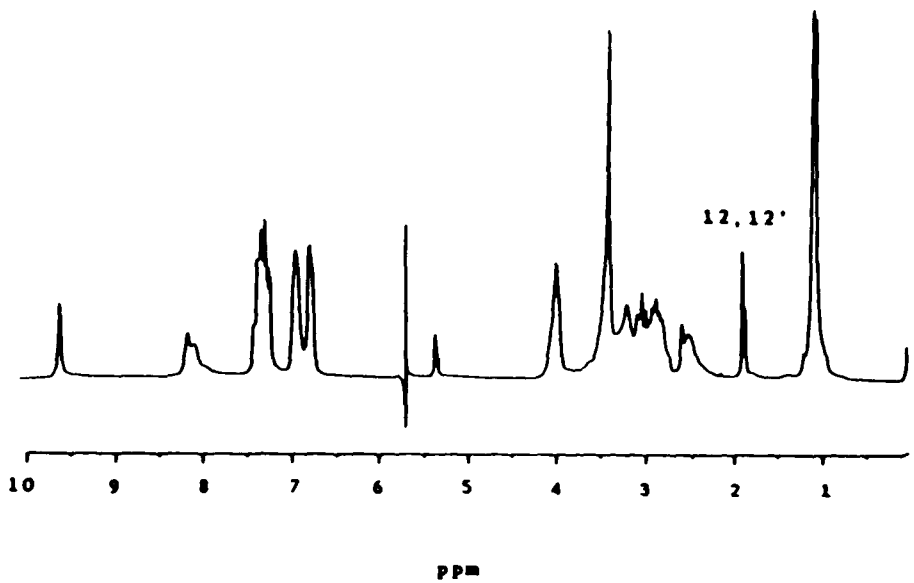


Figure 3-10a Homonuclear decoupling NMR spectrum of IPOHTP polymer (bulk, 150 °C) in DMSO-d_6 at 27 °C

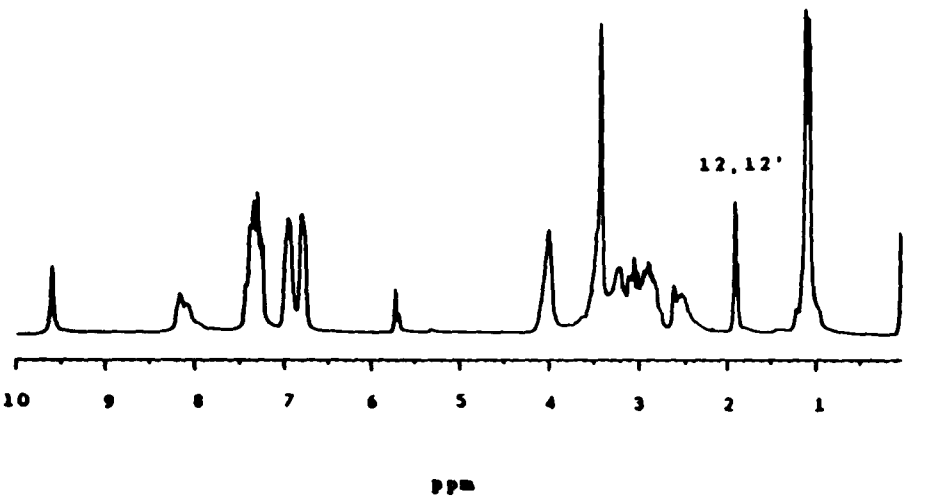


Figure 3-10b Homonuclear decoupling NMR spectrum of IPOHTP polymer (bulk, 150 °C) in DMSO-d_6 at 27 °C

Signals 15 and 15′ and signals 17 and 17′ were overlapped together, respectively. Carbons 14 and 14′ and carbons 16 and 16′ showed separate signals, respectively. XXXI and XXXII formed by an elimination reaction (details in Section 3.6: Polymerization Mechanism of IPOHTP).

3.4.6.3 Bromination

Polymer XXIX was dissolved in DMSO-d_6 and brominated with bromine. The signals of protons 13, 13′, 14 and 14′ completely disappeared and the signals of protons 12 and 12′ moved from 1.8 to 1.9 ppm in the ^{1}H NMR spectrum (Figure 3-11) of the brominated polymer. These changes confirmed the assignment of XXXI and XXXII.

3.5 Molecular Weight Measurements

3.5.1 NMR Measurement

The total amount of XXXI and XXXII increases with polymerization temperature. The peak areas of protons 13, 13′, 14 and 14′ and the total methyl groups (5, 5′, 12, 12′) in ^{1}H NMR spectrum were used to estimate the total amount of XXXI and XXXII. There was 5.2%, 14.8% and 16.7% of XXXI and XXXII out of the total amount of XXXI, XXXII and repeat unit, respectively, in the bulk polymers prepared at 100, 150 and 200 °C; there was 5.0%, 8.7% and 11.2% of XXXI and XXXII out of the total amount of XXXI, XXXII and repeat unit, respectively, in the solution prepared polymer at 100, 150 and 200 °C.

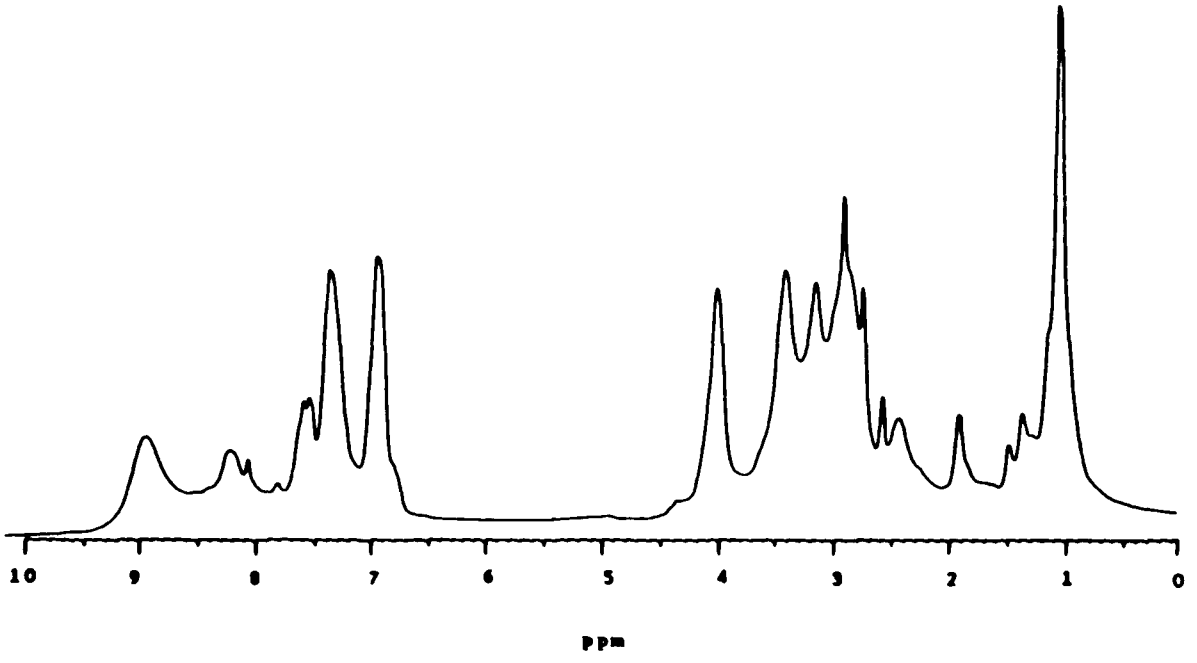


Figure 3-11 200.1 MHz ^{1}H NMR spectrum of brominated IPOHTP polymer (bulk, 200 °C) in DMSO-d_6 at 27 °C

Correspondingly, if one isopropenyl group (in XXXI or XXXII) per polymer chain is
assumed, the number-average molecular weights of the IPOHTP polymers were calculated and shown in Table 3-4.

3.5.2 VPO Measurement

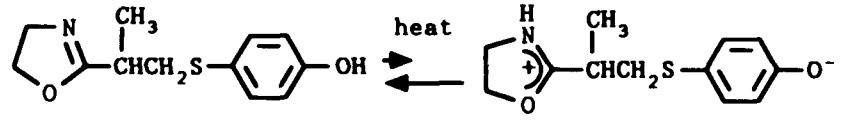
In Table 3-4 are also listed the number-average molecular weights determined by VPO. AS shown in Table 3-4, the molecular weight decreases with polymerization temperature, which is understandable because the elimination reaction gets more serious with increasing temperature.

3.5.3 Comparison of the Molecular Weights Obtained from NMR and VPO

Comparing the molecular weights calculated from NMR to the ones determined by VPO, we see that for the bulk polymer prepared at 100 °C the molecular weight calculated by NMR is greater than the one determined by VPO and for the bulk polymers prepared at 150 and 200 °C the molecular weights by NMR are smaller than the one by VPO. This indicates that the amount of isopropenyl group increases with temperature, from being less than one isopropenyl group per chain for the polymer prepared at 100 °C, to more than one per chain for the polymers prepared at 150 and 200 °C (some chains have one XXXI and one XXXII per chain or two XXXII's per chain). The total amount of XXXI and XXXII in solution prepared polymers also increased with temperature, but the polymers have less than one XXXI or XXXII per chain.

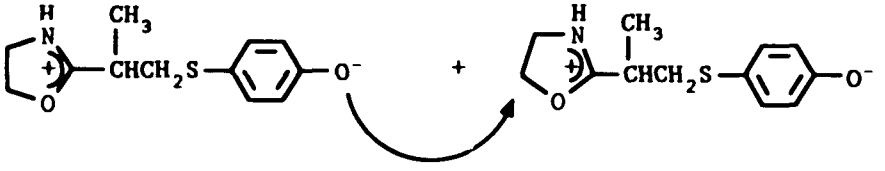
3.6 Polymerization Mechanism of IPOHTP

From the chemical structure analysis of the polymers, we propose the following polymerization mechanism:

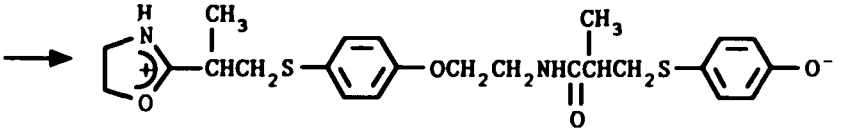


(16)

XVI XXXIII

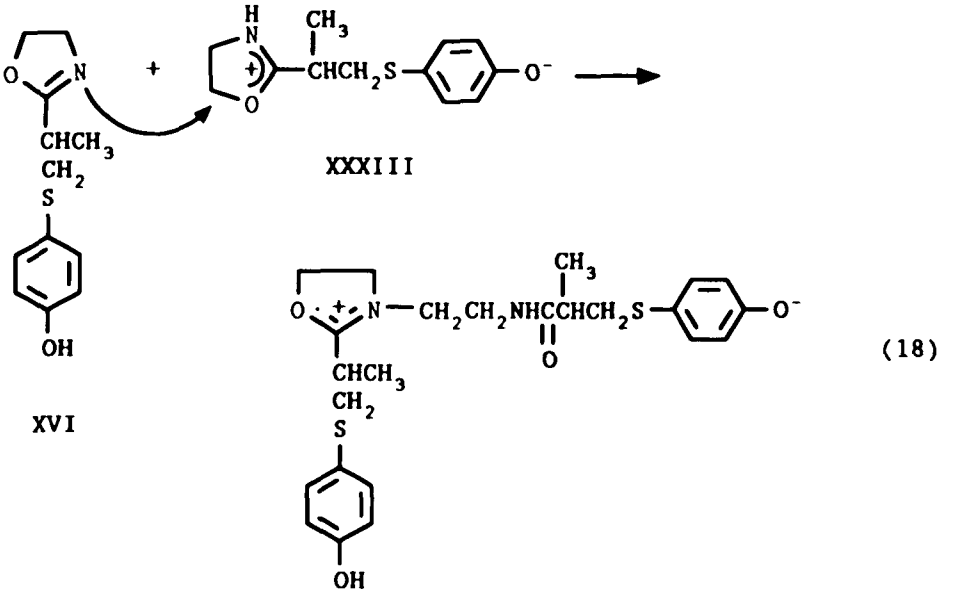


XXXIII XXXIII



(17)

XXXIV



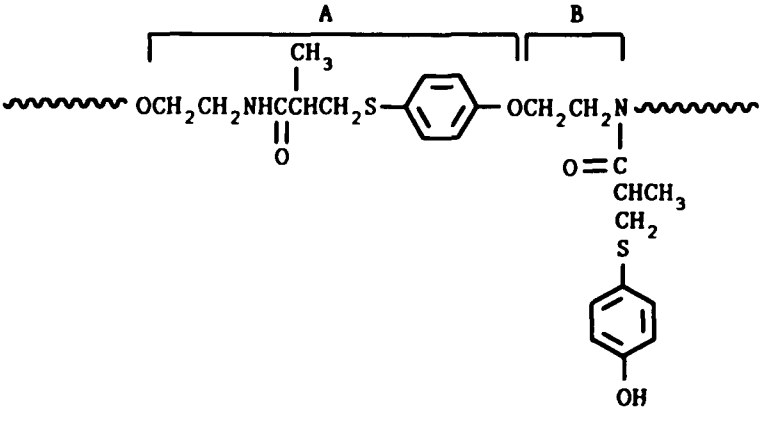
XXXIII

XVI

XXXV

(18)

