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Modification of tetrahydrothiophenium arene oxide systems

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Modification of Tetrahydrothiophenium Arene Oxide Systems

by

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1990

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1.0 BACKGROUND

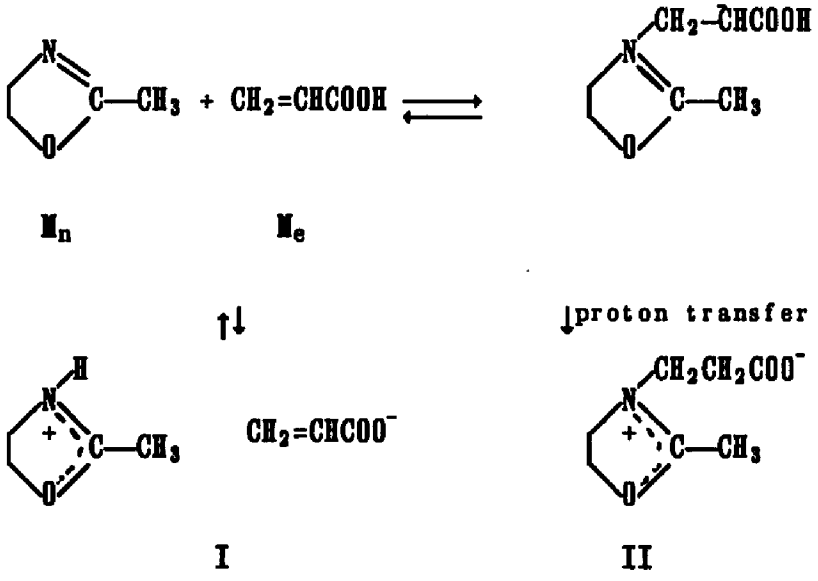
Zwitterionic polymerization, also known as spontaneous polymerization, is based upon the organic reaction which occurs when a nucleophilic monomer (M_n) is mixed with an electrophilic monomer (M_e) resulting in the formation of a genetic zwitterion intermediate, $^{+}M_n\text{-}M_e^{-}$, which proceeds to polymerize. Since the zwitterions are responsible for both initiation and propagation, it is not necessary to use a catalyst, initiator, or high-energy irradiation to induce the polymerization. Three distinct approaches have been used to investigate polymerizations in which the propagating species is a zwitterion. A discussion of the three methods used seems necessary in order to obtain a sense of the field before presenting a detailed discussion of the experimental results.

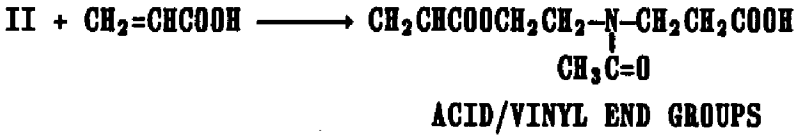
1.1 Direct Mixing of Nucleophilic and Electrophilic Monomers

A significant portion of the work done in the field of zwitterion polymerizations has been accomplished by the use of this approach. The technique used in this approach is fairly crude; it involves the direct mixing of a nucleophilic and electrophilic monomer either in solution or neat and allowing the reaction mixture to stand at the reaction temperature for a specified time. Zwitterions have been proposed as the intermediates through which polymerization occurs. Several pairs of monomers possessing interesting functional groups which can be incorporated into the polymer backbone or pendant to the polymer backbone have been investigated, i.e. 2-methyl-2-oxazoline (M_n) and N-phenyl maleimide (M_e)[1], 2-phenoxy-1,3,2-dioxaphospholane

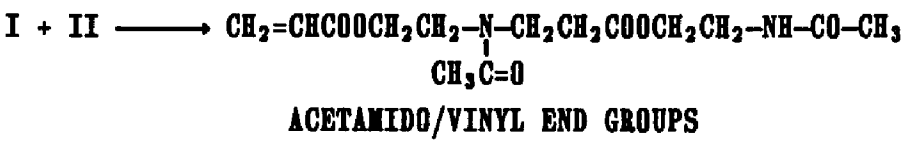
(M_n) and acrylic acid (M_e)[2], and 2-methyl-2-oxazoline (M_n) and acrylic acid (M_e).[3,4] The approach of reacting nucleophilic and electrophilic pairs directly has lead without exception to low molecular weight products, with the largest reported value found being Mn=19,000.[5] A possible explanation for the failure to achieve high molecular weights with this approach lies in the fact that many copolymer systems contains the seeds of their own destruction. This fact was demonstrated in a detailed study of the zwitterionic polymerization of 2-methyl-2-oxazoline with acrylic acid.[3,4] For this system the genetic zwitterion (II) (which is responsible for initiation and propagation) can react with either acrylic acid or a betaine intermediate (I) that forms, causing termination to be favored over chain growth (Scheme I). The termination reactions involved were derived by the analysis of the polymer end groups of the samples by the use of NMR spectroscopy.

Scheme I:





ACID/VINYL END GROUPS



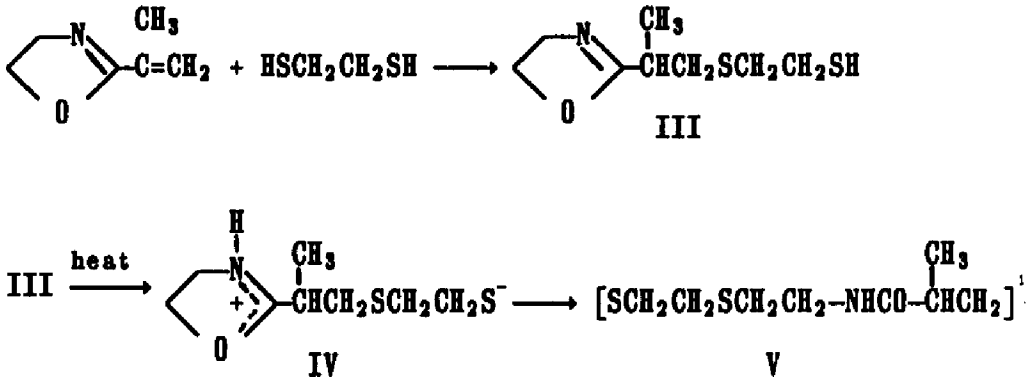
ACETAMIDO/VINYL END GROUPS

1.2 Isolation of a Nonionic Adduct

A more successful approach being pursued to achieve high molecular weight polymers involves the isolation and purification of neutral adducts which are capable of forming and propagating by means of zwitterionic intermediates. By isolating and purifying the neutral adduct, termination by reaction with excess reactants and by-products becomes obsolete and a stoichiometric balance is imposed upon the subsequent polymerization of the neutral adduct.

The neutral adducts of 2-(mercaptoalkyl)-2-oxazolines and 2-(carboxyalkyl)-2-oxazoline have been isolated by the reaction between 2-isopropenyl-2-oxazoline with hydrogen sulfide or 1,2-ethanedithiol and 2-isopropenyl-2-oxazoline with 3-mercaptopropionic acid respectively.[6,7] This approach has met with success as a molecular weight as high as 42,900 has been obtained from the adduct of 2-isopropenyl-2-oxazoline/1,2-ethanedithiol, structure III in Scheme II. The polymerization reaction is proposed to go through the zwitterion, IV, to form a polymer of structure V. The zwitterionic intermediate has never been observed in this system.

Scheme II:



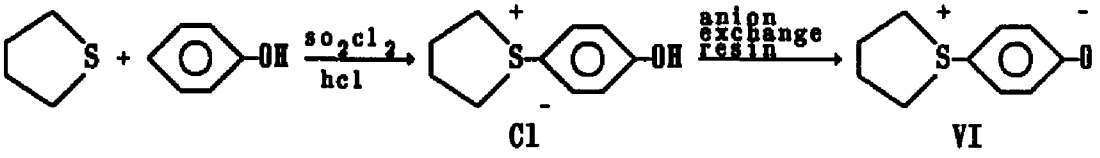
1.3 Stable Zwitterions

The final procedure used to study zwitterionic polymerizations involves the isolation and purification of the zwitterionic specie. Relatively little attention has been paid to zwitterion polymerizations involving stable (isolable) zwitterions. Two classes of zwitterions which have been isolated and polymerized are the sulphonium and ammonium zwitterions.

1.3.1 *Sulphonium Zwitterions*

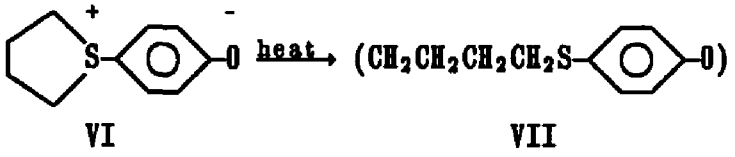
Schmidt and coworkers synthesized and isolated a class of zwitterions entitled tetrahydrothiophenium arene oxide (VI) by reacting the appropriate phenol with tetrahydrothiophene (Scheme III).[8] This class of zwitterions have been isolated as a hydrate in all cases with the exception being the systems where the aromatic ring contains two chlorine atoms. These zwitterions polymerize through a ring opening mechanism where the phenoxide anion attacks the *α*-carbon of the tetrahydrothiophenium ring to form an alternating copolymer

Scheme III:



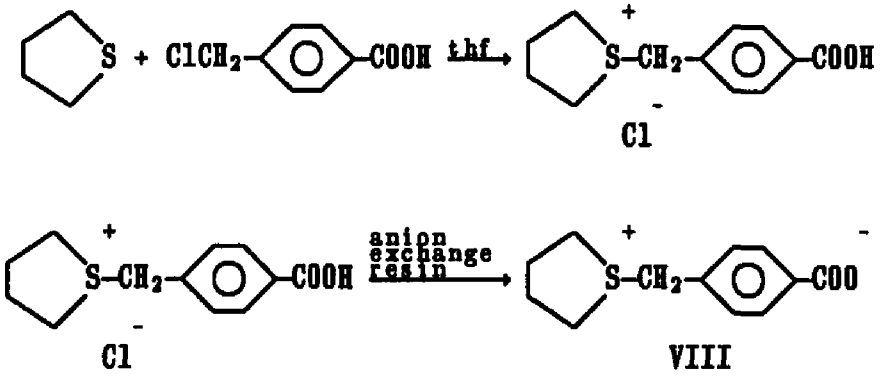
(Scheme IV) with structure VII. Recently Odian, O'Callaghan and

Scheme IV:



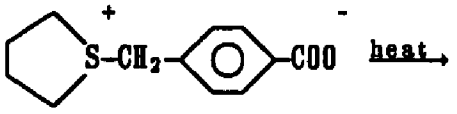
coworkers reported molecular weights of 67,800 for the tetrahydro-1-[4-hydroxy-3-(2-hydroxyethoxy)phenyl]thiophenium hydroxide inner salt which represents the highest yet to be reported for a zwitterion polymerization.[9] Gunatillake, Odian, and Schmidt reported the synthesis and isolation of 1-[(4-carboxyphenyl)methyl]tetrahydrothiophenium hydroxide inner salt, VIII, prepared by reacting tetrahydrothiophene with 4-(chloromethyl)benzoic acid (Scheme V).[10]

Scheme V:

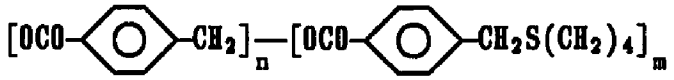


Zwitterion VIII was also isolated as a hydrate and on polymerizing resulted in the formation of random copolymer IX (Scheme VI). The

Scheme VI:



VIII



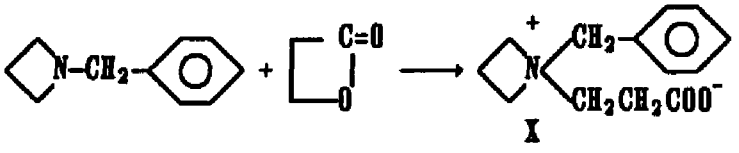
IX

polymerization preceeds 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 weights as high as 41,000 were obtained with this zwitterion.

1.3.2 *Ammonium Zwitterions*

S. Hashimoto and T. Yamashita synthesized and isolated ammonium zwitterions by reacting 1-benzylazetidine with cyclic ester such as β-propiolactone to form 3-(N-benzylazetidino)propionate (X) as shown in Scheme VII.[11] Compound X polymerized when heated by ring opening of the azetidinium ring by the carboxylate anion to form a polymer with structure XI with a molecular weight of 6000 as shown in

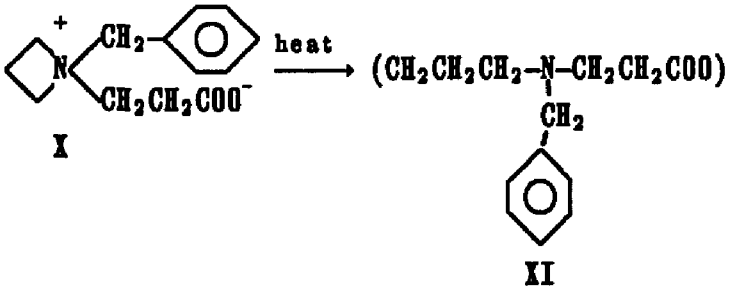
Scheme VII:



X

Scheme VIII.

Scheme VIII:



X

XI

1.4 Methodolgy

The purpose of this investigation was to prepare new zwitterions by the modification of tetrahydrothiophenium arene oxide systems. Information regarding the types of monomers which can successfully be used to obtain high molecular weight polymers can be obtained by understanding the termination mechanism of the polymerization. Tetrahydrothiophenium arene oxides represent an interesting class of zwitterions to study. Since they are isolable, they lend themselves to modification by reactions with either electrophiles or nucleophiles. However, due to the fact that they are highly reactive and bifunctional, attempts to modify the electrophilic portion of the zwitterion, thiophenium ring, by the addition of a nucleophile would

result in competition between the nucleophilic end of the zwitterion, phenoxide anion, and the added nucleophile for the thiophenium ring. The reverse scenario is also true for modification of the nucleophilic end by the addition of an electrophile. Modification of the hydrochloride salt of the tetrahydrothiophenium arene oxide system represents a wiser route in the preparation of new zwitterion systems. By blocking the phenoxide functionality, the thiophenium ring could be modified by the addition of a nucleophile without any competing side reactions.

Cyclic amines have been reported by Wilson and Beaman to be incorporated into the polymer main chain when used as initiators for the polymerization of pivalolactone.[12] When the cyclic amine was 1,4-ethylene piperidine up to 18 monomer units were incorporated into the polymer backbone. For this study tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide hydrochloride salt was chosen as the tetrahydrothiophenium arene oxide system to be modified since the polymer has been characterized previously and 1,4-ethylene piperidine as the nucleophlic monomer since its quaternary salt has been demonstrated to undergo ring opening reactions and it is commercially availabile.

Since there is no synthetic way to reduce the reactivity of the thiophenium ring, attempts to modify the nucleophilic end of tetrahydrothiophenium arene oxides by the addition of electrophiles would require mild conditions in order to avoid competition. β-Lactones have been reported in the literature to react with sodium phenoxides in water at 25-30°C to form β-aroxy carboxylic acids.[13]

The nucleophilic portion of tetrahydro-1-(4-hydroxy-1-naphthyl)-thiophenium hydroxide inner salt was reacted with β-butyrolactone. β-Butyrolactone was chosen as the electrophile due to its low toxicity in comparison to other β-lactones and its commercial availability.

2.0 EXPERIMENTAL

2.1 Experimental for 4-(4-[1,4-Ethylenepiperidinium]butanethio)-1-naphthol Inner Salt

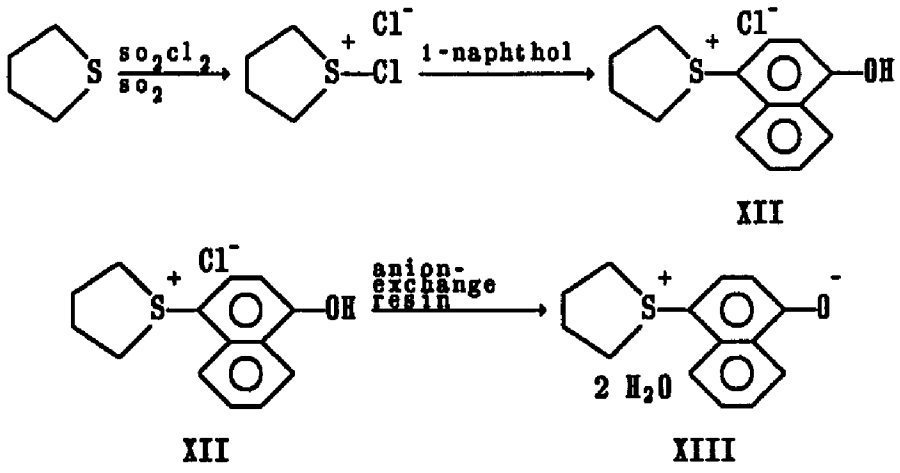
2.1.1 *Synthesis*

2.1.1.1 Synthesis of Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium Hydroxide Inner Salt: 1-naphthol was purified by vacuum sublimation (0.5 mm Hg) at 85°C prior to use. All other reagents were used as received. Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide hydrochloride salt, herein referred to as NZ·HCl salt, was prepared as reported by Schmidt.[14] 10.3 g of tetrahydrothiophene (0.12 moles) and approximately 0.003 g of iodine over nitrogen was cooled to -40°C after which approximately 33 g of sulfur dioxide was condensed into the solution through a dry ice/acetone condenser. Approximately 3 g of gaseous hydrogen chloride was dissolved into the solution followed by the addition of 15 g of sulfuryl chloride (0.11 mole). 16 g of 1-naphthol (0.11 mole) was added to the solution, which was then allowed to warm to reflux for three hours after which 1 ml of distilled water was added to the solution. The solvent, sulfur dioxide, was removed under vacuum (water aspirator) at ambient temperature, and the liquid was poured into excess acetone to form a white precipitate, which was the NZ·HCl salt (XII). The NZ·HCl salt was collected by vacuum filtration, dissolved into methanol and reprecipitated into acetone. The NZ·HCl salt was again collected by vacuum filtration and stored in the freezer until used. The yield was

typically 75%.

The NZ·HCl salt was converted to the tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt, herein referred to as NZ zwitterion or NZ monomer (XIII), by dissolving 4.0 g of the NZ·HCl salt into 12 ml of CH_3OH. The methanol solution was treated with Dowex 1x2 200 anion-exchange resin which was activated by stirring over 3M sodium hydroxide. The resin was collected by vacuum filtration, washed with distilled water until neutral (pH paper), and further washed with methanol to remove the water. The activated resin was added slowly into the methanol solution of the NZ·HCL salt to a pH of 10.5 was obtained (monitored with a pH meter). The resin was filtered off and the solution was added to ether to precipitate the crude NZ zwitterion (Scheme IX).

Scheme IX:



The crude NZ zwitterion was recrystallized from ethanol and diethyl ether. Diethyl ether was added at ambient temperature to a

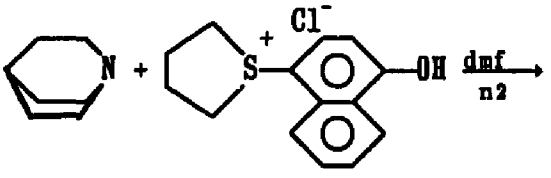
25% solution of the NZ zwitterion in ethanol, until the solution turned slightly cloudy and then the solution was maintained overnight at 0°C. A white powder was filtered and more ether was added to the filtrate which was again maintained overnight at 0°C. The second crop was used in our experiments after drying overnight in a desiccator in the dark at atmospheric pressure at ambient temperature. The purified NZ zwitterion, which is sensitive to heat and light, was refrigerated in the dark.

2.1.1.2 Synthesis of 4-(4-[1,4-Ethylenepiperidinium]butanethio)-1-naphthol inner salt: 4-(4-[1,4-ethylenepiperidinium]butanethio)-1-naphthol inner salt, herein referred to as the NEP zwitterion or NEP monomer, was prepared from its corresponding hydrochloride salt as indicated in Scheme X. 1,4-ethylene piperidine was purified prior to use by vacuum sublimation (0.5 mm Hg) at room temperature. N,N-Dimethylformamide (DMF) was dried over 3Å molecular sieves and distilled under vacuum in a nitrogen atmosphere. DMF was stored in a dry box until used. 6.0 g of the NZ·HCl salt (0.02 moles) and 3.3 g of 1,4-ethylene piperidine (0.03 moles) was added to a round-bottom flask to which 37 ml of DMF was added. The heterogeneous mixture was stirred overnight with nitrogen bubbling through it. The resulting homogeneous light yellow solution was added to rapidly stirring ether (400 ml) yielding a white gum. The ether was decanted off and the residue was dried in a vacuum oven (1 mm Hg) at 50°C overnight to afford 4-(4-[1,4-ethylenepiperidinium]butanethio)-1-naphthol hydrochloride salt, XIV, herein referred to as the NEP·HCl salt. The

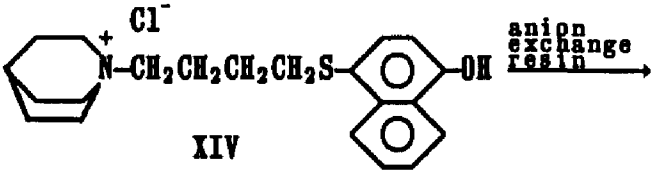
yield was 90%.

4.0 g of the NEP·HCl salt was dissolved into 12 ml of methanol to afford a golden solution. Dowex 1x2 200 anion exchange resin (activated as described previously in section 2.1.1.1) was added to the solution. The resin (approximately 35 g) was added to the methanol solution of the NEP·HCL salt until a pH of 10.5 was reached (monitered with a pH meter). The resin was filtered off and the solution (≈ 30 ml) was added to 200 ml of acetone. The flask was scratched with a glass rod to induce crystallization. Once the solution became cloudy it was placed in a freezer overnight. The NEP zwitterion, XV, which had a light green color, was isolated by vacuum filtration and then dried in a vacuum oven (1 mm Hg) at room temperature for 3 hours. The NEP zwitterion was stored in the dry box until used. The yield was 58.3%.

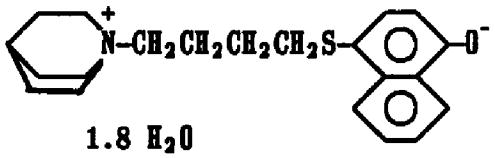
Scheme X:



XII



XIV



1.8 H_2O

XV

2.1.1.3 Anhydrous 4-(4-[1,4-Ethylenepiperidinium]butanethio)-1-naphthol: Isolation of the anhydrous NEP zwitterion was achieved by the use of Thermogravimetric Analysis. 10-15 mg samples of the NEP zwitterion was placed inside of an aluminum pan and weighed to ±.01 mg. The sample was heated to 175°C under a nitrogen atmosphere at a rate of 10°C per minute to observe weight loss due to the water of hydration, cooled to room temperature and then reheated to 175°C. On the second heating cycle no weight loss was observed. The sample was removed from the aluminum pan and dissolved into CD_3OD in order for ^1H NMR to be taken to ensure that no polymerization occurred.

2.1.1.4 Synthesis of Poly(1,4-piperidineylethyleneoxy-1,4-naphthylthiotetramethylene): Poly(1,4-piperidinedylethyleneoxy-1,4-naphthylenethiotetramethylene), herein referred to as the NEP polymer, was prepared by the bulk polymerization of the NEP zwitterion. The polymerization was studied over a termperature range of 175-225°C under both sealed tube and continuous vacuum conditions. For the sealed tube method 0.20 g of the NEP zwitterion was placed in a polymerization tube, evacuated at approximately 1 mm Hg for 20 minutes, and sealed under vacuum. The polymerization tube was covered with aluminum foil (to keep out the light) and heated at the reaction

temperature for a specified time. Water condensed at the top of the polymerization tube as the NEP zwitterion lost its water of hydration upon heating. The polymerization tube was broken and the green glass was stirred over methylene chloride and precipitated into rapidly stirring methanol forming a beige solid. The methanol/methylene chloride solution was decanted off and the polymer was dried in a vacuum oven at room temperature for 24 hours. The yield was typically around 75%. The same procedure was followed for the samples polymerized under continuous vacuum except that the tube was not sealed but heated under continuous vacuum (approximately 1 mm Hg).

2.1.2 *End Group Analysis*

2.1.2.1 Bromination of the NEP polymer: 0.050 g of the NEP polymer was added into 0.5 ml of acetic acid-d_4 and stirred for 1 hour. After 1 hour methanol-d_4 was added dropwise to afford a clear light tan colored solution. On addition of a drop of Br_2 the solution turned green in color and a green precipitate formed on the bottom of the vial. The solution was decanted off and the precipitate was dissolved into 0.50 ml of DMSO-d_6. ^1H NMR was performed on the DMSO-d_6 solution.

2.1.2.2 Acetylation of the NEP Polymer: The NEP polymer (0.15 g) was dissolved into CH_2Cl_2 (1.0 ml) and triethylamine (0.02 g) was added while stirring. Acetyl chloride (0.02 g) in CH_2Cl_2 (0.3 ml) was added while stirring to the polymer solution at ambient temperature. After the reaction mixture stirred for four hours it was precipitated

into excess methanol. The methanol/methylene chloride solution was decanted off and the acetylated polymer was dried in a vacuum oven (1 mm Hg) at room temperature overnight.