XXXIV + XXXV ⟶



XXXVI

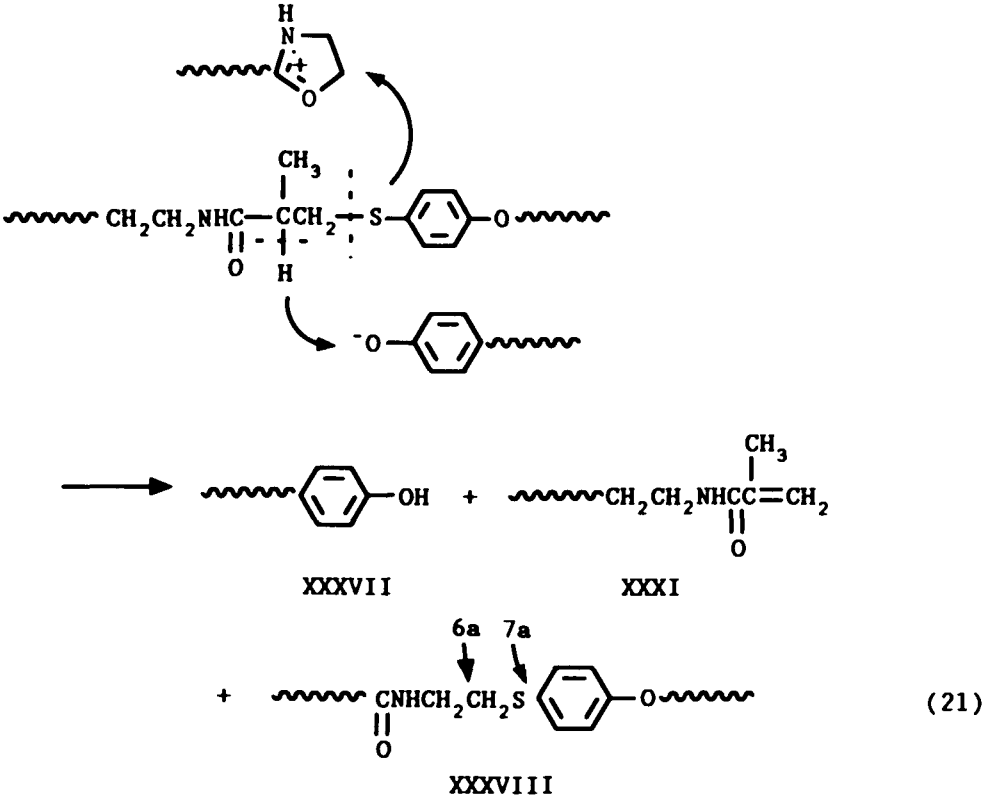
(19)

XXXVI + (x+y-1) XVI + (z-3) XXXIII ⟶ XXIX (20)

At the elevated temperature, an equilibrium (Eq. 16) between

IPOHTP (XVI) and its zwitterion (XXXIII) establishes in favor of IPOHTP. Two zwitterions (XXXIII) react by O^- attack on oxazolinium ring (oxygen attack) (Eq. 17) to form a dimer zwitterion (XXXIV). One IPOHTP (XVI) attacks one zwitterion (XXXIII) (nitrogen attack) to form a different dimer zwitterion (XXXV) (Eq. 18). XXXIV reacts with XXXV to give a tetramer zwitterion XXXVI containing both unit A and unit B (Eq. 19). XXXVI continues to react with zwitterions (XXXIII) and IPOHTP (XVI) to produce polymer XXIX (Eq. 20).

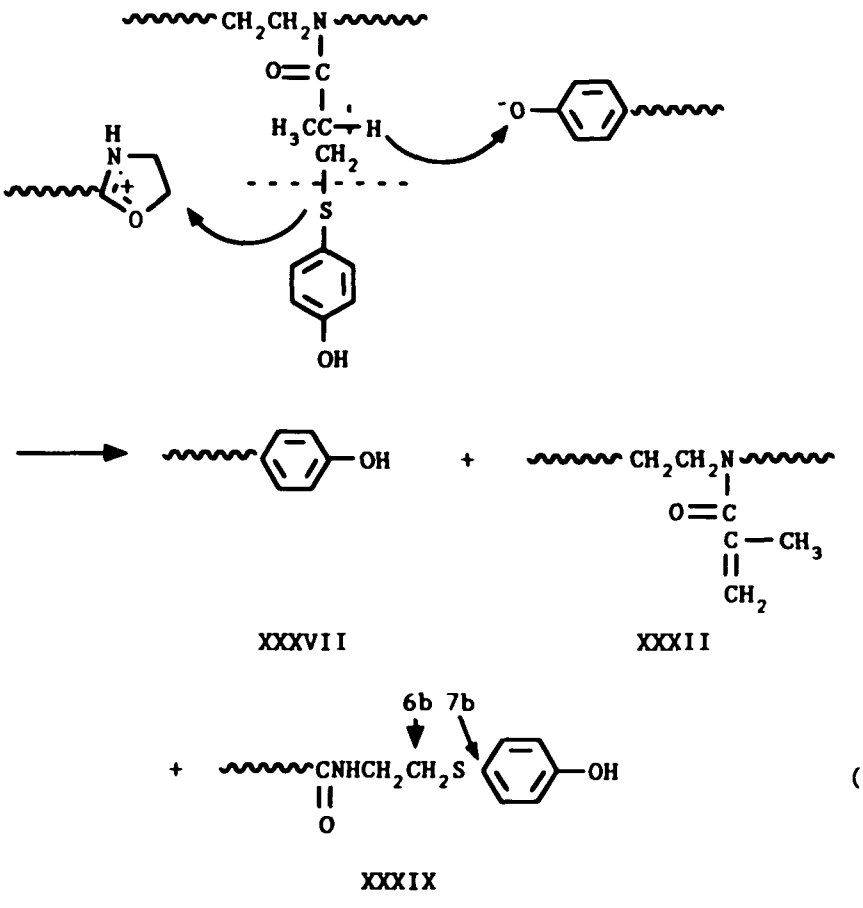
The polymerization terminates mainly due to an elimination reaction, especially at high temperature (above 150 °C). The elimination reaction can occur in backbones as shown in Eq. 21, and can also occur in side-chains as shown in Eq. 22.



XXXVII XXXI

XXXVIII

(21)



XXXVII XXXII

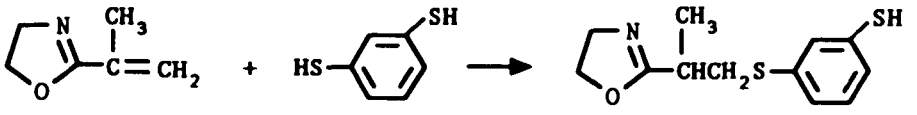
XXXIX

(22)

The eliminated H^+ protonates $^-OAr\sim$ to form XXXVII. Carbon 7′ was detected by ^{13}C NMR spectroscopy as shown in Figure 3-8. The eliminated fragments $^-SAr\sim$ and ^-SArOH from CH_2-S bond cleavage attack the oxazoline rings to produce XXXVIII and XXXIX. As seen in Figure 3-8, there were two or three signals near carbons 6 and 6′ and two other signals near carbons 7 and 7′. These signals probably correspond to carbons 6a and 7a in XXXVIII and 6b and 7b in XXXIX. XXXI and XXXII result directly from the elimination reaction. The assignments of XXXI and XXXII in Figures 3-7 and 3-8 have been discussed in Section 3.4.6: End-group Analysis.

4.0 Results and Discussion on Zwitterion Polymerization of IPOBDT (System II)

4.1 Synthesis of IPOBDT (XVIII)



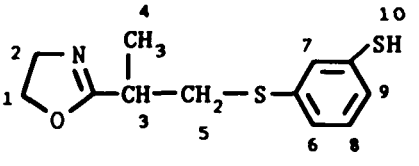
(10)

VIII XVII XVIII

This reaction was conducted in acetonitrile at 0 °C and monitored by ^{1}H NMR spectroscopy. The reaction was fast, almost complete immediately after the addition of IPO (VIII) to BDT (XVII) and a small portion of IPOBDT polymerized. The polymerization of IPOBDT prevented the isolation of IPOBDT.

4.2 Characterization of IPOBDT

4.2.1 ^{1}H NMR Spectroscopy



XVIII

The ^{1}H NMR spectrum (Figure 4-1) of the IPOBDT-acetonitrile solution supported structure XVIII. As

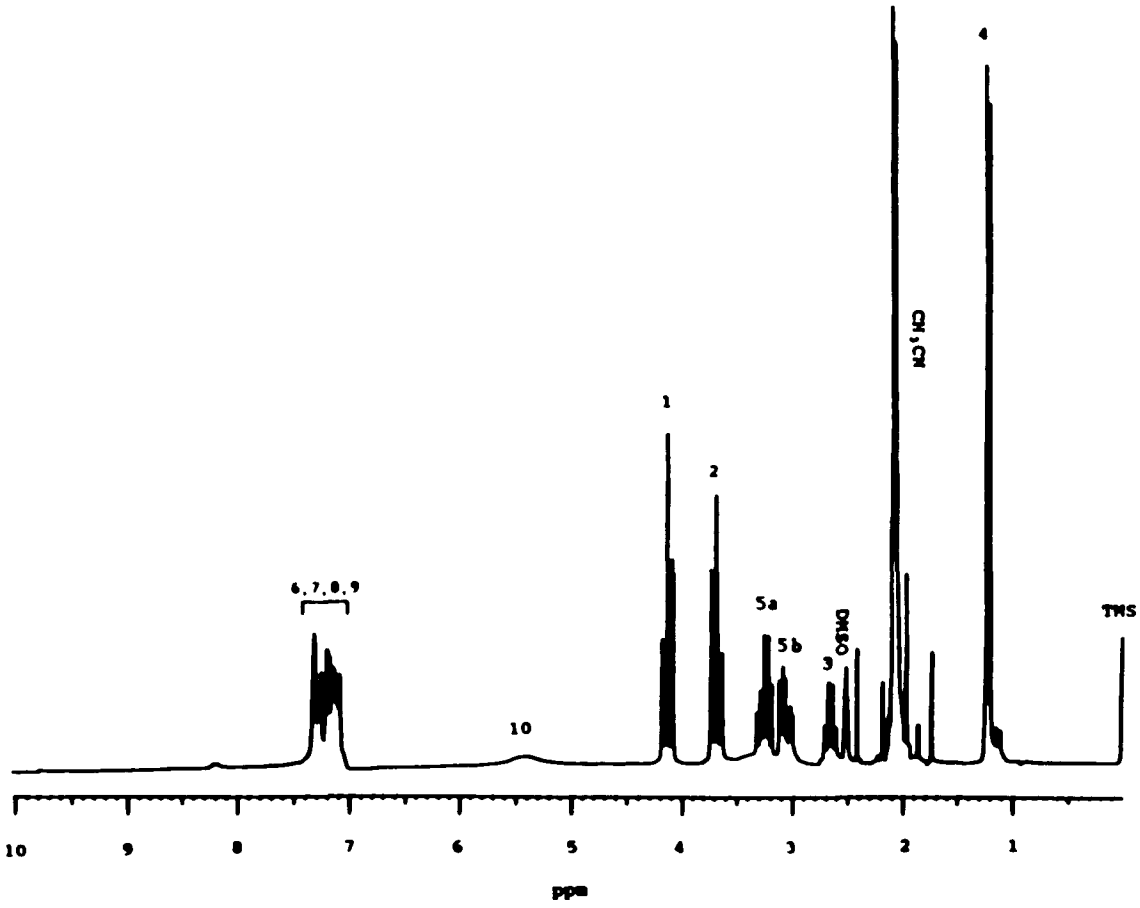
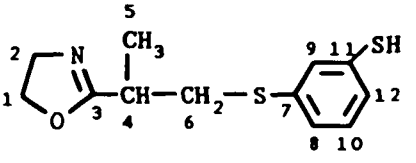


Figure 4-1 200.1 MHz ^{1}H NMR spectrum of IPOBDT-acetonitrile solution in DMSO-d_6 at ambient (ca. 25 °C)

shown in Figure 4-1, the two triplets at 4.15 ppm and 3.68 ppm are protons 1 and 2. The multiplets in the region of 2.9 ppm to 3.4 ppm correspond to protons 5a and 5b. The multiplet centered at 2.66 ppm is due to proton 3. The complexity of the signal pattern of protons 3, 5a and 5b is because protons 3, 5a and 5b constitute an ABX system -- the chirality of the carbon proton 3 is attached to give proton 5a and 5b different chemical environments. The doublet at 1.25 ppm is methyl protons 4. The aromatic protons are the signals from 7.0 ppm to 7.4 ppm. The small singlet at 8.2 ppm and doublet at 1.15 ppm are signals from IPOBDT polymer -- the doublet at 1.15 ppm grew 10 times bigger after sitting at room temperature for 1.5 h in DMSO-d_6 at a concentration of 30 vol-% of the IPOBDT-acetonitrile in DMSO-d_6. The broad peak around 5.4 ppm is proton 10. The multiplet at 2.5 ppm and large singlet at 2.1 ppm are DMSO and acetonitrile, respectively. The singlets around the acetonitrile peak are spinning side bands.

4.2.2 ^{13}C NMR Spectroscopy



XVIII

The ^{13}NMR spectrum (Figure 4-2) was taken to confirm the chemical structure of XVIII. The assignments of the signals are shown in Table 4-1. The assignments of aromatic

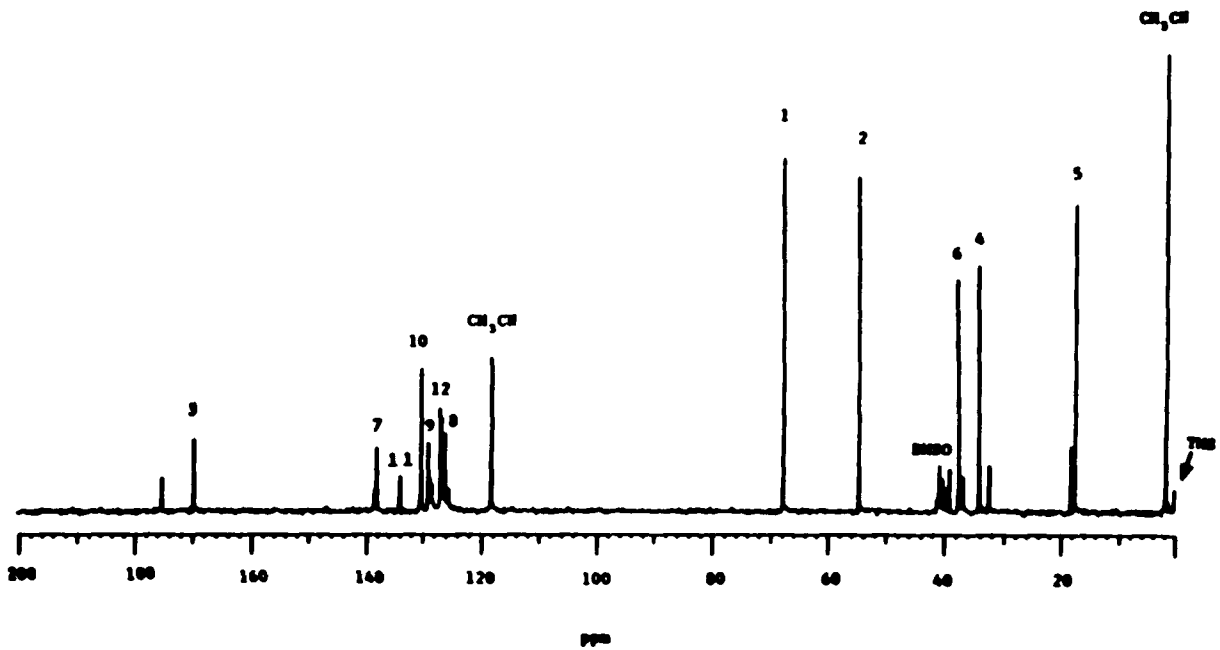


Figure 4-2 ^{13}C NMR spectrum of IPOBDT-acetonitrile solution in DMSO-d_6 at ambient (ca. 25 °C)

Table 4-1

The Assignment of Carbon Signals in IPOBDT

# of carbon	chemical shift (ppm)
C1	67.5
C2	54.4
C3	169.5
C4	33.8
C5	17.3
C6	37.2
C7	139.8
C8	123.6
C9	127.7
C10	128.3
C11	134.1
C12	126.4

carbons are assisted by calculations[38]. The observed and calculated chemical shifts of the aromatic carbons are compared in Table 4-2. The signals at 2.1 ppm and 118.2 ppm are from acetonitrile which was used as a solvent in the preparation of IPOBDT monomer. The multiplet around 40.0 ppm is due to DMSO-d_6. The rest of the relatively small signals are from the IPOBDT polymer formed by a small portion of polymerization.

4.3 Solution Polymerizations of IPOBDT

Solution polymerizations were carried out in acetonitrile and tetrahydrofuran (THF) in the temperature range of -27-70 °C and in N,N'-dimethylformamide (DMF) at the temperature range of -27-150 °C in a concentration of 60 vol-%. The polymer gradually precipitated out of acetonitrile during polymerization while remaining in THF and DMF during the whole period of polymerization. The polymers after purification were all white and foam-like. They are soluble in THF, DMF, tetrachloroethane (TCE) and dimethylsulfoxide (DMSO) with no insoluble portion.

4.4 Bulk Polymerization of IPOBDT

IPOBDT was also polymerized in bulk at -27, 0, ambient (ca. 25), 70 and 150 °C. IPO and BDT were mixed together in ether to form IPOBDT, the ether evaporated, and the residue maintained at desired temperature. The polymers prepared below 150 °C were colorless and the one prepared at 150 °C was slightly yellow. All the polymers were white solids

Table 4-2

Comparison of Calculated and Observed Chemical Shifts of Aromatic Carbons in IPOBDT

	Calculated (ppm)	Observed (ppm)
C7	139.8	138.1
C8	123.6	125.9
C9	127.8	127.7
C10	130.0	128.3
C11	131.2	134.1
C12	126.0	126.4

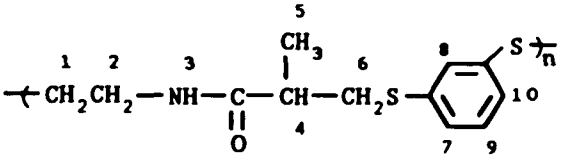
after purification.

4.5 Characterization of IPOBDT Polymers

The chemical structure of IPOBDT polymers was determined by ^{1}H NMR (Figures 4-3 and 4-4), ^{13}C NMR (Figures 4-5 and 4-6), DEPT (Distortionless Enhancement by Polarization Transfer Spectroscopy) (Figure 4-7), IR spectroscopy (Figure 4-8) and elemental analysis.

4.5.1 ^{1}H NMR Spectroscopy

Figure 4-3 was taken with DMSO-d_6. The assignments of the signals in Figure 4-3 are shown below:



XXXX

The complex signals in the region from 2.9 to 3.5 ppm correspond to protons 1,2,4,and 6 and water. Protons 7,8,9 and 10 constitute the multiplet between 7.1 ppm and 7.4 ppm. The singlet at 8.2 ppm and doublet at 1.1 ppm are protons 3 and 5, respectively. ^{1}H NMR spectrum in TCE-d_2 (Figure 4-4) gave a different pattern from Figure 4-3 although both of them are ^{1}H NMR spectra of the same IPOBDT polymer sample. In Figure 4-4, aromatic protons 7,8,9,10 and 3 are overlapped together in the region of 6.6 ppm and 7.5 ppm; the complex signals from 2.3 ppm to 3.6 ppm are protons 1,2,

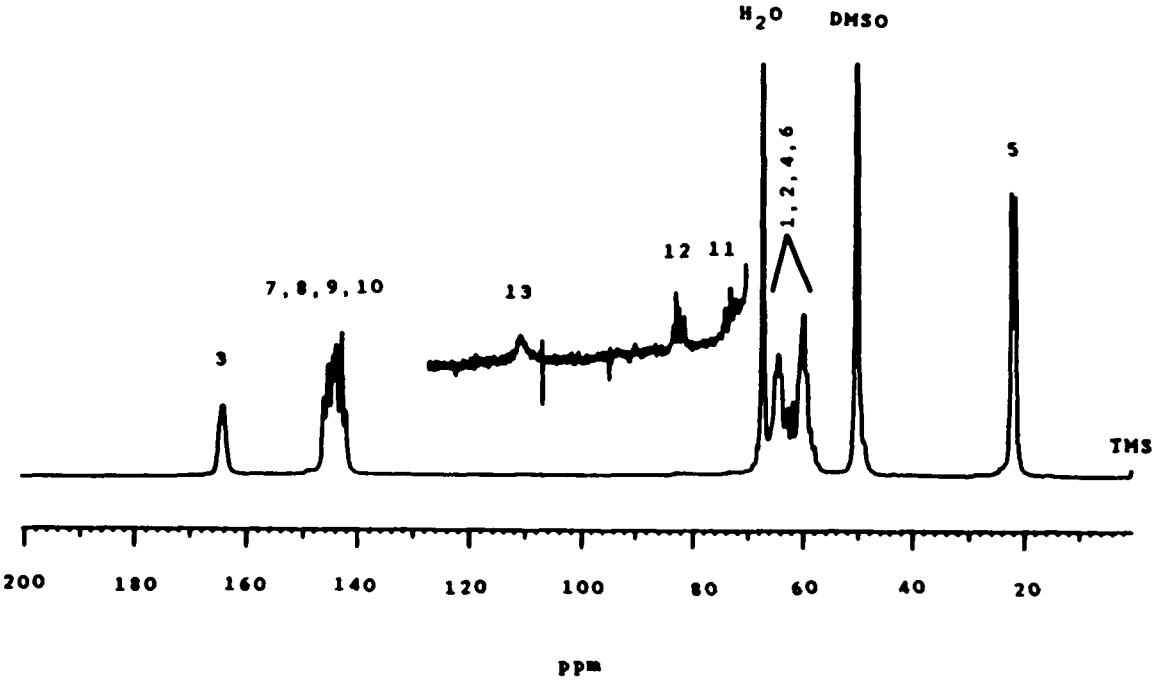


Figure 4-3 200.1 MHz ^{1}H NMR spectrum of IPOBDT polymer (in acetonitrile, 0 °C) in DMSO-d_6 at 27 °C

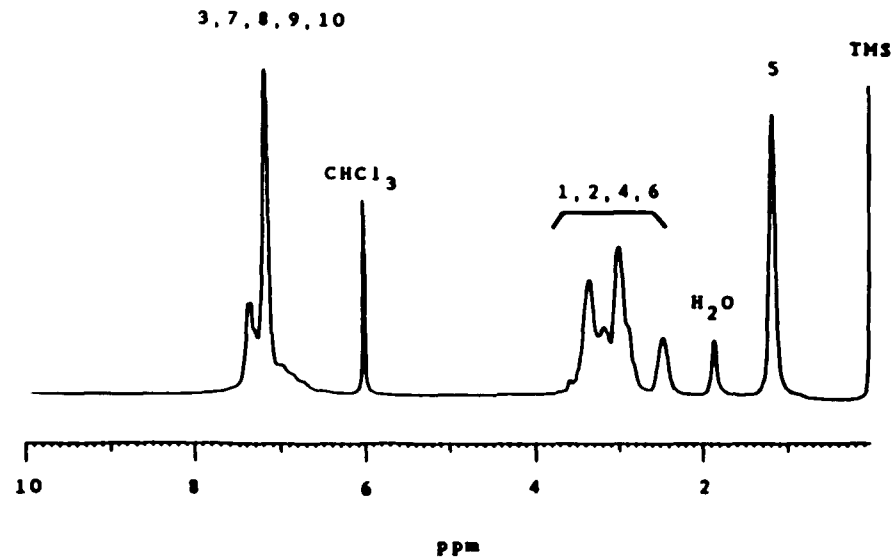
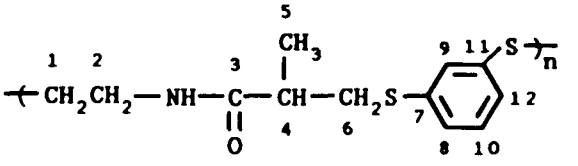


Figure 4-4 200.1 MHz ^1H NMR spectrum of IPOBDT polymer (in acetonitrile, 0 °C) in TCE-d_2 at 27 °C

4 and 6; the singlet at 1.2 ppm is an unresolved doublet which is assigned to proton 5; the two singlets at 6.0 ppm and 1.9 ppm are TCE and H_2O, respectively.

4.5.2 ^{13}C NMR Spectroscopy

The ^{13}C NMR spectra (Figure 4-5 and Figure 4-6) support structure XXXX:



XXXX

The assignments of the carbon signals in Figure 4-5 are shown in Table 4-3. The assignments are assisted by DEPT (Figure 4-7) and calculation[38]. In the DEPT spectrum, methyls and methines are upward, methylenes are down, and quaternary carbons do not appear. From Figures 4-5 and 4-7, we see four signals in between 17.9 ppm and 39.7 ppm. The signals at 17.9 and 39.7 ppm were assigned to carbons 5 and 4, respectively, because methyl and methine carbons go up in DEPT and the three methylene signals at 31.3, 35.6, 38.2 ppm were assigned to carbons 6, 1, and 2 based on calculation. The three quaternary carbons absent in DEPT and present in Figures 4-5 are carbon 3 at 175.2 ppm, carbon 11 at 137 ppm and carbon 7 at 138 ppm; the other aromatic carbons were assigned by calculation. The observed and calculated chemical shifts are compared in Table 4-4.

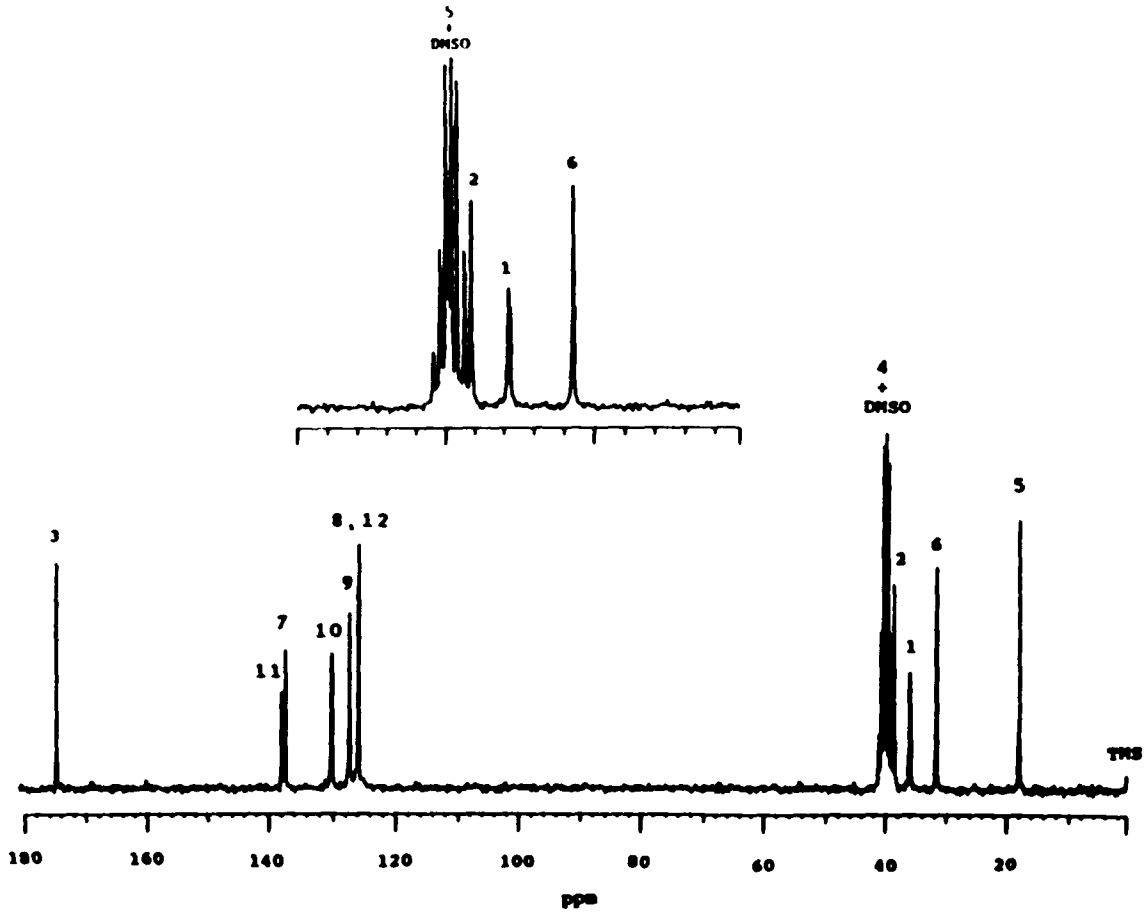


Figure 4-5 50.3 MHz ^{13}C NMR spectrum of IPOBDT polymer (bulk, 75 °C) in DMSO-d_6 at 27 °C