2.1.3 *Spectroscopic Analysis*

2.1.3.1 Nuclear Magnetic Resonance Spectroscopy (NMR):

2.1.3.1.a. Proton (^1H) and Carbon (^{13}C) NMR spectra were obtained at 25°C on an IBM WP 200SY FTNMR spectrometer using a 5-mm dual $^{13}C/^1H$ probe for ^1H and a 10-mm dual $^{13}C/^1H$ probe for ^{13}C, operating at 200 MHz for ^1H and 50 MHz for ^{13}C. The ^1H spectra of the NEP·HCl salt and NEP zwitterion were obtained in a 5% (w/v) solution of methanol-d_4 while ^{13}C spectra were obtained in a 10% (w/v) solution of methanol-d_4, CD_3OD. ^1H and ^{13}C spectra of NEP polymer were obtained, respectively, in 5% and 10% (w/v) solutions of chloroform-d_1, $CDCl_3$ at 25°C. The spectra were either referenced to an internal standard, tetramethylsilane, or to the solvent signals, 4.78 ppm for CD_3OD, and 7.24 ppm for $CDCl_3$ for the proton spectra and 49.0 ppm for CD_3OD and 77.0 ppm for $CDCl_3$ for the carbon spectra.

2.1.3.1.b Distortionless Enhancement by Polarization Transfer (DEPT) spectra for the NEP·HCl salt, NEP zwitterion, and NEP polymer were obtained in 10% (w/v) solutions in their respective solvents at 25°C in order to determine the multiplicities of each ^{13}C resonance. The following standard pulse sequence was used (where D1 is the relaxation delay):[15]

^{1}H: D1——90°——1/2J——180°——$1/2J_{C-h}$——PO——$1/2J_{C-h}$——BB

^{13}C: ————————————90°————180°————————FID

PO is a variable depending on the desired multiplicities selection; i.e. for PO=135° signals of positive intensity represents methyl and methine carbons and signals of negative intensity represents methylene carbons. For all reported DEPT results PO was chosen as 135°. J_{C-h} is the one bond J scalar coupling constant between carbon and hydrogen. A value of 135 Hz was used for the experiments. Quaternary carbons have zero intensity. A relaxation delay, D1, of 2 seconds was used between pulses.

2.1.3.1.c ^{1}H -^{1}H Correlated Spectroscopy (COSY) were obtained on 5% (w/v) solutions on the NEP·HCl salt, NEP zwitterion and NEP polymer in their respective solvents at 25°C in order to correlate homonuclar coupling. The frequency axes F1 and F2 contain the ^{1}H chemical shift values while the 1-D spectrum appears along the diagonal. Smaller off-diagonal cross peaks arise from coupling between the protons. The COSY spectrum was obtained by the use of the standard pulse sequence:[16]

^{1}H: D1——90°——D0——90°——FID

A total of 256 experiments of 1K data points were obtained. 16 scans were obtained for each experiment with sweep widths of 1592.357 Hz for the NEP·HCl salt , 2202.643 Hz for NEP zwitterion, and 1915.709 Hz for NEP polymer. A relaxation delay, D1, of 1 second was used between scans. The data was processed on a SUN work station. The raw FIDs were processed by using a phased shifted sine apodization, with a

phase of 0.5, endpoint of 1 and an integer exponent of 2, function prior to the first Fourier transformation. The resulting interferogram were processed by using a phased shifted sine apodization factor with a phase of 0.5, endpoint of 1 and an integer exponent of 2, followed by zero-filling to 512 data points before the second Fourier transformation. The spectrum was symmetrized and plotted as a contour map.

2.1.3.1.d ^{1}H - ^{13}C Correlated Spectroscopy (HCCORR) were obtained on 10% (w/v) solutions of the NEP·HCl salt and NEP polymer using the 10 mm probe dual $^{13}C/^{1}H$ probe and a 25% (w/v) solution of the NEP zwitterion using the 5 mm dual $^{13}C/^{1}H$ probe at 25°C in order to correlate carbons with their directly attached protons. The frequency axes F1 and F2 contain the ^{1}H and ^{13}C chemical shift values respectively. Connectivities were determined by noting the frequency at which the peak occurs on both the ^{1}H and ^{13}C chemical shift axes. Quaternary carbons do not give any peaks since they are not attached to a proton. The HCCORR spectra were obtained by use of the following pulse sequence:[17]

^{1}H: D1——90°——D0——D3——90°——D4——BB

^{13}C:————————180°——90°————FID

A total of 512 experiments of 1K data points were obtained for the NEP·HCl salt, NEP zwitterion, and NEP polymer samples. A relaxation delay, D1, of 2 seconds was used between scans. Correlations for the C-H bond are most efficient when the delay period, D3, is approximately 1/(2J), 3.3 msec, and D4 is between 1/(3J) and 1/(4J),

1.7 msec. Twenty-four scans were obtained for the NEP·HCl salt and NEP polymer and 88 scans were obtained for the NEP zwitterion for each experiment with a sweep width of 1798.561 Hz for proton and 7462.687 Hz for carbon for the NEP·HCl salt, and 2202.643 Hz for proton and 8064.516 Hz for carbon for both the NEP zwitterion and NEP polymer. The data was processed on a SUN work station. The raw FIDs were processed by using a phased shifted sine apodization function, with a phase of 0.5, endpoint of 1, and an integer exponent of 2, prior to the first Fourier transformation. The resulting interferogram were processed by using a phased shifted sine apodization function, with a phase of 0.5, endpoint of 1, and an integer exponent of 2, folowed by zero-filling to 1K data points for the NEP·HCl salt, NEP zwitterion and NEP polymer prior to the second transformation. The spectrum was plotted as a contour map.

2.1.3.2 Infrared Spectroscopy (I.R.): I.R. spectra were recorded on a Bio-Rad Digilab FTS-40 spectrometer. The NEP·HCl salt and NEP zwitterion were deposited as a thin film on a NaCl plate from a dilute ethanol solution; the solvent was evaporated in a vacuum oven (at approximately 1 mm Hg) at ambient temperature for four hours. The NEP polymer and NEP acetylated polymer were deposited as a thin film on a NaCl plate from a methylene chloride solution; the solvent was evaporated in a vacuum oven (about 1 mm Hg) at ambient temperature for 4 hours.

2.1.4 *Thermal Analysis*

2.1.4.1 Thermal Gravimeteric Analysis (TGA): TGA was performed on the NEP zwitterion to determine the amount of water of hydration present. A Dupont 990 Thermal Analyzer coupled to a 950 Thermogravimetric Analyzer module was used for the determination. The NEP zwitterion (6-10 mg) was weighed to the nearest 0.01 mg at ambient temperature in an aluminium pan in the TGA module, heated to 175°C at a rate of 10°C per minute under a nitrogen atmosphere with a flow rate of 50 ml/min. The pan was cooled to room temperature and reweighed to determine the amount of water lost.

2.1.4.2 Differential Scanning Calorimetry (DSC): DSC was carried out with the Dupont 990 coupled with a 910 Differential Scanning Calorimeter module. DSC was performed on the NEP zwitterion in order to determine the melting point of the monomer. 8 to 10 mg of the NEP zwitterion was heated from room temperature to 225°C under a N_2 atmosphere with a flow rate of 50 ml/min at a rate of 10°C per minute, cooled slowly and subjected to a second heating cycle. DSC was performed on the NEP polymer to determine the presence of heat transitions (i.e. glass transition temperature, melting temperature). The NEP polymer sample (2 mg) was weighed to the nearest 0.1 mg, compressed sealed in an aluminium pan and heated at 10°C per minute under a nitrogen atmosphere (flow rate 50 ml/min) to 160°C. The sample was cooled slowly or fast cooled by use of an ice bath before a second heating scan was taken.

2.1.5 *Molecular Weight Determination*

2.1.5.1 Nuclear Magnetic Resonance Spectroscopy (NMR): ^1H NMR was used to determine the number average molecular weight of the NEP polymer by comparing the sum of the integral value for the olefinic end group centered at 5.02 ppm and 5.79 ppm with the main chain methylene proton signal adjacent to the aryl ether linkage centered at 4.15 ppm. In using this procedure an assumption that each polymer molecule contains only one olefinic end group was made.

2.2 Experimental for the Copolymerization of Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt and β-Butyrolactone

2.2.1 *Materials*

Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt, herein referred to as the NZ monomer or NZ zwitterion, was prepared and purified as reported in Section 2.1.1.1. β-Butyrolactone, herein referred to as β-BL, was purified by fractional distillation over calcium hydride, CaH_2, under a nitrogen atmosphere at reduced pressure. Crotonic acid was purified by recrystallization from water. N,N-Dimethylformamide, herein referred to as DMF, was purified by repeated drying over molecular sieves and distillation under a nitrogen atmosphere at reduced pressure. Toluene was purified by distillation over CaH_2 under a nitrogen atmosphere at reduced pressure. All the other reagents were used as received.

2.2.2 *Synthesis*

2.2.2.1 Synthesis of Poly(oxytetramethylenethio)-1,4-naphthalene: Poly(oxytetramethylenethio)-1,4-naphthalene, herein referred to as poly-NZ or the naphthyl polymer, was prepared by the thermal polymerization of the NZ zwitterion. 0.20 g of the NZ zwitterion was placed in a polymerization tube, evacuated at approximately 1 mm Hg for 15 minutes, and sealed under vacuum. The polymerization tube was covered with aluminum foil (to keep out the light) and then heated at

135°C for 20 hours. Water condensed on top of the polymerization tube as the zwitterion lost its water of hydration. The polymerization tube was broken and the light yellow reaction mixture was stirred for 4 hours over methylene chloride. The naphthyl polymer which precipitated as a white solid, was collected by vacuum filtration and washed with methylene chloride followed by methanol. The naphthyl polymer was dried at 40°C in a vacuum oven at approximately 1 mm Hg overnight.

2.2.2.2 Synthesis of Poly[(oxycarbonyl)propylene]: Poly[(oxycarbonyl)propylene], herein referred to as poly-β-BL, was prepared as described in the literature.[18] 0.50 ml of β-BL (6.13 mmoles) was dissolved in 0.50 ml of toluene to which 15.1 μl of boron trifluoride etherate, $(C_2H_5)_2O \cdot BF_3$ (2 mole %) was added. The reaction mixture was heated at 60°C for 2 days under a nitrogen atmosphere. On heating, the reaction mixture turned from colorless to gold. On cooling to room temperature the reaction mixture became extremely viscous. Poly-β-BL was isolated by distilling off the toluene to leave an oily product.

2.2.2.3 Copolymerization of Tetrahydro-1-(4-hydroxy-1-naphthyl)-thiophenium hydroxide inner salt and β-Butyrolactone: The copolymerization of the NZ zwitterion and β-BL was investigated in solution between the temperature range of 35-100°C. Equimolar mixtures of the NZ monomer and β-BL were dissolved in DMF in a polymerization tube under a nitrogen atmosphere. The polymerization

tube was sealed under vacuum (approximately 1 mm Hg) by use of the freeze-thaw technique. The polymerization tube was covered by aluminum foil (to keep out the light), and then heated at the reaction temperature for the specified time. The reaction mixture turned from a light green color to a tan color upon heating. The polymerization tube was broken and the reaction mixture was precipitated into diethyl ether. After centrifugation a transparent film formed on the bottom of the vessel. The diethyl ether/DMF mixture was decanted off. The resulting film was dissolved into a minimum of methylene chloride, CH_2Cl_2, and reprecipitated into excess methanol, CH_3OH, at 0°C. After centrifugation the methanol/methylene chloride solution was decanted off and the resulting clear film was dried in a vacuum oven (approximately 1 mm Hg) at 40°C for 2 days.

2.2.2.4 Preparation of 1-(Tetramethylenethio)-4-naphthol β-methyl acrylate: The model end group compound 1-(tetramethylenethio)-4-naphthol β-methyl acrylate, herein referred to as the vinyl-naphthol model compound, was prepared by the reaction between crotonic acid and the NZ monomer. 0.49 g of crotonic acid (5.5×10^{-3} moles) was dissolved in 3.0 ml of DMF and heated to 40°C. 1.00 g of the NZ zwitterion (3.8×10^{-3} moles) was dissolved in 6.5 ml of DMF and added drop wise in the crotonic acid solution at 40°C. The reaction mixture was stirred at 40°C for 4 hours. The DMF was removed under vacuum (approximately 2 mm Hg) at 40°C to afford a golden color oil. The target compound was isolated from a silica gel column using 90/10 (v/v) ethyl acetate/methylene chloride mixture as the eluting solvent.

2.2.2.5 Acetylation of 1-(Tetramethylenethio)-4-naphthol β-methyl acrylate: 0.150 g of the vinyl-naphthol model compound was dissolved into 1.00 ml of CH_2Cl_2 to which 0.100 g of triethyl amine was added while stirring. Acetyl chloride (0.070 g) dissolved in 0.50 ml of CH_2Cl_2 was added slowly to the vinyl-naphthol model compound solution. The reaction mixture was stirred at room temperature for 4 hours. After the reaction time was complete, the reaction mixture was poured into excess hexane to precipitate the triethyl amine·HCl salt. The triethyl amine·HCl salt was collected by vacuum filtration. The filtrate was placed in a roto-vap and the solvent was removed at room temperature under reduced pressure. The target compound was isolated from a silica gel column using ethyl acetate as the eluting solvent. The target compound was dried at 40°C in a vacuum oven (approximately 1 mm Hg) overnight.

2.2.2.6 Bromination of 1-(tetramethylenethio)-4-naphthol β-methyl acrylate: A 10% (v/v) solution of bromine in $CDCl_3$ was added drop wise to a 5% solution of the vinyl-naphthol model compound in $CDCL_3$ in an ice bath until the color of bromine persisted. The solution was allowed to stand overnight at room temperature. The sample retained the color of the added bromine and was not purified, but examined directly by ^1H NMR.

2.2.3 *End Group Analysis*

2.2.3.1 Bromination of the Copolymer: A 1% solution of bromine in chloroform (d_1), $CDCl_3$, was added drop wise to a 5% solution of the

copolymer in $CDCl_3$ in an ice bath until the red color of bromine persisted, and then let stand overnight at room temperature. The copolymer solution retained the color of the added bromine and was not purified, but examined directly by ^1H NMR spectroscopy.

2.2.3.2 Acetylation of the Copolymer: The copolymer (0.060 g) was dissolved into CH_2Cl_2 (0.60 ml) to which 0.20 g of pyridine was added while stirring. Acetyl chloride (0.020 g) in CH_2Cl_2 (0.30 ml) was added slowly while stirring to the polymer solution at ambient temperature. After the reaction mixture was stirred for 4 hours, it was added to excess methanol and centrifuged. The methanol/methylene chloride solution was decanted off and the resulting film was dried in a vacuum oven at 40°C for 2 days.

2.2.4 *Spectroscopic Analysis*

2.2.4.1 Nuclear Magnetic Resonance Spectroscopy (NMR):

2.2.4.1.a Proton (^1H) and (^{13}C) NMR spectra were obtained at 25°C on 5% (w/v) solution and 10% (w/v) solutions, respectively, in dimethyl sulfoxide, DMSO (d_6), for the NZ/β-BL monomer mixture, chloroform, $CDCl_3$ (d_1), for poly-β-BL, the copolymer and the vinyl-naphthol end group, and 1,1,2,2-tetrachloroethane, TCE (d_4) for poly-NZ at 60°C as described in Section 2.1.3.1.a.

2.2.4.1.b Distortionless Enhancement by Polarization Transfer (DEPT) spectra was obtained via the method described in Section 2.1.3.1.b on the copolymer sample in a 10% (w/v) solution in $CDCl_3$ at 25°C.

2.2.4.1.c ^{1}H-^{1}H Correlated Spectroscopy (COSY) spectra was obtained on 5% (w/v) of the NZ monomer and poly-NZ in their respective solvent via the method described in Section 2.1.3.1.c. A total of 256 experiments of 1K data points was obtained for each. Sixteen scans were obtained for each experiment with a sweep width of 1851.852 Hz for the NZ monomer and 1639.344 Hz for poly-NZ. A one second delay, D1, was used between scans. The data was processed in an identical manner as described previously in Section 2.1.3.1.c.

2.2.4.1.d ^{1}H-^{13}C Correlated Spectroscopy (HCCORR) were obtained on a 10% solution of the NZ monomer in DMSO (d_6) by using a 10-mm dual $^{13}C/^{1}H$ probe at 25°C, and on a 25% (w/v) solution of poly-NZ in TCE (d_4) at 60°C by using a 5-mm dual $^{13}C/^{1}H$ probe via the method described in Section 2.1.3.1.d. A total of 512 experiments of 1K data points were obtained for the NZ monomer and 256 experiments of 512W points were obtained for poly-NZ. A two second delay (D1) was used between pulses. Twenty-four scans were obtained for each experiment with a sweep width of 1650.165 Hz for proton and 7462.687 Hz for carbon for the NZ monomer; 88 scans were obtained for each experiment with a sweep width of 2200.643 Hz for proton and 8064.515 Hz for carbon for poly-NZ. The data was processed in a manner identical to that described in Section 2.1.3.1.d.

2.2.4.2 Infrared Spectroscopy (IR): IR spectra were obtained on the instrument described in Section 2.1.3.2 on samples of poly-NZ, and 1:1 molar mixture of poly-NZ/poly-β-BL deposited as a film on a NaCl

plate from a dilute solution of bromobenzene. The film was dried in a vacuum oven (approximately 1 mm Hg) at 40°C for 4 hours. The copolymer was deposited as a film on a NaCl plate from a dilute solution of chloroform which was dried at room temperature for 4 hours in a vacuum oven (approximately 1 mm Hg).

2.2.5 *Molecular Weight Determination*

2.2.5.1 Gel Permeation Chromatography (GPC): GPC of the copolymer obtained by heating the NZ zwitterion with β-BL was carried out on a Waters 150C instrument with a 840 workstation using DMF containing 0.05 M LiBr as the mobile phase at a flow rate of 1.0 ml/min at 100°C. The stationary phase consisted of four ultrastryagel columns of 10^5, 10^4, 10^3, and 5×10^2 Å sizes. The GPC calibrations were based on polystyrene standards.

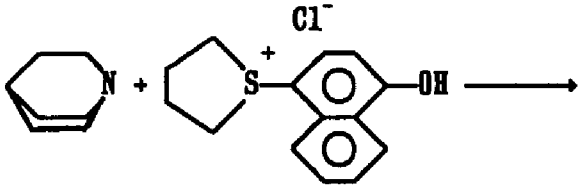
3.0 RESULTS AND DISCUSSION

3.1 Results and Discussion for 4-(4-[1,4-ethylenepiperidinium]-butanethio)-1-naphthol Inner Salt

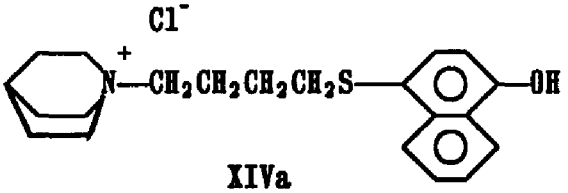
3.1.1. *Synthesis of the NEP Hydrochloride Salt*

NEP·HCl (XIVa) was prepared by the nucleophilic attack of the nitrogen atom, in 1,4-ethylene piperidine, on either carbons *a* to the sulphonium center of the NZ·HCl salt to cause ring opening of the thiophenium ring to occur as shown in Scheme XI. Whereas the

Scheme XI:



XII



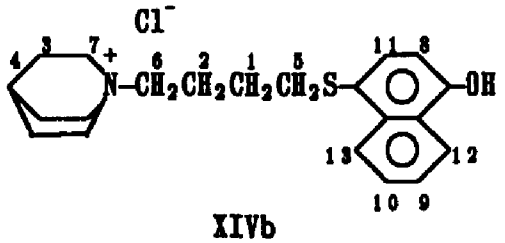
XIVa

thiophenium ring in the NZ·HCl salt has a high degree of reactivity due to the ring strain, the 1,4-ethylene piperidinium ring in the NEP·HCl salt was found to be relatively stable and was heated to 50°C without the chloride ion opening the ring.

3.1.2 *Characterization of the NEP Hydrochloride Salt*

3.1.2.1 NMR Spectroscopy: The NEP·HCl salt was characterized by the use of ^{1}H, and ^{13}C NMR, DEPT, COSY, and HCCORR techniques.

3.1.2.1.a Proton Assignments of the NEP·HCl Salt: Figure 1 and Table 1 show the ^{1}H spectrum and δ values of the NEP·HCl salt. The signal assignments shown in XIVb were based on the observed splitting pattern, signal areas, and the results from the COSY experiment (Figure 2). The sharp singlet at 4.89 ppm is due to the presence of



XIVb

the residual OH group from the solvent, methanol-d_4. The solvent signal for the methyl group is hidden under the triplet center at 3.27 ppm. The COSY spectrum (Figure 2) of the NEP·HCl salt contains a computer generated 1-D spectrum along the F1 and F2 axes in order to aid in the interpretation. Cross peaks indicating coupling between proton pairs 1 and 5, 2 and 6, and 3 and 7 are evident. On closer examination of the spectrum cross peaks also exist for proton pairs 1 and 2, and 3 and 4. Cross peaks are also present in the aromatic region for proton pairs 8 and 11, 9 and 12, and 10 and 13. A small cross peak is even observed for the proton pair 9 and 10 even though their signals are partial overlapping in the proton spectrum. The

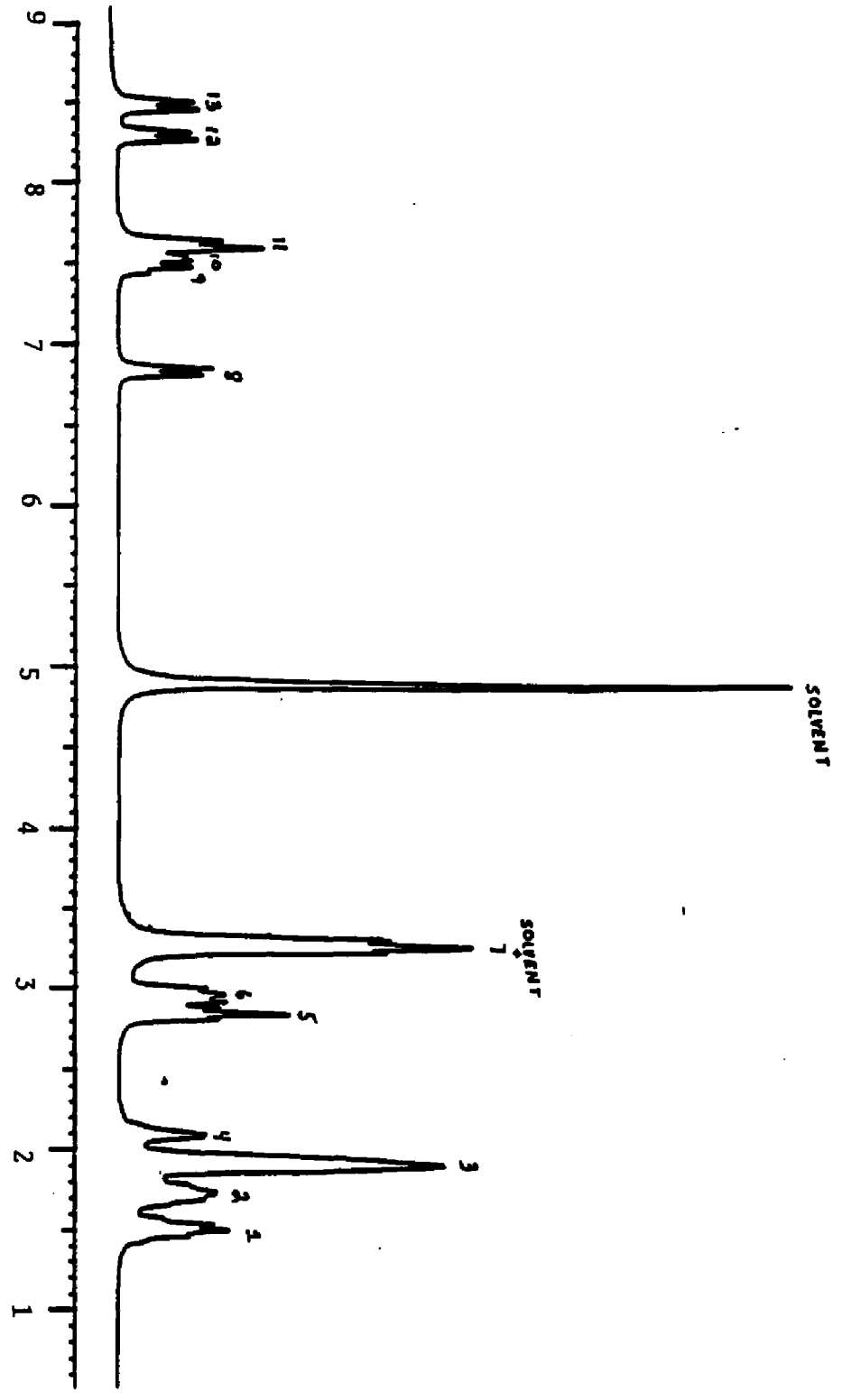


FIGURE 1
^{1}H SPECTRUM OF NEP·HCl Salt
CD_3OD SOLVENT

TABLE 1

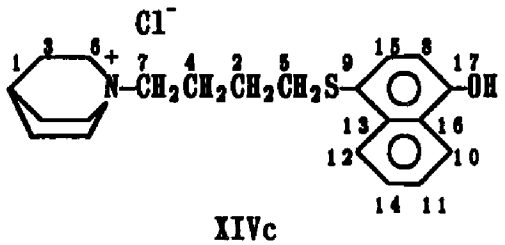
Assignments of the ^{1}H Spectrum of the NEP•HCl Salt

Proton Number	Chemical Shift (ppm)
1	1.49
2	1.73
3	1.92
4	2.09
5	2.84
6	2.95
7	3.27
8	6.82
9	7.46
10	7.53
11	7.60
12	8.25
13	8.43

FIGURE 2
COSY SPECTRUM OF NEP·HCl Salt
CD_3OD SOLVENT

assignments of protons 9 and 10, and 12 and 13 are made somewhat arbitrarily and hence may be interchanged, i.e. protons 9 and 12 may be signals 10 and 13 and protons 10 and 13 may be signals 9 and 12. However it is clear from the COSY spectrum that protons 9 and 10 are adjacent to protons 12 and 13, respectively.