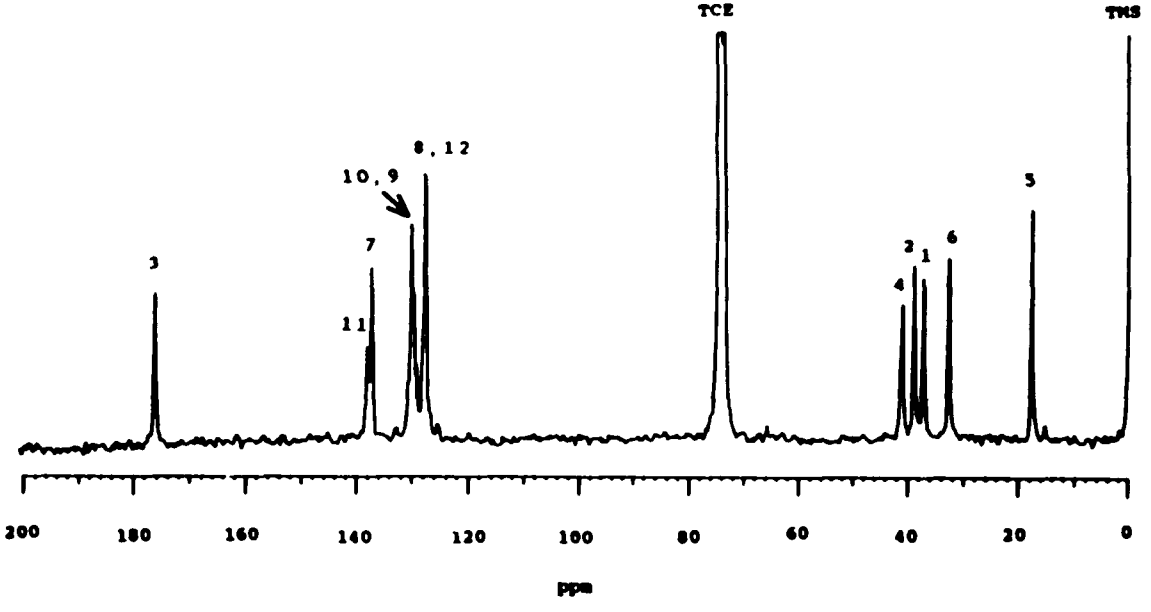


Figure 4-6 50.3 MHz ^{13}C NMR spectrum of IPOBDT polymer (bulk, 75 °C) in TCE-d_2 at 27 °C

Table 4-3

The Assignment of Carbon Signals in IPOBDT Polymers

# of carbon	chemical shift (ppm)
C1	35.6
C2	38.2
C3	175.2
C4	39.7
C5	17.9
C6	31.3
C7	137.5
C8	126.6
C9	125.0
C10	129.5
C11	136.9
C12	125.0

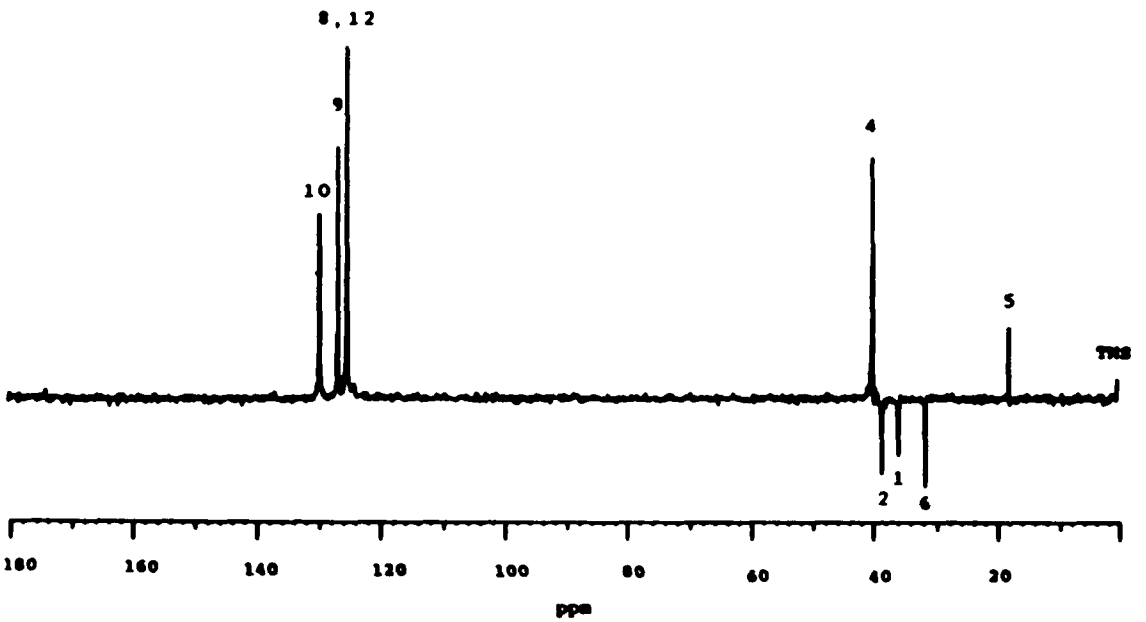


Figure 4-7 DEPT spectrum of IPOBDT polymer (bulk, ambient (ca. 25 °C)) in DMSO-d_6 at 27 °C

Table 4-4

Comparison of the Calculated and Observed Chemical Shifts of Carbon Signals in IPOBDT Polymer

	Calculated (ppm)	Observed (ppm)
C1	39.6	35.6
C2	44.4	38.2
C4	44.2	39.7
C6	22.1	31.3
C7	139.1	137.5
C8	123.1	126.6
C9	124.9	125.0
C10	129.3	129.5
C11	139.1	136.9
C12	123.1	125.0

It is interesting that the aromatic region shows a different pattern in the ^{13}C NMR spectrum (Figure 4-5) taken in DMSO-d_6 compared to the ^{1}H NMR spectrum (Figure 4-6) taken in TCE-d_2. The aromatic carbon signals are broad and less resolved in Figure 4-6 than in Figure 4-5. For example, carbons 9 and 10 are overlapped together in Figure 4-6 but separated in Figure 4-5.

4.5.3 IR Spectroscopy

The structure of polymer XXXX was also confirmed by IR spectrum (Figure 4-8):

N-H stretching: 3279.0 cm^{-1} (strong); aromatic C-H stretching: 3070.7 cm^{-1} (medium); C-H stretching in $-CH_3$: 2966.5 cm^{-1} (weak); C-H stretching in $-CH_2$: 2924.1 cm^{-1} (medium); C-H stretching in -CH: 2878.1 cm^{-1} (weak); C=O stretching: 1643.3 cm^{-1} (very strong); mainly NH in-plane deformation (amide II): 1570.1 cm^{-1}, 1554.6 cm^{-1} and 1545.0 cm^{-1} (strong); C-H deformation in $-CH_3$: 1462.0 cm^{-1} (sharp and weak); aromatic C-H deformation in-plane: 1226.7 cm^{-1} (medium); aromatic C-H deformation out-of-plane: 775.4 cm^{-1} and 662.8 cm^{-1}.

4.5.4 Elemental Analysis

The elemental analysis results also showed great agreement with theoretical values:

	C	H	N	S
Found:	56.88	5.83	5.58	25.38
Theory:	56.88	5.97	5.53	25.31

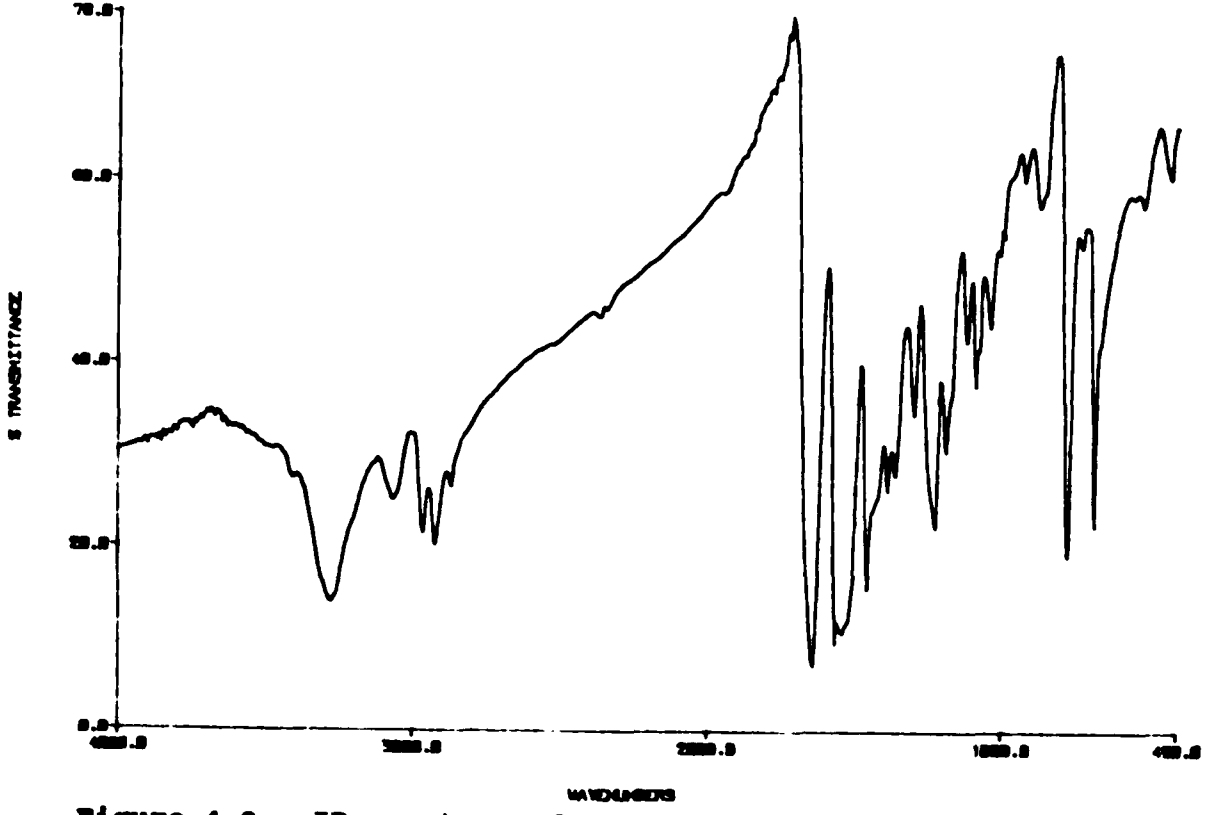
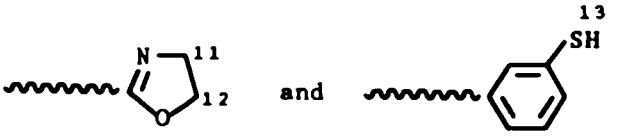


Figure 4-8 IR spectrum of IPOBDT polymer (bulk, 0 °C) in KBr

4.6 Discussions on End-groups

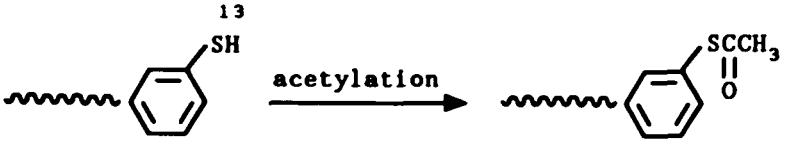
The ^1H NMR spectroscopy (Figure 4-3) of IPOBDT polymer prepared below 150 °C detected the following end-groups:



XXXXI XXXXII

where ~~~ stands for polymer chain

Protons 11 and 12 showed two triplets at 4.21 ppm and 3.69 ppm, respectively. A singlet at 5.58 ppm was due to proton 13. The IPOBDT polymer was acetylated to confirm the existence of XXXXII:



(23)

XXXXII XXXXIII

The ^1H NMR spectrum of the acetylated polymer showed a singlet at 2.19 ppm and no signal for proton 13. The singlet at 2.19 ppm was assigned to the methyl group in XXXXIII. The ^1H NMR spectrum (Figure 4-9) of IPOBDT polymer prepared at 150 °C showed the disappearance of XXXXI and the additional end-groups XXXXIV and XXXXV:

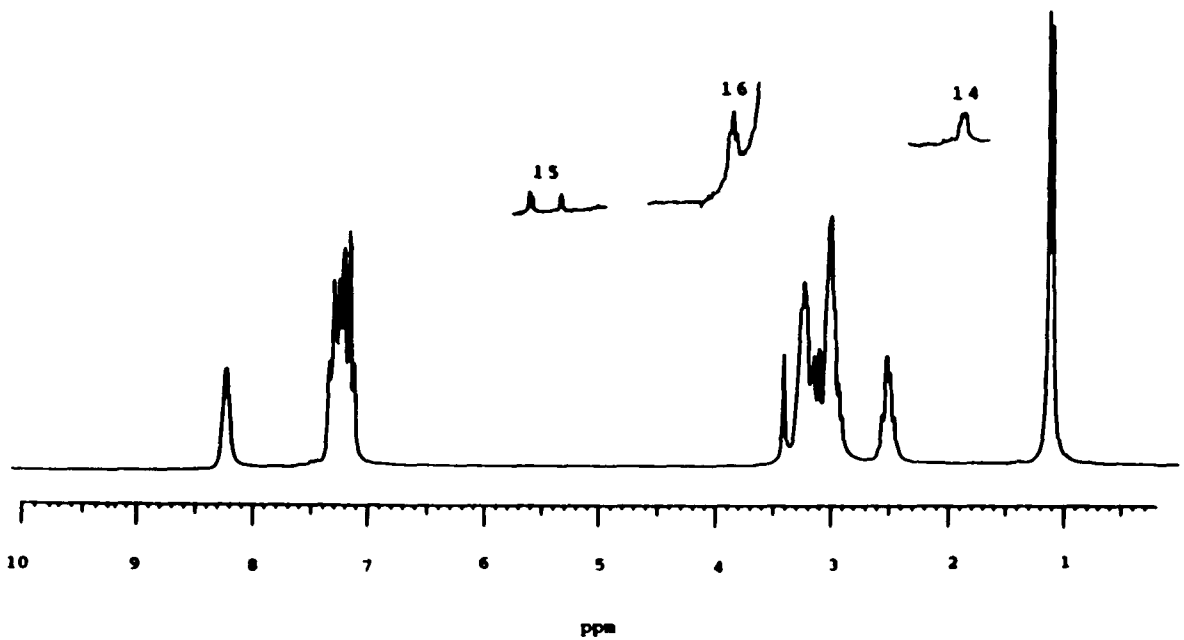
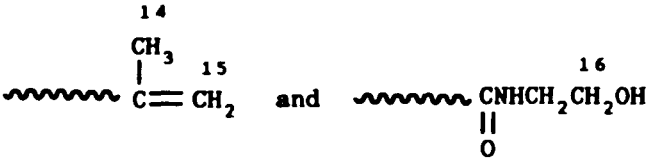
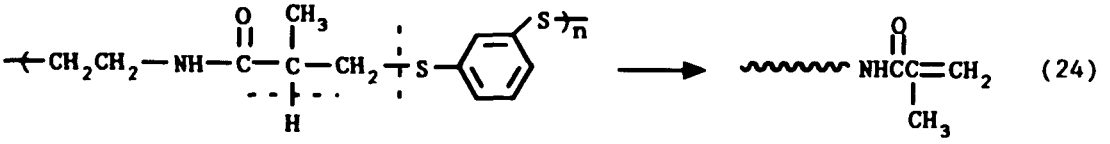


Figure 4-9 200.1 ^{1}H NMR spectrum of IPOBDT polymer (bulk, 150 °C) in DMSO-d_6 at 27 °C



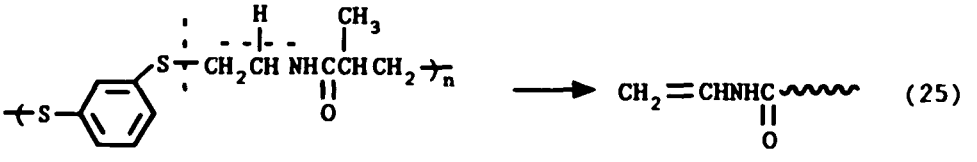
XXXXIV XXXXV

Proton 14 showed a singlet at 1.85 ppm. Proton 15 gave the signals from 5.28 to 5.69 ppm. A triplet at 3.86 ppm was assigned to proton 16. The signal of proton 15 in XXXXIV disappeared upon additon of bromine. XXXXIV was produced by the elimination reaction as follows.



XXXX XXXXIV (24)

Another speculated elimination reaction would give end-group XXXXVI instead of XXXXIV:



XXXX XXXXVI (25)

The existence of end-group XXXXVI was excluded by using the following two model compounds, acrylamide (XXXXVII) and methacrylamide (XXXXVIII):

XXXXVII

XXXXVIII

Protons 1 and 2 in XXXXVII give two groups of multiplets in a region of 5.3 to 6.4 ppm; Proton 1′ in XXXXVIII give two groups of multiplets in the region of 5.3 to 5.6 ppm. The signals in Figure 4-9 are from 5.3 to 5.7 ppm, which fits well with the signal pattern of XXXXVIII.

4.7 Molecular Weight Measurements

The molecular weight measurement of all the polymers was done on gel permeation chromatography and some on vapor pressure osmometry. The results are shown in Table 4-5. The molecular weight of the polymers of IPOBDT is not temperature dependent below and at 70 °C for the solution polymerization while the bulk polymerization gave a higher molecular weight polymer at 70 °C than the ones below 70 °C. The polymerization at 150 °C was carried out in both DMF and bulk, and both gave higher molecular weight compared to the polymerizations below 150 °C. Comparing the solution polymerizations in the three solvents, the polymers prepared in DMF and acetonitrile show higher molecular weight than the polymers prepared in THF indicating that solvent polarity affects molecular weight.

Table 4-5

Number-Average Molecular Weight ($\bar{M}_n$) of IPOBDT Polymers

Polymerization Temperature (°C)	Solution Polymerization					Bulk Polymerization
	in CH_3CN		in THF		in DMF	
	$\bar{M}_n$ by GPC	$\bar{M}_n$ by VPO	$\bar{M}_n$ by GPC	$\bar{M}_n$ by VPO	$\bar{M}_n$ by GPC	$\bar{M}_n$ by GPC
-27	11,330	9,171				9,187
0	12,105	8,996			18,027	
25	15,400	10,544	8,320	6,607		
70	10,570	8,896	7,417	6,039	17,390	19,831
150					19,232	21,828

The number-average molecular weight of the polymers prepared in acetonitrile below 150 °C was calculated by the area ratio of proton 12 in XXXXI to proton 5 in the ^1H NMR spectrum (Figure 4-1) assuming one end-group XXXXI per polymer chain. The results were as follows: 11,500 for the polymer prepared at -27 °C, 16,300 for the polymer made at 0 °C, 17,100 for the polymer prepared at 70 °C. Compared with Table 4-5, the determinations by GPC check the calculations by NMR for the polymers prepared at -27 and 0 °C while for the polymer prepared at 70 °C the calculation by NMR gave a larger molecular weight probably because some of XXXXI was transformed to XXXXVIII by water at 70 °C resulting in the loss of XXXXI for some polymer chains. The molecular weight of the polymer prepared at 150 °C was also calculated by NMR, but end-group XXXXIV was used instead of XXXXI since XXXXI is not present in the polymer prepared at 150 °C. Based on the assumption of one XXXXIV per chain the area ratio of proton 15 in XXXXIV to proton 5 was used to calculate the molecular weight and gave a molecular weight, 21,500 which is in good agreement with the one determined by GPC.

4.8 TGA

The polymers were also characterized by thermal gravimetric analysis (TGA) (Figure 4-10). As shown in Figure 4-10, the polymer decomposes at 250 °C, which indicates that the polymer is pretty much heat-resistant.

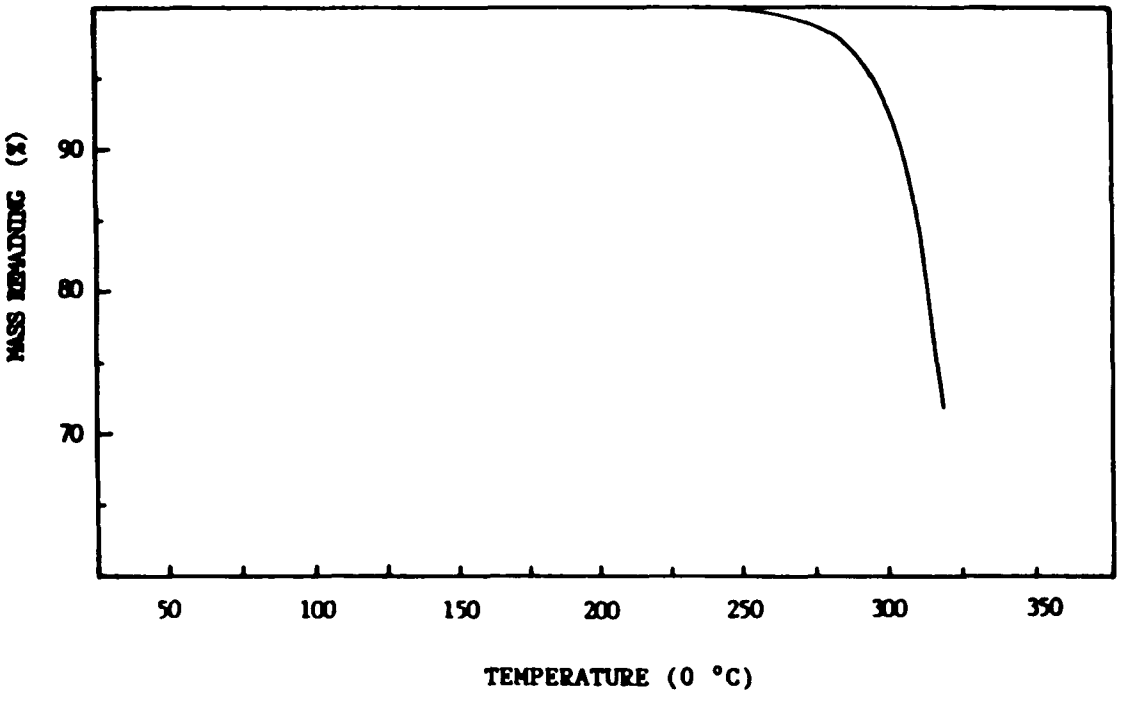
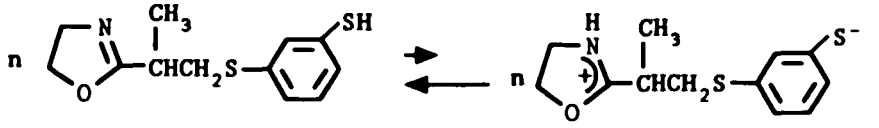
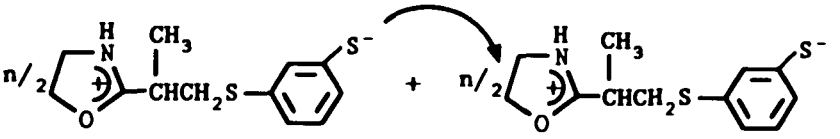


Figure 4-10 Thermal Gravimetric Analysis (TGA) diagram of IPOBDT polymer (in DMF, 75 °C) under nitrogen

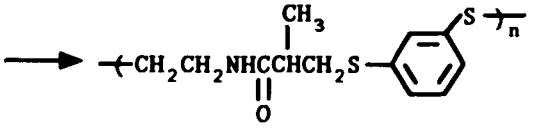
4.9 Polymerization Mechanism of IPOBDT



XVIII XXXXIX (26)



XXXXIX XXXXIX



XXXX (27)

Polymer XXXX has an unbranched chain structure because S^- in IPOBDT zwitterion is much more nucleophilic than N in IPOBDT neutral molecule and the latter can not compete with the former to produce a branched polymer as in the IPOHTP system. Also because S^- is very nucleophilic the establishment of the equilibrium (26) between IPOBDT monomer and its zwitterion does not need heat and the polymerization occurs at -27 °C. The effort was made to look for the zwitterions, but no zwitterions were detected by NMR spectroscopy. The reason could be that the concentration of the zwitterions was too low to be detected by NMR spectroscopy. The termination reactions were dependent on polymerization temperature. For the polymerizations below

150 °C both XXXXI (electrophile) and XXXXII (nucleophile) were found indicating an "automatic termination" possibly because of the short life-time of zwitterions and lower concentration of zwitterions as the polymer chain grows. For the polymerization at 150 °C, both elimination and water attack occurred to terminate the polymerization.

4.10 Comparison between System I and System II

The chemical structure and molecular weight of the polymers depend strongly on the nucleophilicity of the anionic end (nucleophilic) of a zwitterion. Comparing IPOHTP and IPOBDT systems, we see that because of low nucleophilicity of ArO^- in IPOHTP zwitterion, the polymers have a branched structure due to the successful competition of N in IPOHTP neutral molecule also acting as a nucleophile. Also, have low molecular weights are produced because of the high tendency of the elimination reaction. ArS^- in IPOBDT zwitterion has a high nucleophilicity and gave higher molecular weight and unbranched polymers.

The chemical structure and molecular weight of the polymers also depend on the rigidity of the backbone chain. This was concluded from the comparison of the polymerization of IPOHTP to the polymerization of 3-[[2-(2-oxazolin-2-yl)propyl]thio]propionic acid (XIII)[4] (Eq. 8). The nucleophilic center ArO^- in the former system is more nucleophilic than COO^- in the latter system, but ArO^- could not compete as well as COO^- with nitrogen in the neutral molecule. The result was 18% of branched polymer

repeat unit from nitrogen attack in the polymer (XIV) of 3-[[2-(2-oxazolin-2-yl)propyl]thio]propionic acid compared to 48% of branched polymer repeat unit from nitrogen attack in IPOHTP polymer. We propose the following explanation: the concentration of the zwitterions is very low (too low to be detected by NMR spectroscopy), so most of the zwitterions, especially long chain zwitterions, stabilize themselves by the adoption of conformations having the two chain ends close together. The introduction of the phenyl ring, besides the rigid amide bond, to the backbone of IPOHTP polymer makes the chain more rigid. IPOHTP zwitterions have difficulty stabilizing themselves by having the two chain ends close together. The less stable IPOHTP zwitterions tend to convert to their neutral molecules (monomer or polymer) more favorably. The result is that the concentration of IPOHTP zwitterions is lower, which gives less opportunity for zwitterions to attack each other to form straight chain polymers and more opportunity for N in IPOHTP neutral molecule to attack zwitterions to form polymers with side chains.