3.1.2.1.b Carbon Assignments of the NEP·HCl Salt: The proton-decoupled ^{13}C spectrum (Figure 3, Table 2) of the NEP·HCl salt supports structure XIVa. The carbon signals were assigned as shown in XIVc based on the results from DEPT (Figure 4, Table 3), HCCORR (Figure 5a and 5b) experiments, and chemical shifts values for similar carbons.[19] From the DEPT spectrum (Figure 4) the assignments of the



XIVc

methine carbon, 1, at 20.7 ppm and the four quaternary carbons, 9, 13, 16, and 17 at 122.1, 127.2, 136.6, and 155.6 ppm were obvious. Direct calculations for the chemical shift of carbons 9 and 17 could not be made for the NEP·HCl salt since the appropriate substituent chemical shift parameters for the naphthalene ring were not available. However, chemical shifts of 125.5 and 153.9 ppm were calculated for carbons 9 and 17, respectively, assuming that the substituent parameters for substituted benzenes were applicable to substituted naphthalenes and the substitutents parameters for S-CH_3 and Ar–OH

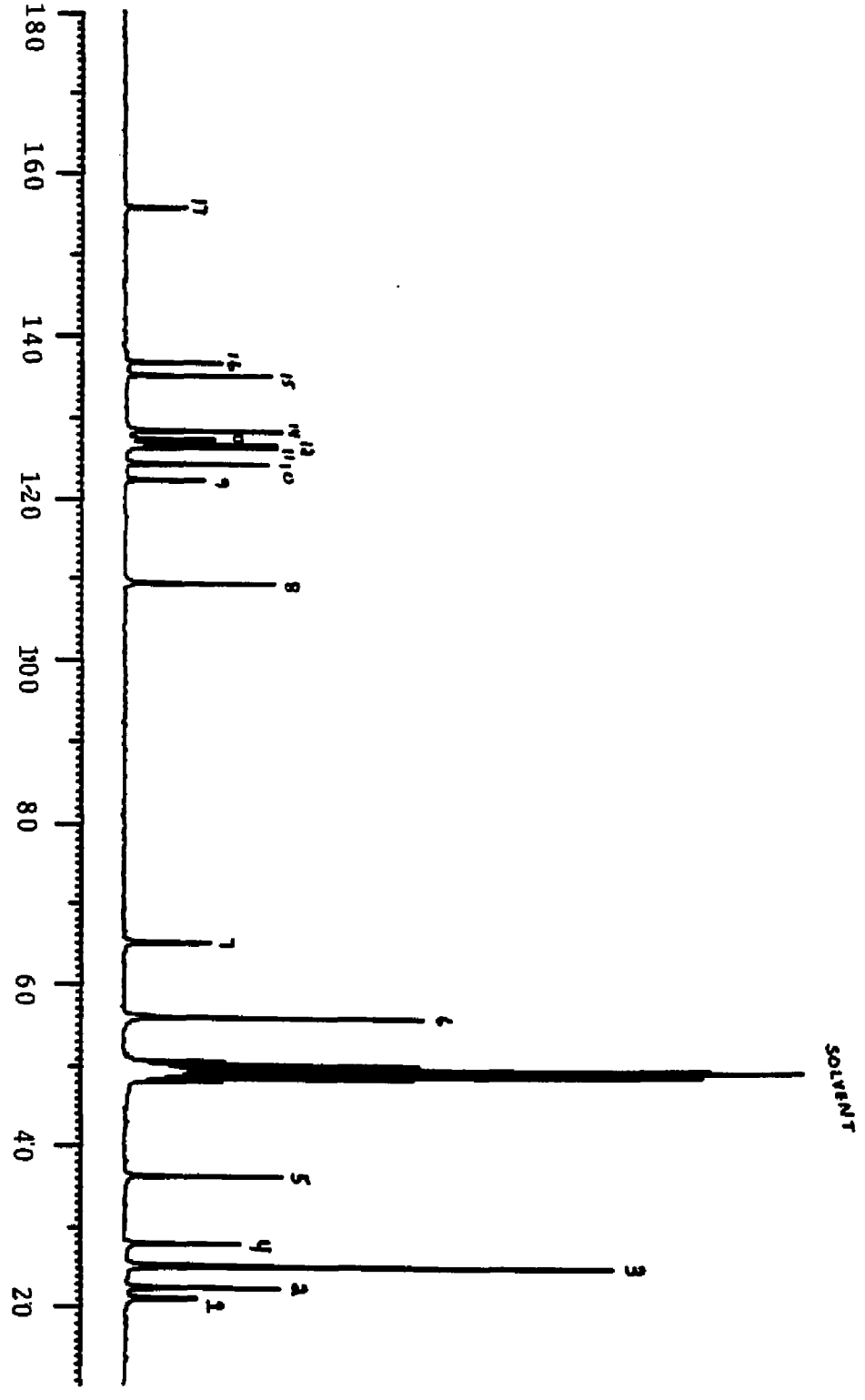


FIGURE 3
^{13}C SPECTRUM OF NEP·HCl Salt
CD_3OD SOLVENT

TABLE 2

Assignments of the ^{13}C Spectrum of the NEP•HCl Salt

Carbon Number	Chemical Shift (ppm)
1	20.7
2	22.0
3	24.7
4	27.5
5	35.9
6	55.6
7	64.8
8	109.2
9	122.1
10	124.1
11	126.1
12	126.5
13	127.2
14	128.1
15	135.0
16	136.6
17	155.5

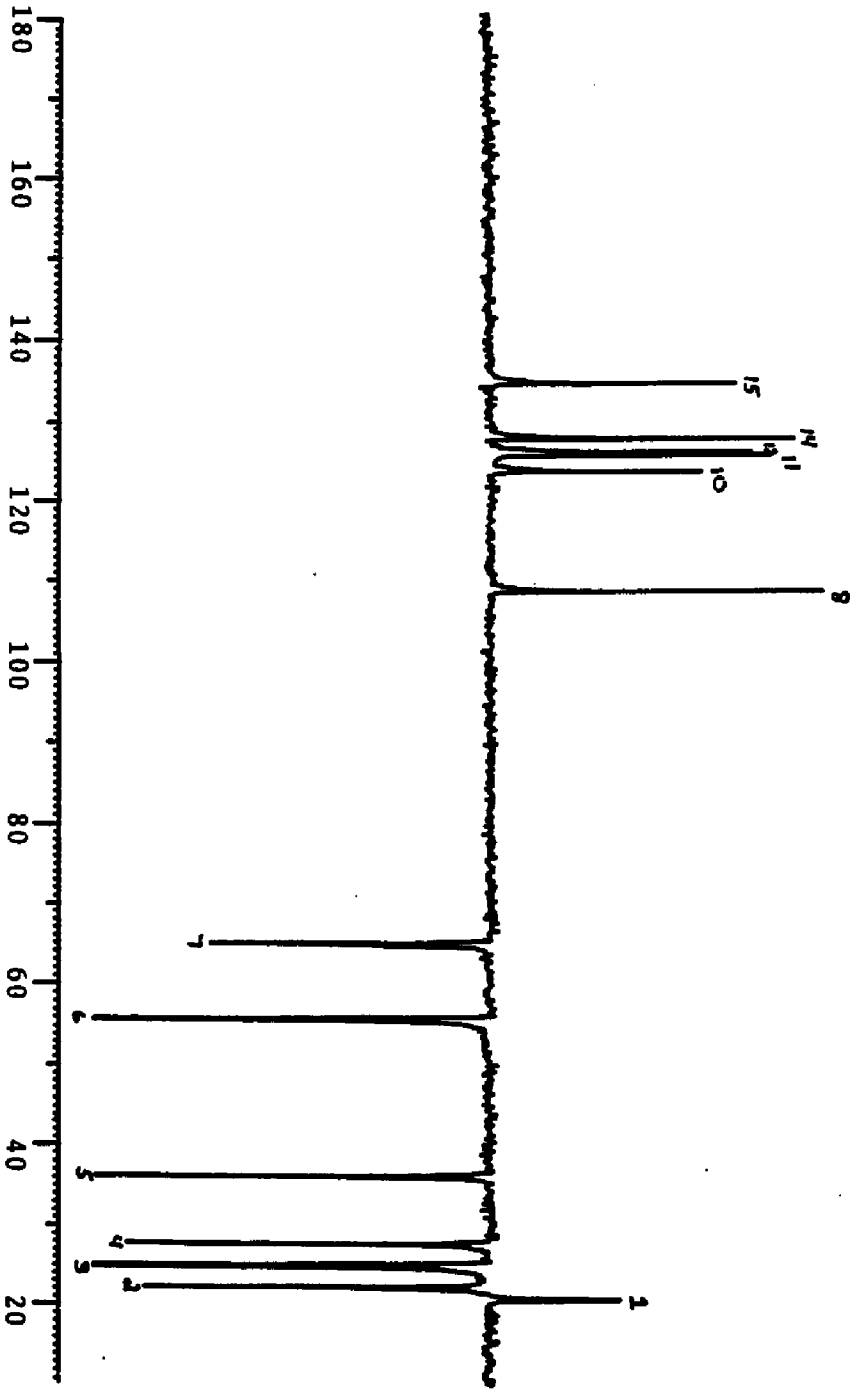


FIGURE 4
DEPT SPECTRUM OF NEP·HCL Salt
CD_3OD SOLVENT

TABLE 3

Assignments of the DEPT Spectrum of the NEP•HCl Salt

Carbon Number	Chemical Shift (ppm)
1	20.6
2	22.0
3	24.7
4	27.4
5	35.9
6	55.5
7	64.7
8	109.1
10	124.0
11	126.1
12	126.5
14	128.1
15	135.0

simulate those of S-CH_2 and Ar'–OH where Ar represents benzene and Ar' represents naphthalene.[20] The observed chemical shift of carbons 9 and 17 were assigned as 122.1 and 155.6 ppm respectively. The assigned value of carbon 17 is in good agreement with the calculated value. However, the calculated value for carbon 9 is intermediate between that of the assigned value, 122.1, and a second quaternary carbon, 127.2 ppm hence the assignment is not unambiguous and is made arbitrary. The assignments of carbons 9, 13, and 16 were made arbitrary and may be interchanged. Figure 5a and b shows the HCCORR spectrum of the NEP·HCl salt with high resolution 1-D spectrum for proton and carbon along the F1 and F2 axes, respectively, to aid in the interpretation of the spectrum. For HCCORR experiments the proton and carbon are related through scalar coupling. Figure 5a represents the aliphatic region of the NEP·HCl salt. The following proton/carbon connectivities were deduced by using the labelling of the diagram XIVb for the proton and XIVc for the carbon assignments: H-1/C-4, H-2/C-2, H-3/C-3, H-4/C-1, H-5/C-5, H-6/C-7, and H-7/C-6. Figure 5b represents the HCCORR spectrum of the aromatic region of the NEP·HCl salt. Using the protocol established previously, the following connectivities were established for the aromatic region: H-8/C-8, H-9/C-11, H-10/C-14, H-11/C-15, H-12/C-10, and H-13/C-12. Carbons 9, 13, 16, and 17 show no correlating peaks because they have no directly attached protons and the long range ^{1}H–^{13}C J coupling are too weak to be observed. The assignment of carbons 11 and 12, and 10 and 14 were made somewhat arbitrarily and hence may be interchanged i.e. carbons 10, 11, 12, and 14 may be signals 14, 12, 11 and 10 respectively.

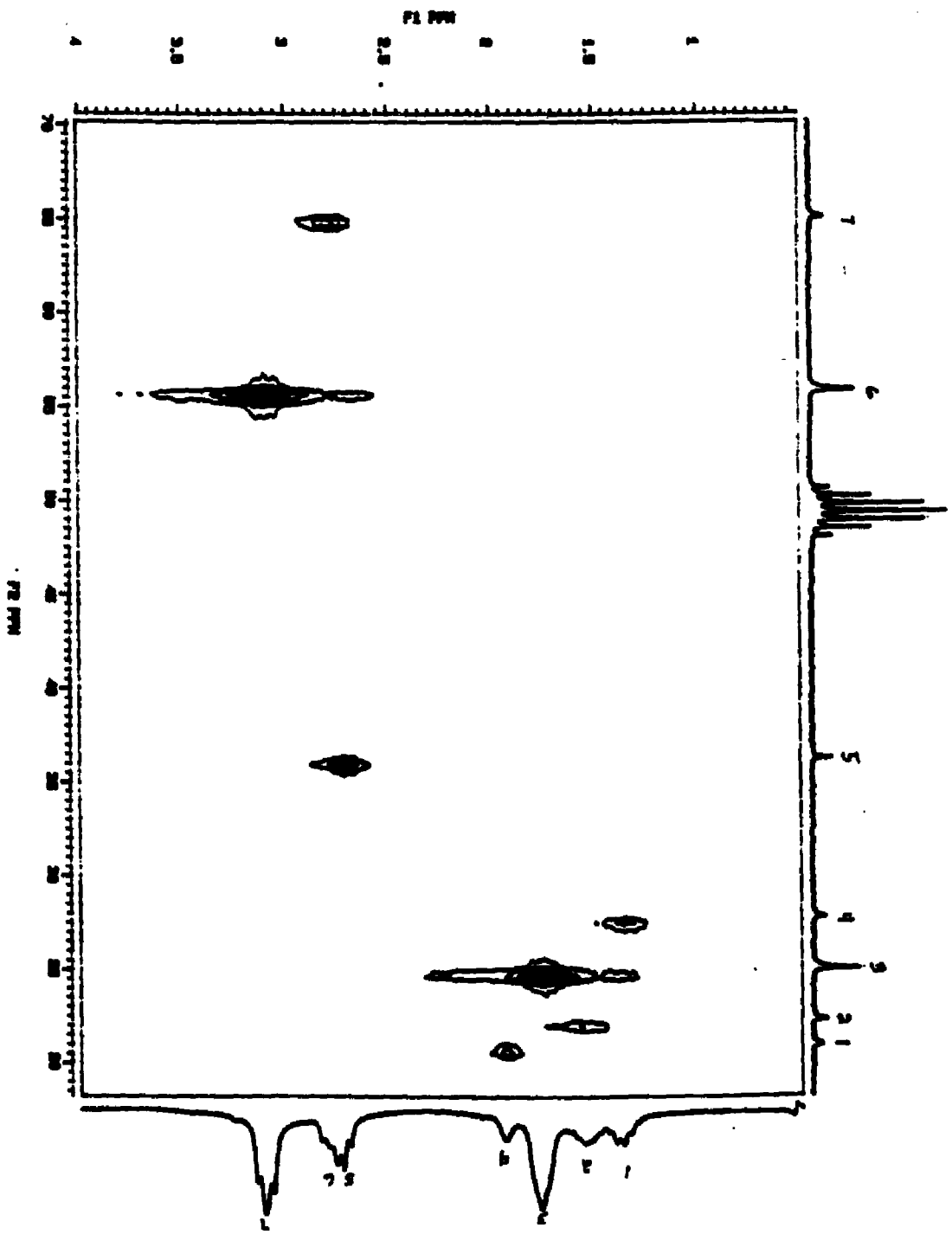


FIGURE 5a
ALIPHATIC REGION OF HCCORR SPECTRUM
OF NEP·HCl SALT
CD_3OD SOLVENT

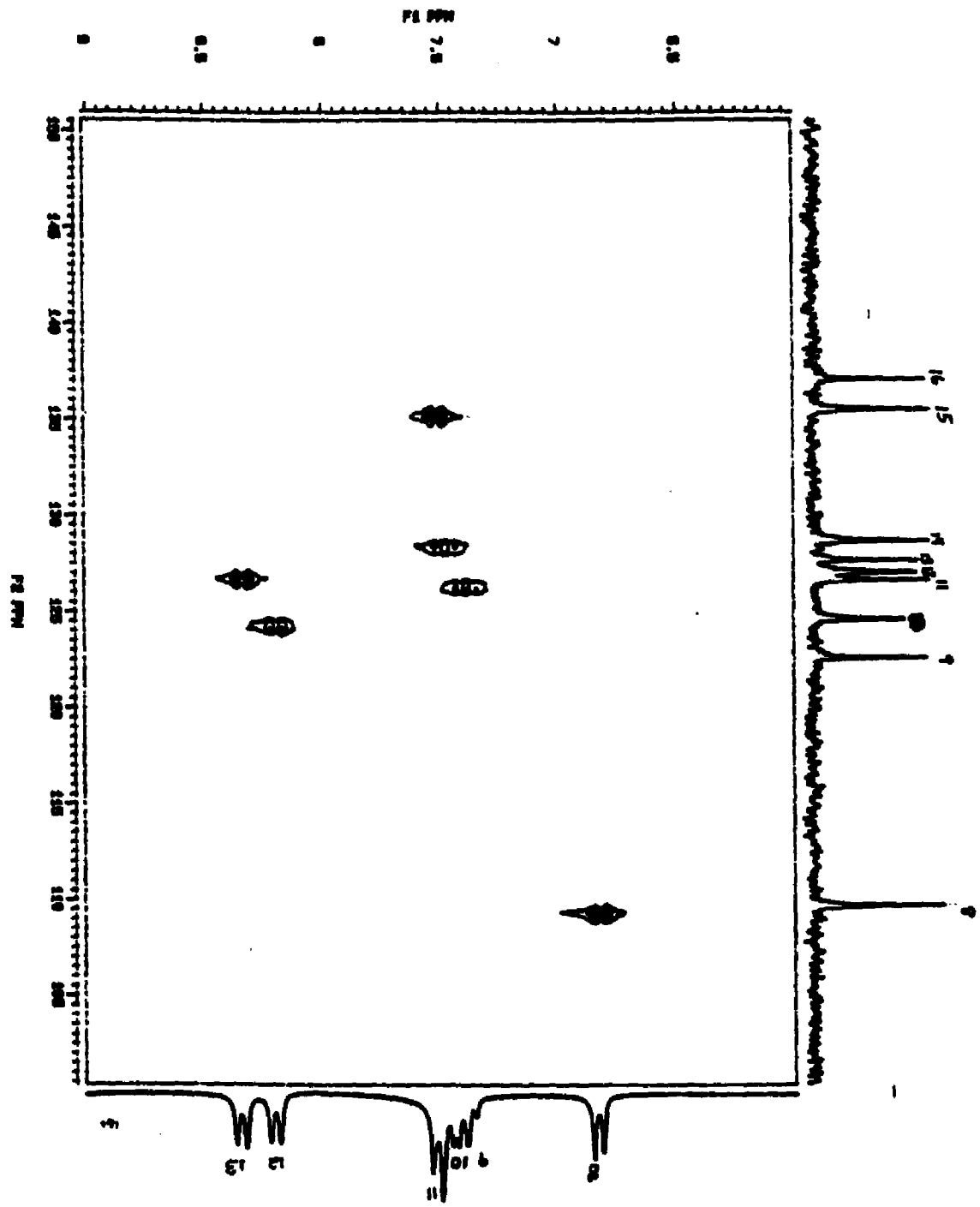


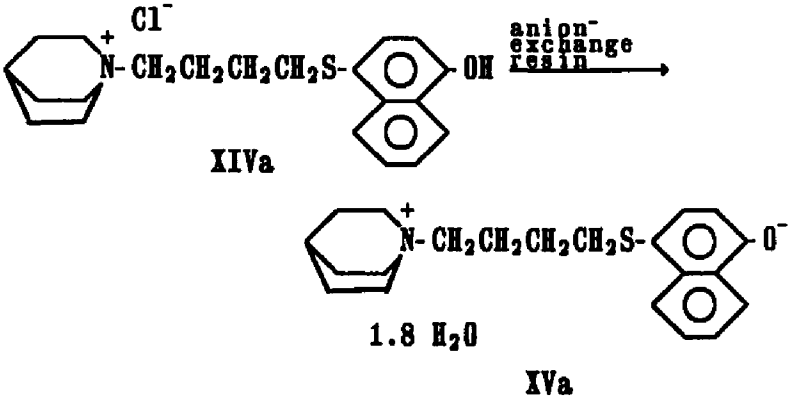
FIGURE 5b
AROMATIC REGION OF HCCORR SPECTRUM
OF NEP·HCl SALT
CD_3OD SOLVENT

3.1.2.2 IR Spectroscopy: The IR spectrum of the NEP·HCl salt is not well defined in the region between 4000 and 2000 cm^{-1} due partially to the broad, overlapping absorption bands of -OH, from water and naphthol. Identifiable bands occur at 3046.7 (aromatic C-H), 2950.8 and 2881.4 (aliphatic C-H and $N-CH_2$), 1585.5 and 1503.5 (aromatic C-C), and 836.4 and 767.7 cm^{-1} (aromatic C-H).

3.1.3 *Synthesis of the NEP Zwitterion*

The NEP zwitterion (XVa) may be prepared by treating the NEP·HCl (XIVa) with a strongly basic anion-exchange resin (Scheme XII) in a manner similar to that used in the preparation of the tetrahydrothiophenium arene oxides zwitterions. The NEP zwitterion is a highly

Scheme XII:



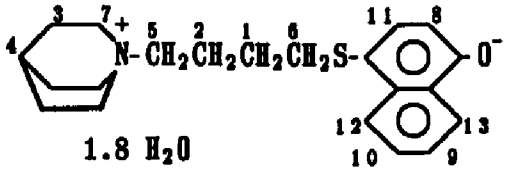
stable molecule which had high solubility in water and methanol and to a lesser extent in dimethyl sulfoxide and was insoluble in acetone and diethyl ether. It was initially isolated as a green tinted powder which discolored on storage periods exceeding one month. Unlike the sulfonium zwitterions which have been investigated previously, the NEP zwitterion has equal stability regardless of the state in which it is isolated (hydrated or anhydrous).

3.1.4 *Characterization of the NEP Zwitterion*

3.1.4.1 NMR Spectroscopy: The NEP zwitterion was characterized by

the use of ^{1}H, and ^{13}C NMR, DEPT, COSY, and HCCORR techniques.

3.1.4.1.a Proton Assignments of the NEP Zwitterion: Figure 6 and Table 4 show the ^{1}H spectrum and δ values of the NEP zwitterion. The signal assignments shown in XVb were based on the observed splitting pattern, signal areas, and results from the COSY experiment (Figure



XVb

7). The sharp singlet at 3.34 ppm was assigned to water from the water of hydration of the NEP zwitterion. This assignment was confirmed by the absence of this signal in the ^{1}H spectrum of the anhydrous NEP zwitterion. The small signal along side of the water peak belongs to the methyl group of the solvent methanol-d_4, and the sharp singlet at 4.93 ppm is attributed to the hydroxy group from the solvent. Figure 7 represents the COSY spectrum of the NEP zwitterion with a computer generated 1-D spectrum along the F1 and F2 axes in order to aid in the interpretation. Off-diagonal cross peaks, indicating coupling, occurs for proton pairs 3-7, 3-4, 6-1, and 5-2. No cross peak was present for the proton pair 1-2 since their signals overlap completely in the ^{1}H spectrum. Analysis of the COSY spectrum for the aromatic region of the NEP zwitterion revealed off diagonal cross peaks for proton pairs 8-11, 9-13, and 10-12 . A cross peak for the proton pair 9-10 is not clearly evident. Possible explanations

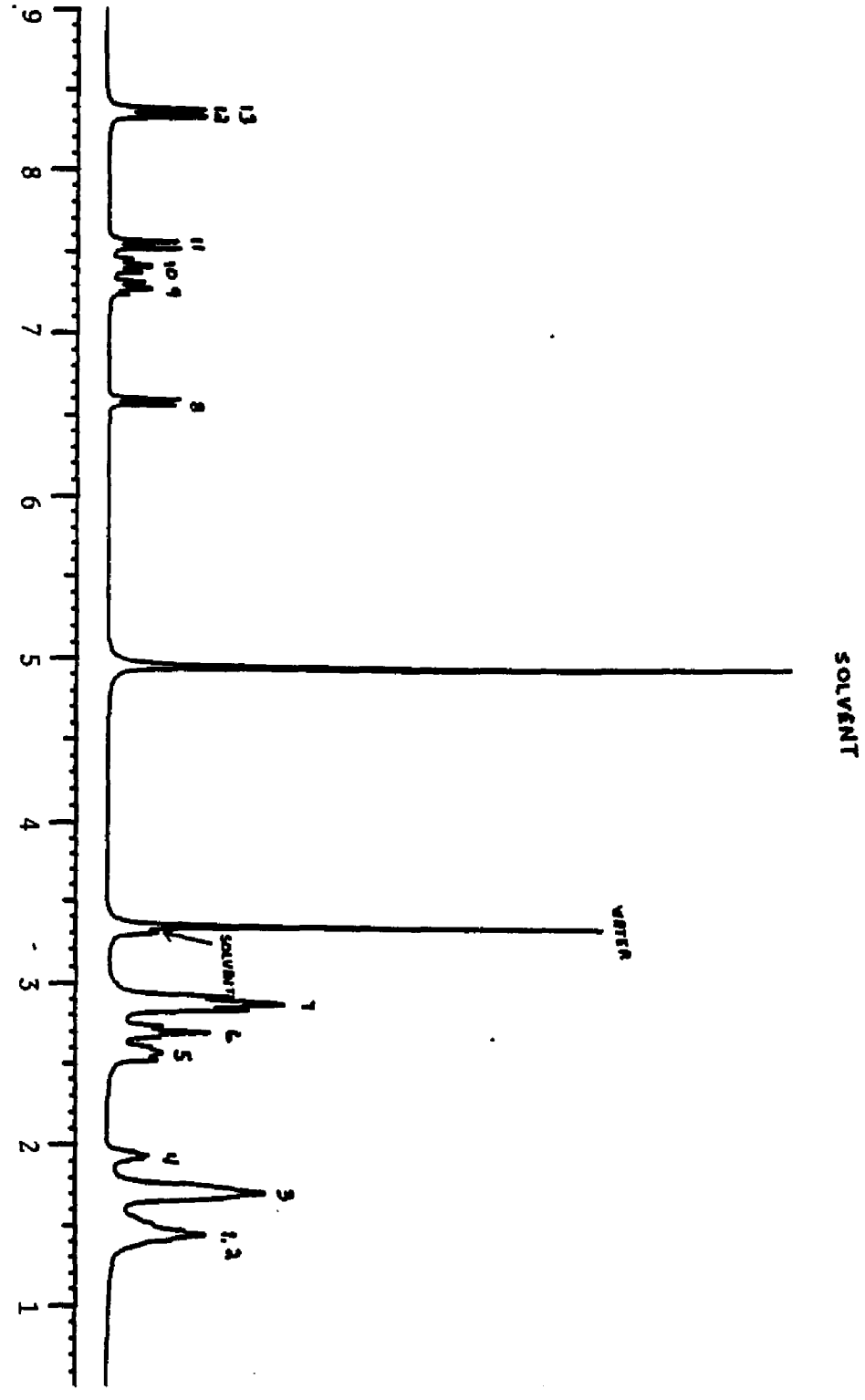


FIGURE 6
^{1}H SPECTRUM OF NEP ZWITTERION
CD_3OD SOLVENT

TABLE 4

Assignments of the ^{1}H Spectrum of the NEP Zwitterion

Proton Number	Chemical Shift (ppm)
1, 2	1.50
3	1.70
4	1.91
5	2.57
6	2.70
7	2.88
8	6.56
9	7.27
10	7.41
11	7.53
12, 13	8.34