5.0 Results and Discussion on Thermal Polymerization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride (System III)

5.1 Synthesis and Characterization of 3-Chloropropyl Thiolacetate (XXXXXII)

3-Chloropropyl thiolacetate was prepared by the addition of thiolacetic acid (XXXXX) to allyl chloride (XXXXXI) under ultraviolet light radiation from a UV lamp. The reaction was

$$\underset{\text{XXXXX}}{CH_3\overset{\overset{O}{\|}}{C}SH} + \underset{\text{XXXXXI}}{CH_2{=}CHCH_2Cl} \xrightarrow{h\upsilon} \underset{\text{XXXXXII}}{CH_3\overset{\overset{O}{\|}}{C}SCH_2CH_2CH_2Cl} \qquad (28)$$

complete in 1 h at reflux temperature. UV light speeds up the reaction. The reaction was run in winter and without UV lamp radiation, and no reaction occurred in 2 h for the same scale of reaction. The reaction was also run without UV lamp radiation in summer and took 6 h period of time for a small scale reaction. The resulting product contains a small amount of impurities which could not be removed by fractional distillation. This product was used for next step preparation without further purification.

The crude 3-chloropropyl thiolacetate was characterized with ^1H NMR spectrum (Figure 5-1). The singlet at 2.37 ppm is

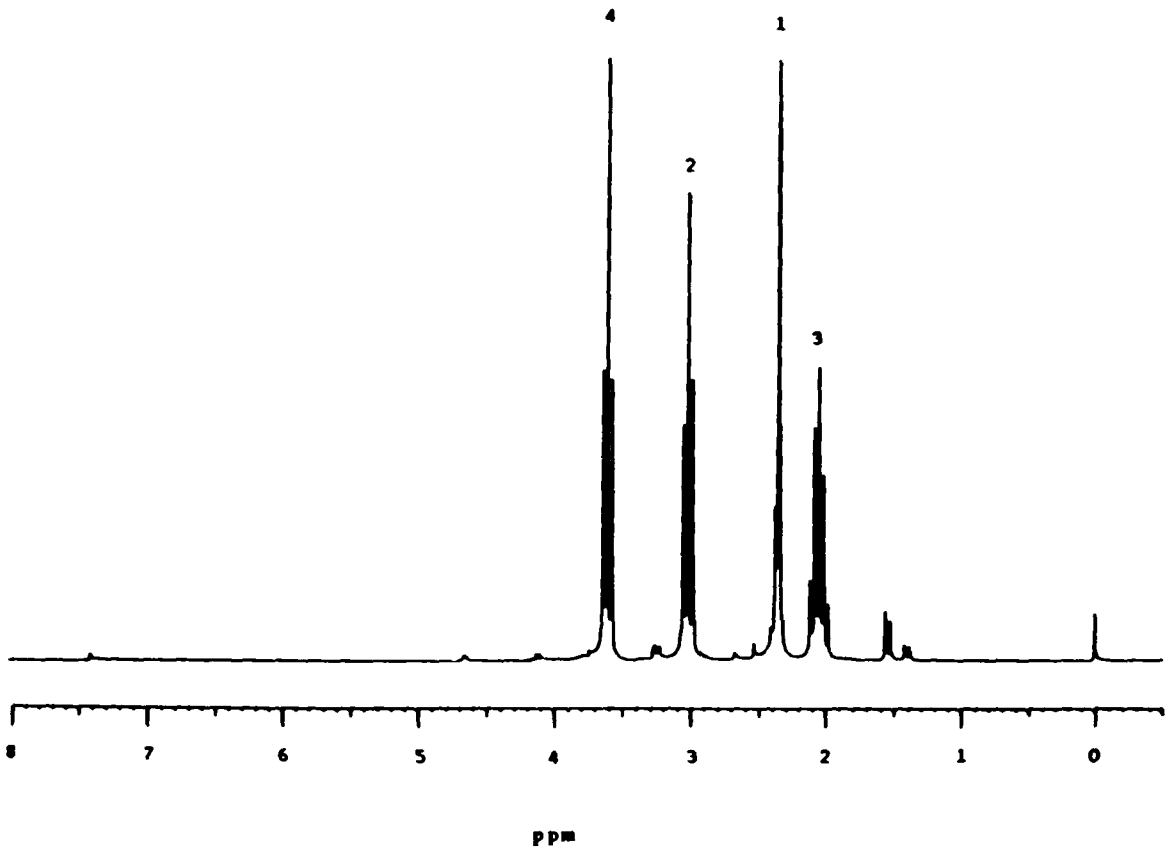
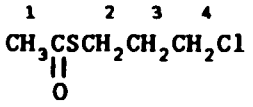


Figure 5-1 200.1 MHz ^{1}H NMR spectrum of 3-chloropropyl thiolacetate in DMSO-d_6 at 27 °C

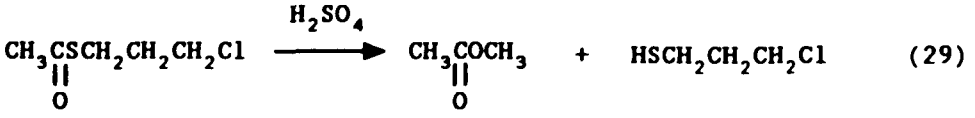


XXXXXII

due to proton 1. The triplet at 3.06 ppm is due to proton 2. the multiplet at 2.07 ppm is proton 3. The triplet at 3.61 ppm is proton 4. The rest of the small signals are due to impurities.

5.2 Synthesis and Characterization of 3-Chloropropanethiol (XXXXXVI)

3-Chloropropanethiol was prepared by hydrolyzing the crude 3-chloropropyl thiolacetate with concentrated sulfuric acid as a catalyst.

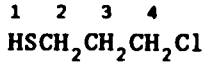


(29)

XXXXXII XXXXXIII XXXXXIV

The product was purified by vacuum distillation and silica gel chromatography. The pure 3-chlorpropanethiol was a colorless liquid.

The chemical structure of 3-chloropropanethiol was characterized by ^{1}H NMR (Figure 5-2) and ^{13}C NMR (Figure 5-3) spectroscopy. The signals in Figure 5-2 were assigned as follows.



XXXXXIV

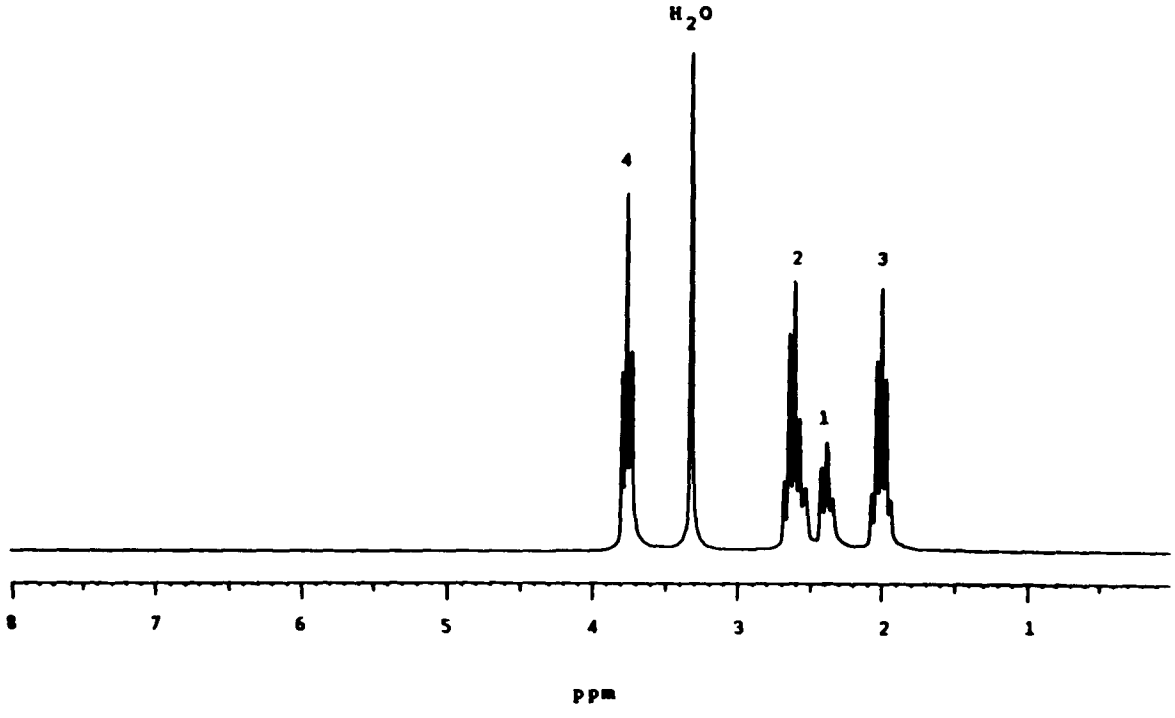


Figure 5-2 200.1 MHz ^{1}H NMR spectrum of 3-chloropropanethiol in DMSO-d_6 at 27 °C

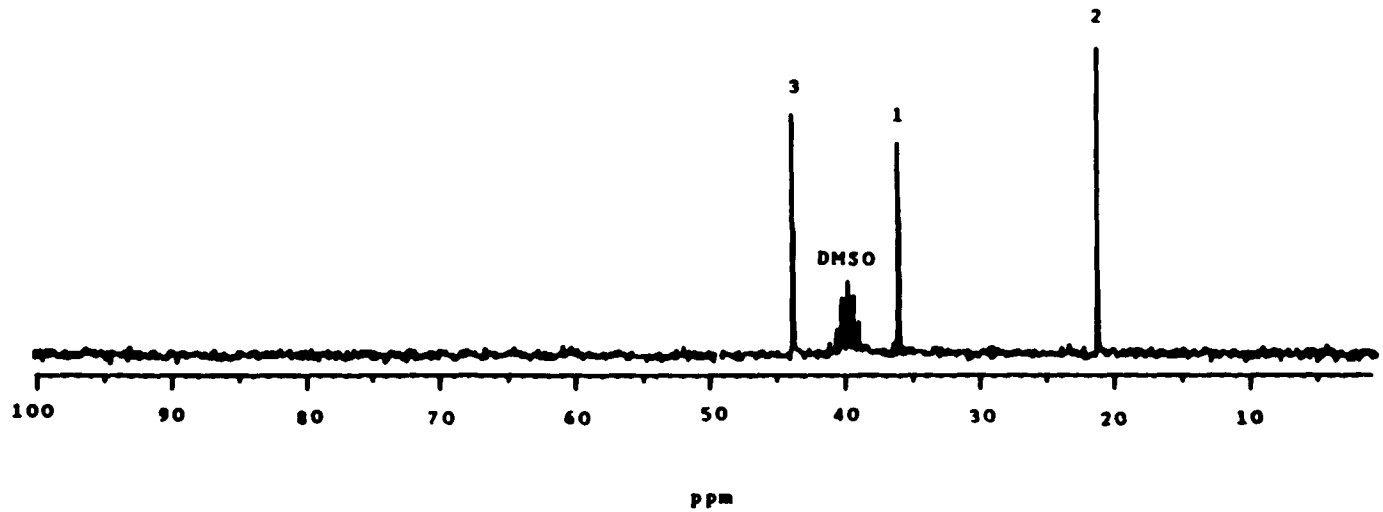


Figure 5-3 50.3 MHz ^{13}C NMR spectrum of 3-chloropropanethiol in DMSO-d_6 at 27 °C

The triplet at 3.75 ppm is proton 4. The multiplet at 2.62 ppm is proton 3. The triplet at 2.38 ppm is proton 1. The multiplet at 2.02 ppm is proton 2. The signal assignment of proton 2 and proton 3 was assisted by Homonuclear Decoupling NMR spectra (Figure 5-4a and Figure 5-4b). Decoupling of the multiplet at 2.62 ppm resulted in a singlet of proton 1 and a triplet of proton 3 as shown in Figure 5-4a, so the multiplet at 2.62 ppm must be proton 2. Decoupling of the multiplet at 2.02 ppm resulted in a singlet of proton 4 and a doublet of proton 2 as shown in Figure 5-4b, so the multiplet at 2.02 ppm must be proton 3. The assignment of carbon signals is shown in Figure 5-3.

$$\overset{1}{H}S\overset{2}{C}H_2\overset{3}{C}H_2CH_2Cl$$

XXXXXIV

5.3 Synthesis and Characterization of 2-Phenyl-1,2-thiaphospholane (XIX)

2-Phenyl-1,2-thiaphospholane was prepared through the following two step reaction:

$$\underset{\text{XXXXXV}}{Ph-PCl_2} + \underset{\text{XXXXXIV}}{HSCH_2CH_2CH_2Cl} \xrightarrow{Py} \underset{\text{XXXXXVI}}{Ph-P\begin{matrix}S-(CH_2)_3-Cl\\ \diagup\\ \diagdown\\ Cl\end{matrix}} \xrightarrow{Li} \underset{\text{XIX}}{\text{(2-phenyl-1,2-thiaphospholane)}} \qquad (30)$$