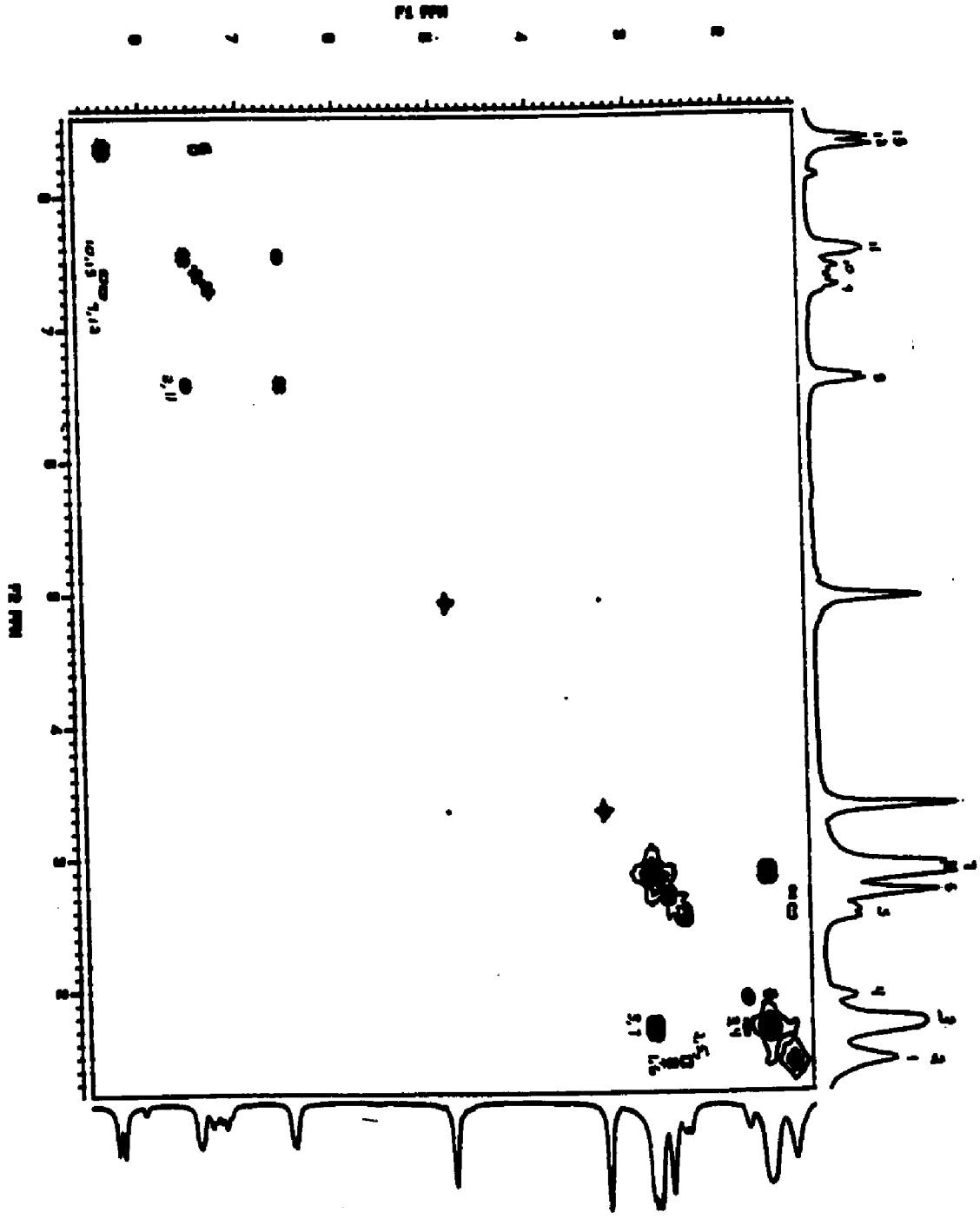
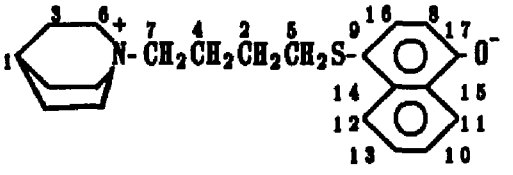


FIGURE 7
COSY SPECTRUM OF NEP ZWITTERION
CD_3OD SOLVENT

for the lack of a clear contour signal for the proton pair 9-10 were a small coupling constant or insufficient digital resolution to resolve the coupling. The assignment of signals 9 and 10 as well as 12 and 13 were arbitrary and may be interchanged i.e. protons 9, 10, 12, and 13 may correspond to signals 10, 9, 13 and 12 respectively.

3.1.4.1.b Carbon Assignments of the NEP Zwitterion: The proton-decoupled ^{13}C NMR spectrum (Figure 8, Table 5) of the NEP zwitterion also supported structure XVa. The carbon signals were assigned as shown in XVc based on results from DEPT (Figure 9, Table 6) and HCCORR (Figure 10a and 10b) experiments, and the chemical shift



XVc

values for similar carbons.[19] The following assignments were made based upon the DEPT spectrum (Figure 9) of the NEP zwitterion: the methine carbon, 1, of the piperidinium ring at 20.5 ppm,and the four quaternary carbons, 9, 14, 15, and 17, of the naphthalene ring were assigned as 111.9, 131.9, 137.9, and 168.2 ppm. Direct calculations for the chemical shift of carbons 9 and 17 could not be made for the NEP zwitterion since the appropiate substituent chemical shift parameters for the naphthalene ring were not available. However, chemical shifts of 125.5 and 164.7 ppm were calculated for carbons 9 and 17, respectively assuming that the substituent parameters for

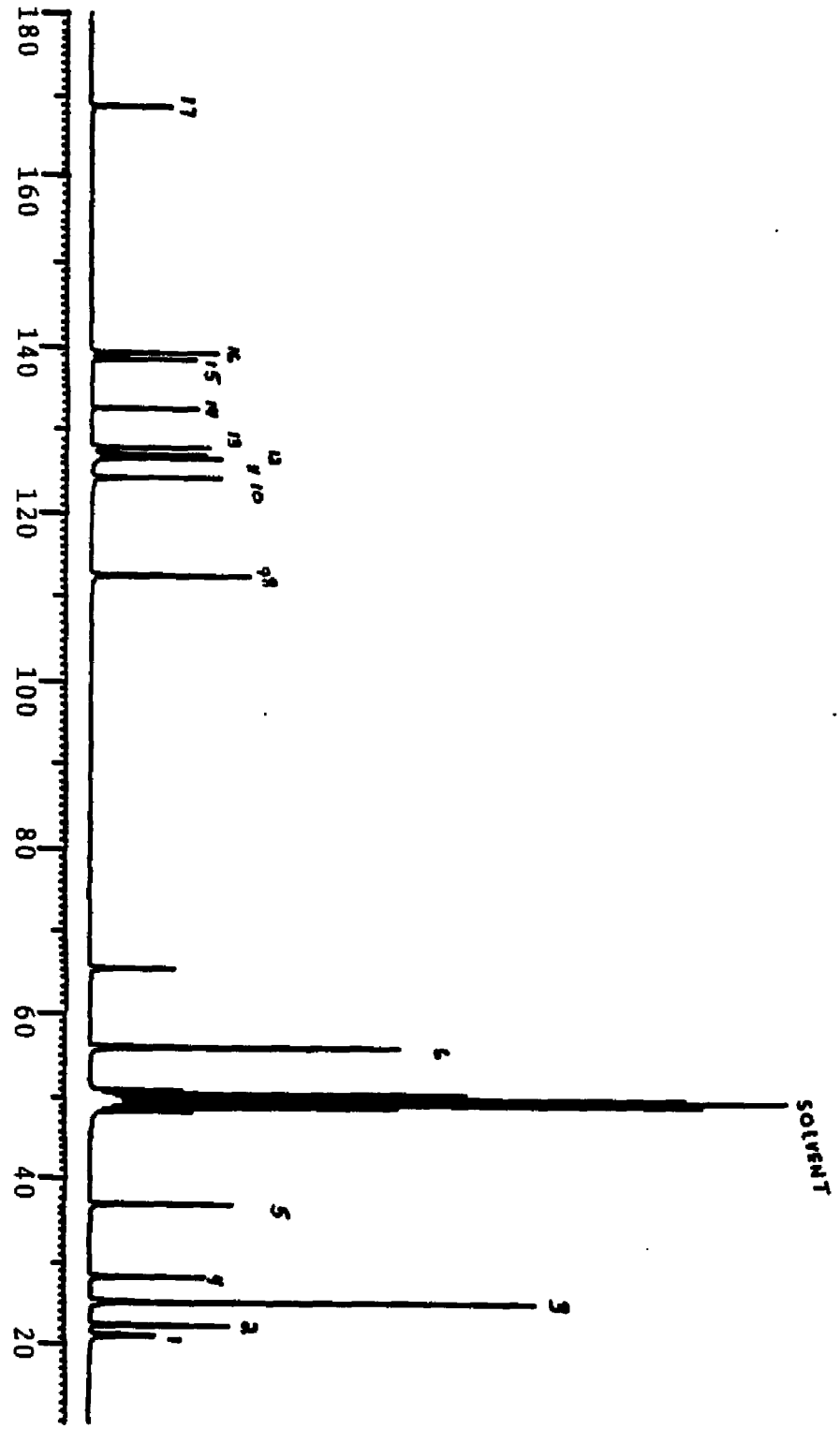


FIGURE 8
^{13}C SPECTRUM OF NEP ZWITTERION
CD_3OD SOLVENT

TABLE 5

Assignments of the ^{13}C Spectrum of the NEP Zwitterion

Carbon Number	Chemical Shift (ppm)
1	20.4
2	21.7
3	24.5
4	27.6
5	36.4
6	55.3
7	64.7
8	111.8
9	111.9
10	123.6
11	125.9
12	126.4
13	127.2
14	131.9
15	137.8
16	138.6
17	168.2