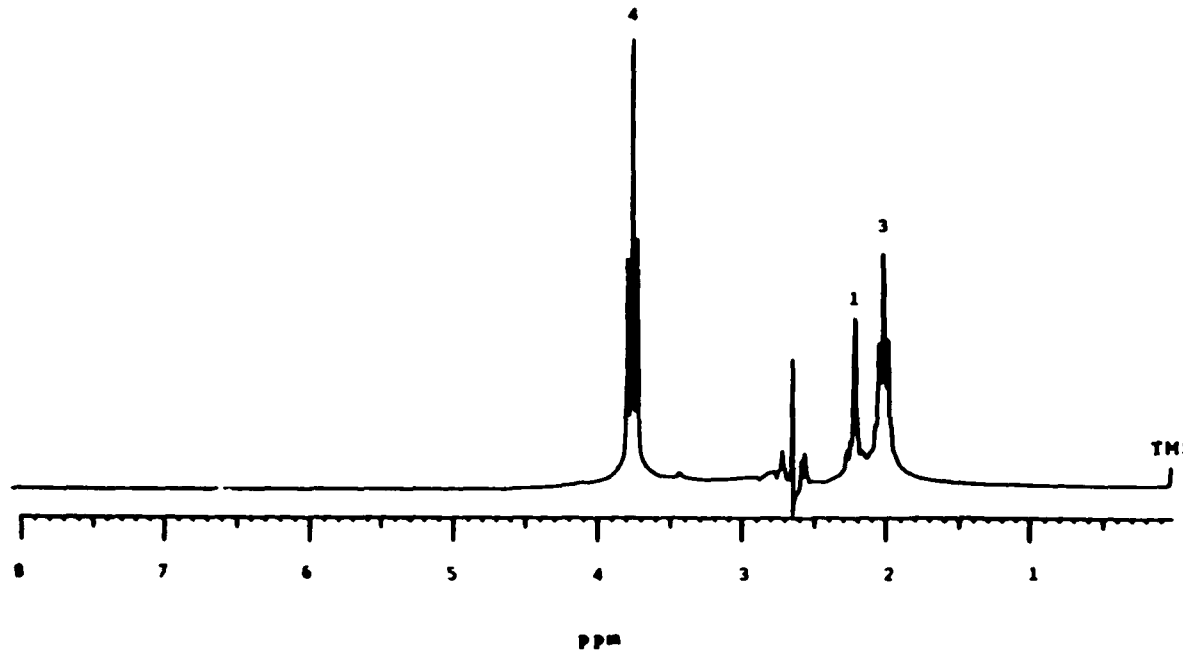


Figure 5-4a Homonuclear decoupling spectrum of 3-chloropropanethiol in DMSO-d_6 at 27 °C

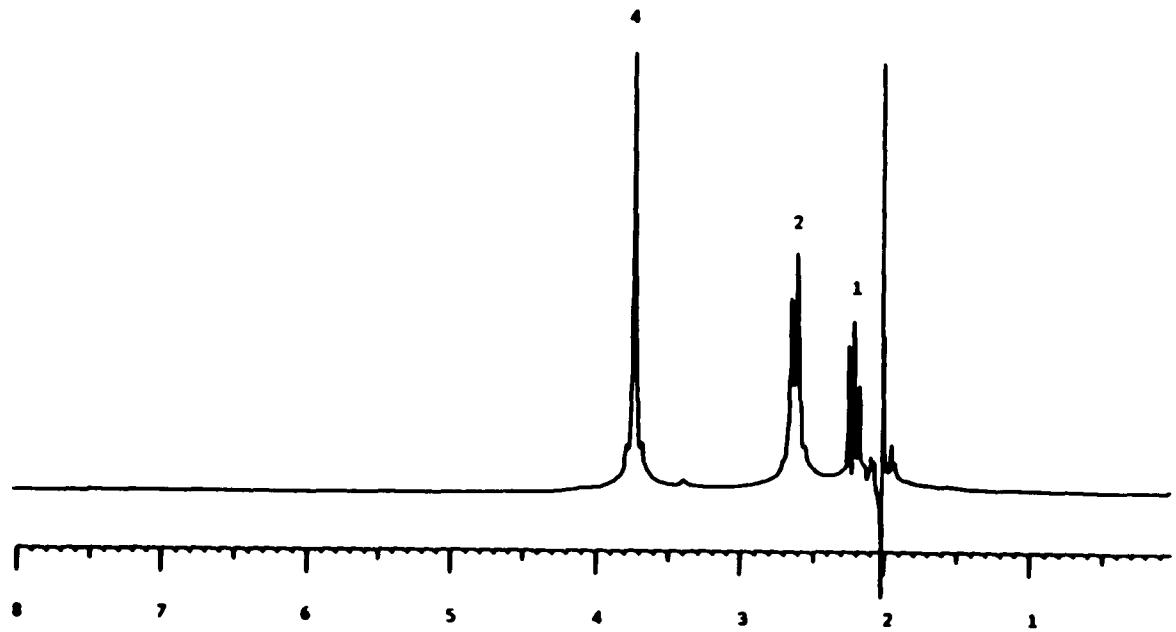
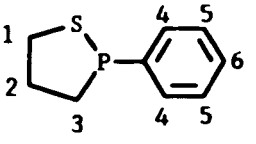


Figure 5-4b Homonuclear decoupling spectrum of 3-chloropropanethiol in DMSO-d_6 at 27 °C

Dichlorophenyl phosphine, 3-chloropropanethiol and pyridine were refluxed together to form compound XXXXXVI in the first step. Compound XXXXXVI then reacted with pieces of lithium at -78 °C overnight to form 2-phenyl-1,2-thiaphospholane (XIX). XIX was a colorless liquid with bp 105-106 °C/0.1 torr. The structure of 2-phenyl-1,2-thiaphospholane was characterized by ^{1}H (Figure 5-5), ^{13}C (Figure 5-6) and ^{31}P (Figure 5-7) NMR spectroscopy. In the ^{1}H NMR spectrum, the signals from 1.41 to



XIX

3.15 ppm are due to protons 1, 2 and 3 which are coupled with ^{31}P and overlapped together, and the signals from 7.16 to 7.50 ppm are due to protons 4, 5 and 6. The ^{13}C NMR spectrum is much better resolved than the ^{1}H NMR spectrum. The carbon signals are assigned as follows:

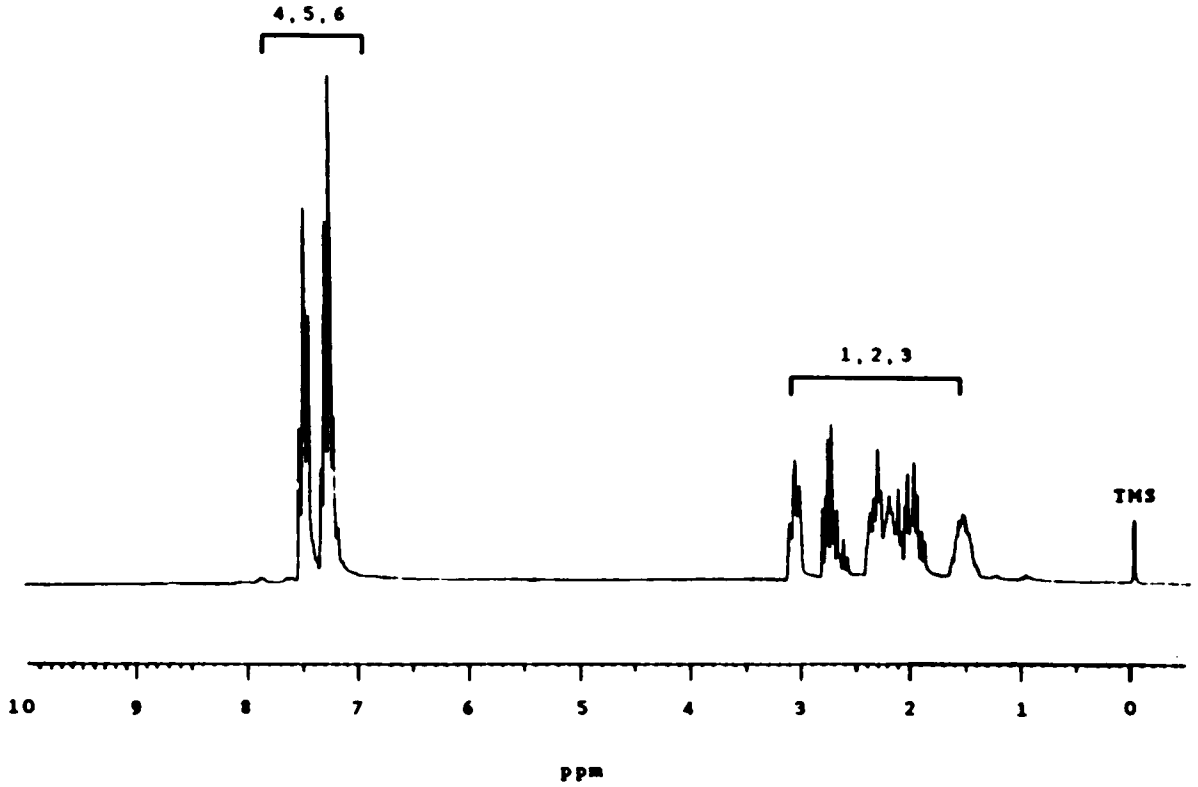


Figure 5-5 200.1 MHz ^{1}H NMR spectrum of 2-phenyl-1,2-thiaphospholane in DMSO-d_6 at 27 °C

Figure 5-6 50.3 MHz ^{13}C NMR spectrum of 2-phenyl-1,2-thiaphospholane in DMSO-d_6 at 27 °C

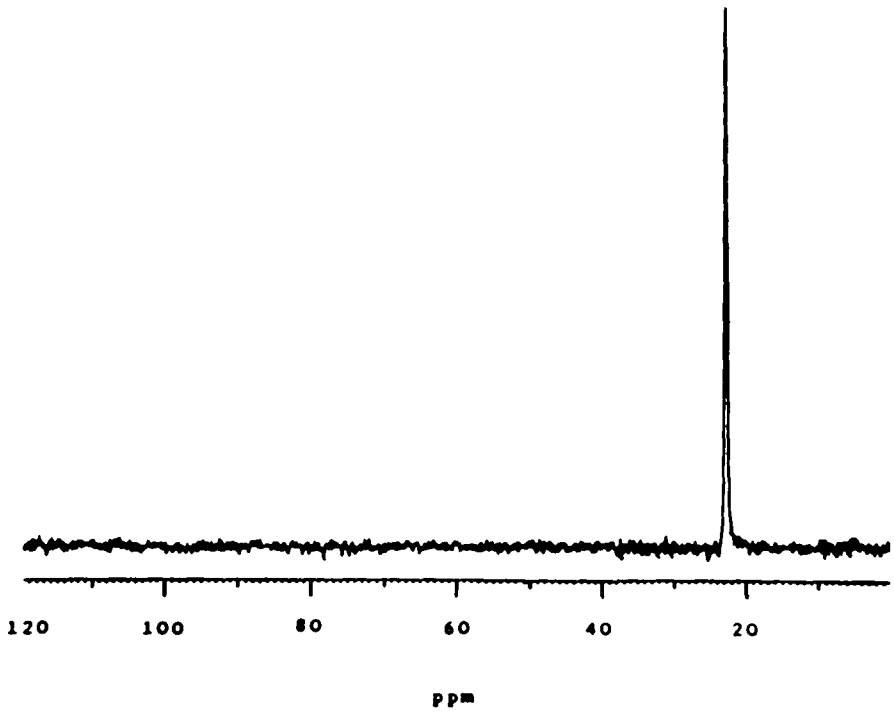
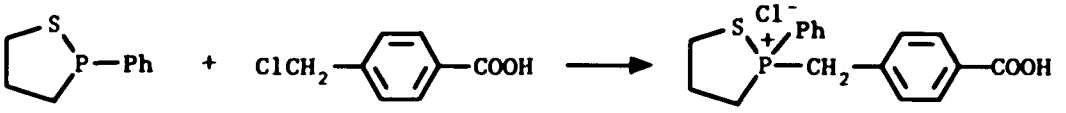


Figure 5-7 80.3 MHz ^{31}P NMR spectrum of 2-phenyl-1,2-thiaphospholane in DMSO-d_6 at 27 °C

5.4 Synthesis and Characterization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride (XXVII)

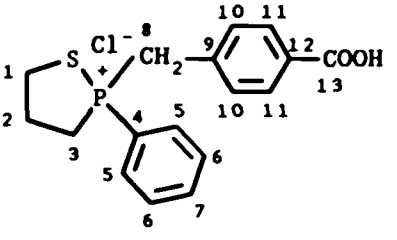
2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride (XXVII) was prepared with 2-phenyl-1,2-thiaphospholane and 4-chloromethyl benzoic acid in a molar ratio of 1:6 at 35 °C.



(31)

XIX XXIV XXVII

Three crops of crude product were collected and combined together. The crude product was recrytallized with methanol and ether to yield pure XXVII as a light green powder. XXVII was kept in a freezer for later use. The chemical structure of XXVII was supported by ^{13}C and ^{31}P NMR spectroscopy. The assignment of the carbon signals in the ^{13}C NMR spectrum (Figure 5-8) is the following:



XXVII

The signal at 173.0 ppm is due to carbonyl carbon 13. The

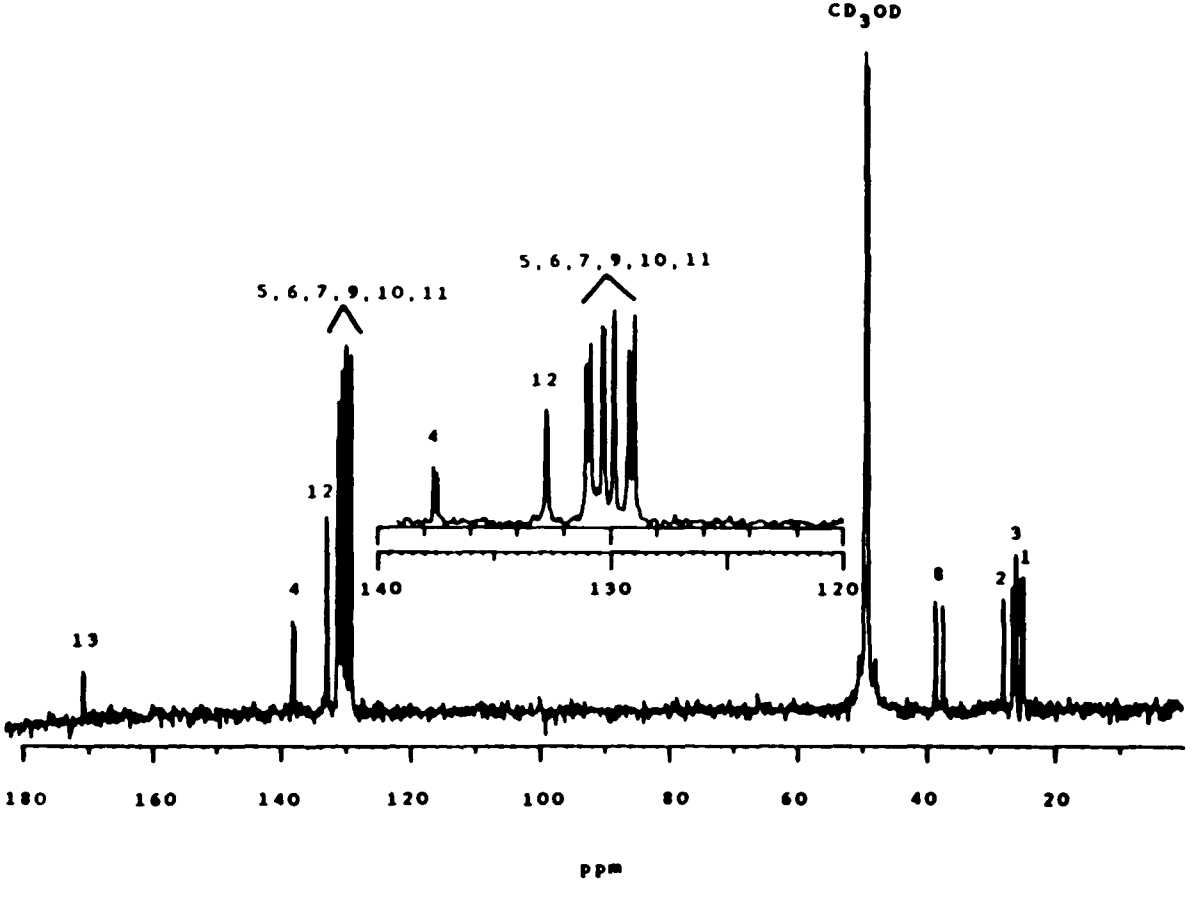


Figure 5-8 50.3 MHz ^{13}C NMR spectrum of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride

doublet at 138.1 ppm is carbon 4 split by ^{31}P. The signal at 132.8 ppm is carbon 12. The signals from 128.2 to 130.7 ppm correspond to carbons 5, 6, 7, 9, 10 and 11. The doublet centered at 30.8 ppm is carbon 8. The signal at 28.0 ppm is carbon 2. The doublets at 20.6 and 24.5 ppm are carbons 3 and 1, respectively, both of which are split by ^{31}P. The ^{31}P NMR spectrum (Figure 5-9) showed one singlet at 83.7 ppm referenced to 85% phosphoric acid. This position is within the chemical shift range of ^{31}P in phosphonium salts.

5.5 Polymerization of 2-Phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium Chloride (XXVII)

The effort to prepare zwitterion XXVIII from XXVII failed because polymerization occurred during process. The thermal polymerizations of XXVII were carried out in bulk under continuous vacuum and in vacuum-sealed tubes in the temperature range of 70-150 °C to give polymers with molecular weight ranging from 1,500 to 3,000. The chemical structure of the polymers was very complicated according to ^{1}H (Figure 5-10) , ^{13}C (Figure 5-11) and ^{31}P (Figure 5-12) spectra. No simple repeat unit structure accounted for the observed spectra.

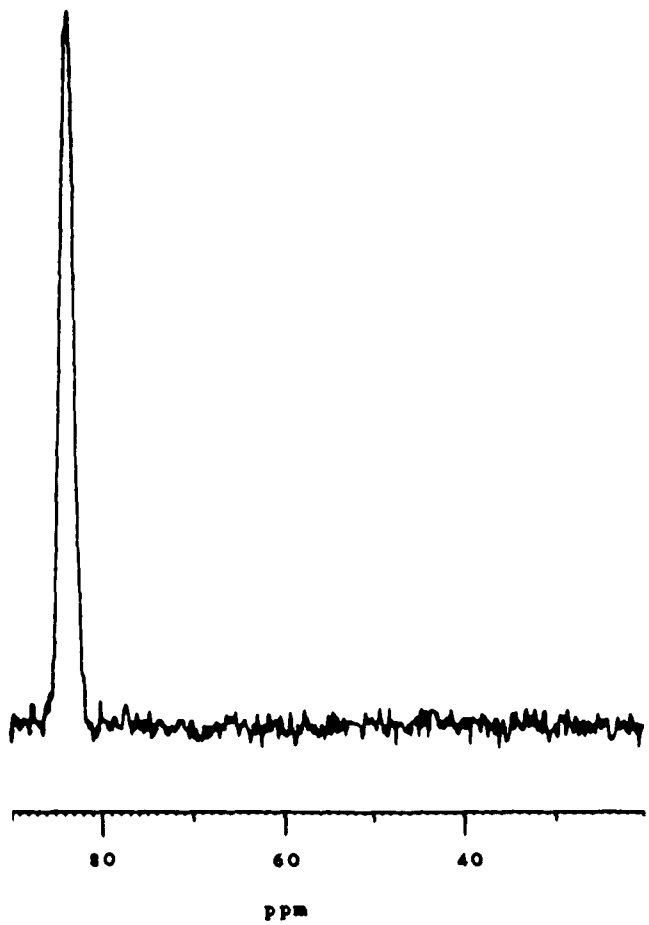


Figure 5-9 80.3 MHz ^{31}P NMR spectrum of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride

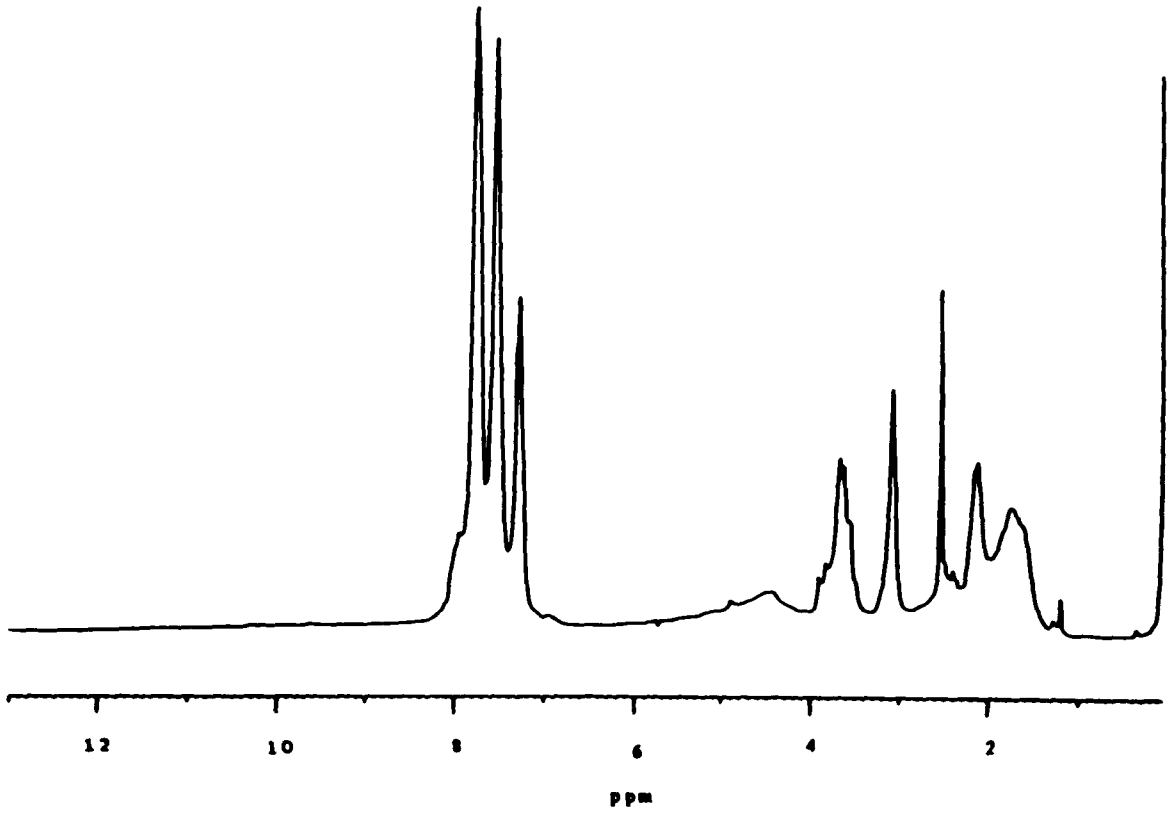


Figure 5-10 200.1 MHz ^{1}H NMR spectrum of the polymer of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride (under continuous vacuum, 100 °C) in DMSO-d_6 at 27 °C.

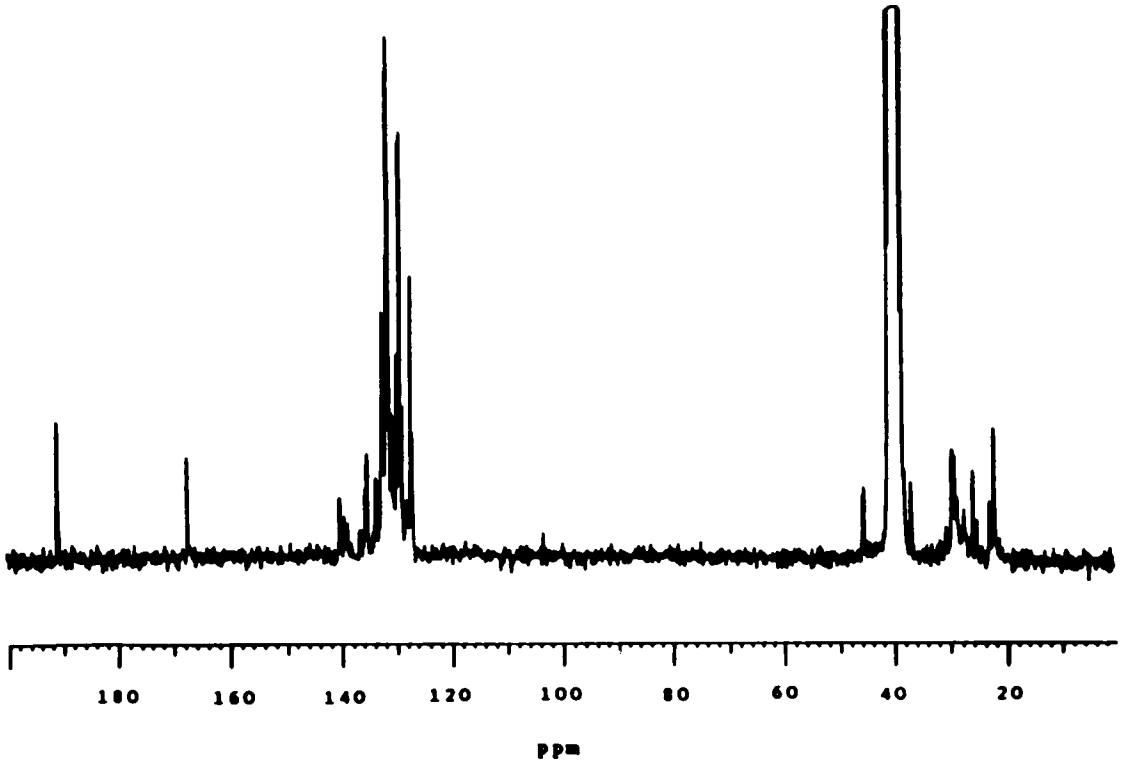


Figure 5-11 50.3 MHz ^{13}C NMR spectrum of the polymer of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride (under continuous vacuum, 100 °C) in DMSO-d_6 at 27 °C.

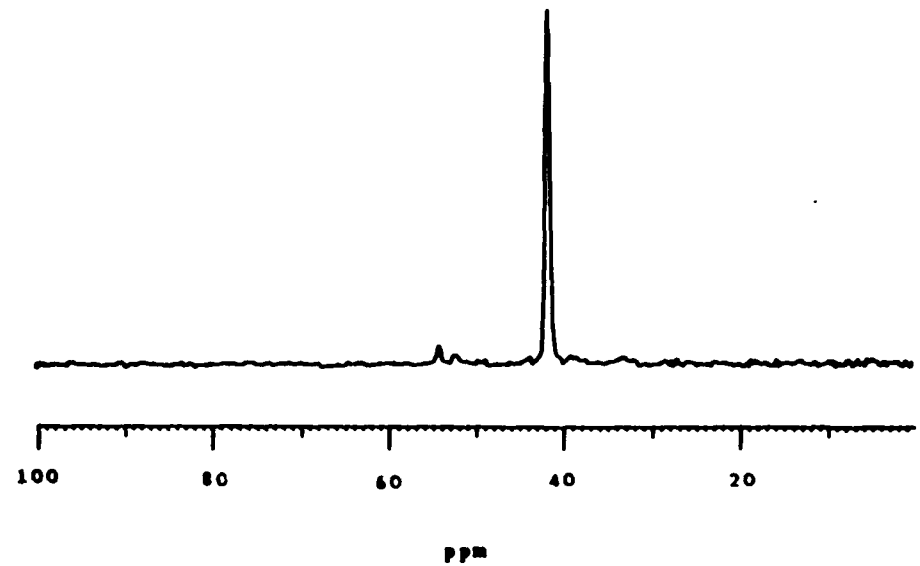


Figure 5-12 80.3 MHz ^{31}P NMR spectrum of the polymer of 2-phenyl-2-[(4-carboxyphenyl)methyl]-1,2-thiaphosphonium chloride (in vacuum-sealed tube, 150 °C) in DMSO-d_6 at 27 °C.

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