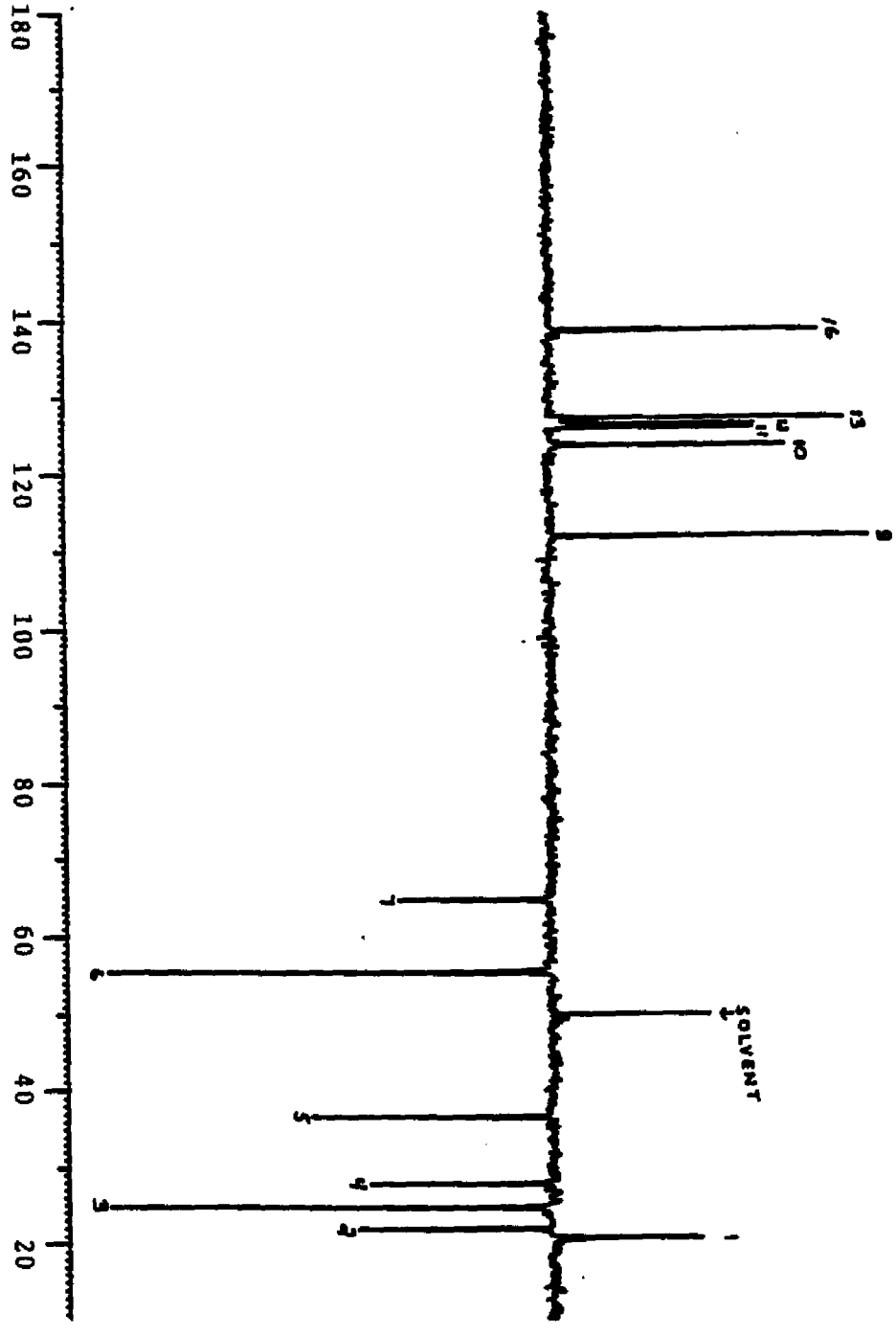


FIGURE 9
DEPT SPECTRUM OF NEP ZVITTERION
CD_3OD SOLVENT

TABLE 6

Assignments of the DEPT Spectrum of the NEP Zwitterion

Carbon Number	Chemical Shift (ppm)
1	20.5
2	21.7
3	24.7
4	27.6
5	36.4
6	49.8
7	55.3
8	111.8
10	123.7
11	125.9
12	126.4
13	127.2
16	138.6

substituted benzenes were applicable to substituted naphthalenes and the substitutents parameters for S-Me and O-Na simulate those for the CH_2-S and O^- respectively.[20] The observed chemical shifts for carbons 9 and 17 were 111.8 and 168.2 ppm, respectively. Thus the signal for carbon 9 exhibited an upfield shift of 13.4 ppm and the carbon 17 signal exhibited no significant shift. In several of the tetrahydrothiophenium-arene oxides systems which have been previously investigated, the carbon analogous to carbon 9 has shown a large upfield shift of 10-15 ppm and no significant shift was observed for the analogous carbon 17. The carbon analogous to 9 from the tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt showed an upfield shift of 28.9 ppm. This large upfield shift has been attributed to the presence of a quinoid-type resonance. Although this type of resonance is not feasible with the NEP zwitterion, other forms of resonance are possible within the aromatic ring system. The assignment of carbons 11 and 12, 14 and 15, and 10 and 13 were made arbitrary and may be interchanged i.e. carbons 10, 11, 12, 13, 14, and 15 may correspond to signals 13, 12, 11, 10, 15, and 14 respectively.

Figure 10a and 10b shows the aliphatic portion and the aromatic portion, respectively, of the HCCORR spectrum of the NEP zwitterion with a high resolution carbon spectrum lying along the F2 axes and a computer generated proton spectrum along the F1 axes in order to aid in the interpretation. The following proton/carbon connectivities were deduced by using the labelling of structure XVb for the proton and XVc for the carbon assignments: H-1/C-2, H-2/C-4, H-3/C-3, H-4/C-1, H-5/C-7, H-6/C-5, and H-7/C-6. The assignment of proton 6

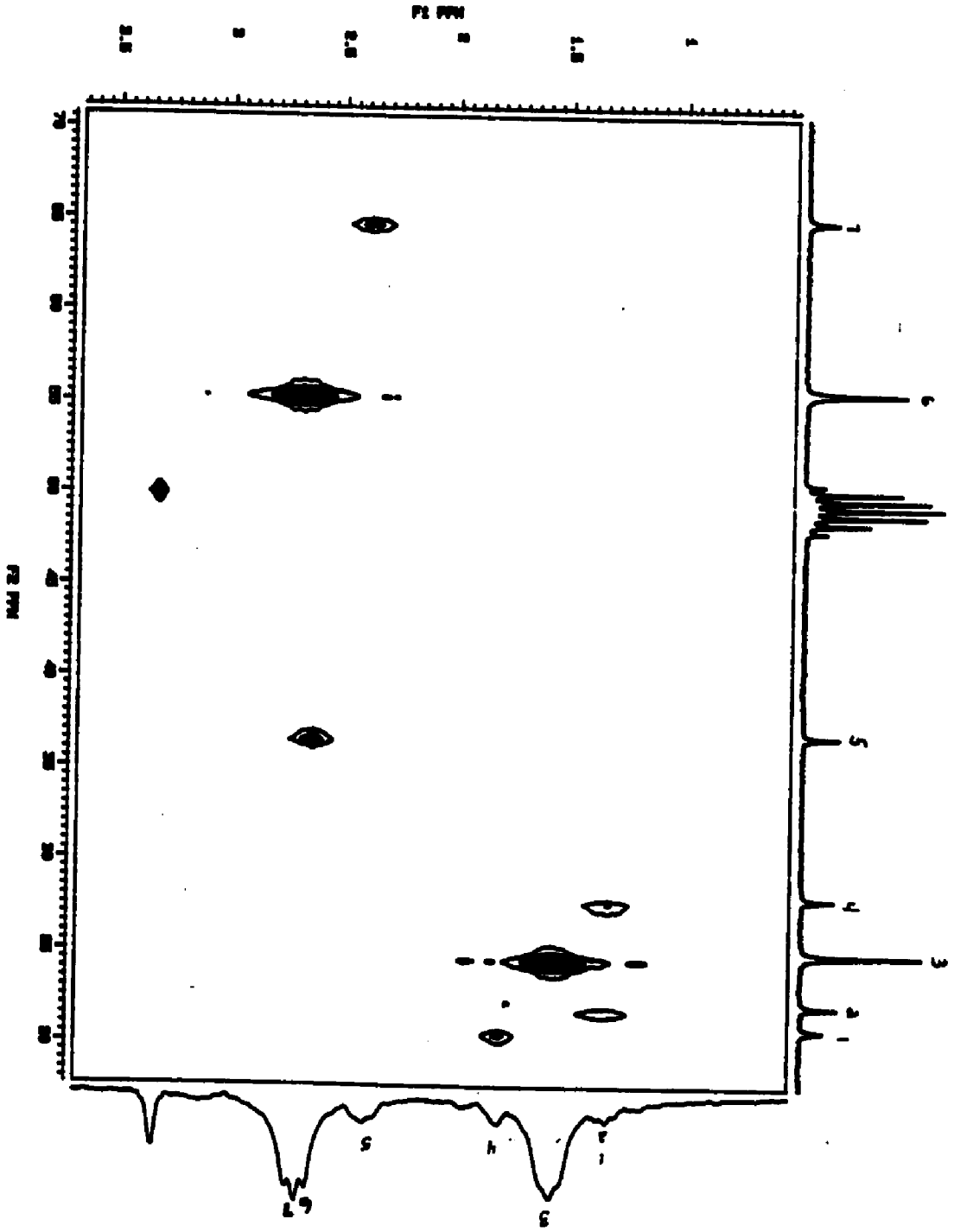


FIGURE 10a
ALIPHATIC REGION OF HCCORR SPECTRUM
OF NEP ZWITTERION
CD_3OD SOLVENT

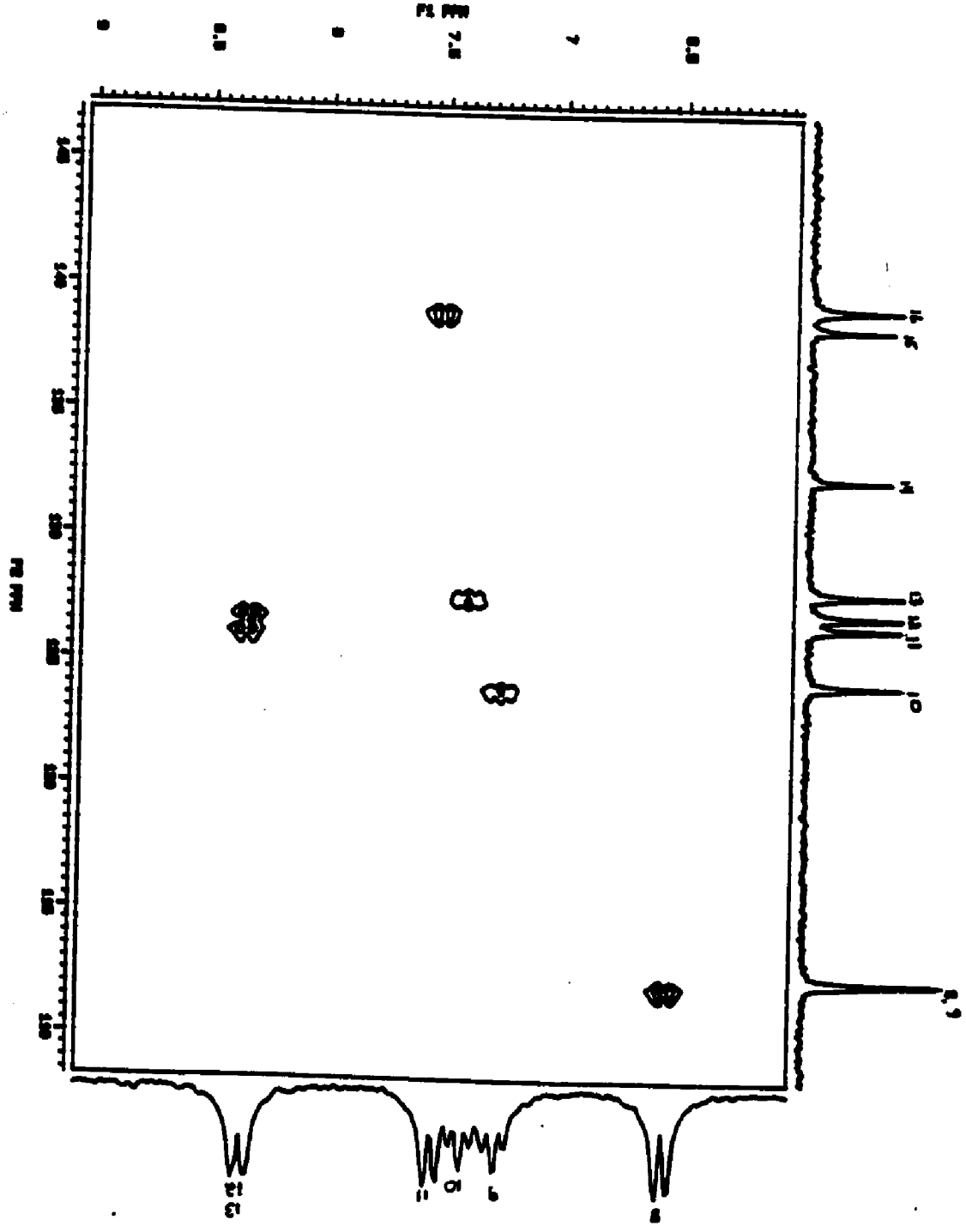


FIGURE 10b
AROMATIC REGION OF HCCORR SPECTRUM
OF NEP ZWITTERION
CD_3OD SOLVENT

was based on the chemical shift of its correlated carbon which was assigned on the basis of the chemical shift of that reported for an analogous carbon in other tetrahydrothiophenium arene oxides polymers.[14] Two contour signals with identical proton chemical shift values but different carbon chemical shift values indicated overlapping proton signals at 1.48 ppm which were assigned to the two sets of acyclic methylene protons β to the ammonium and sulfur atoms of the NEP zwitterion. Examination of Figure 10b reveals the following correlations using the protocol established previously: H-8/C-8, H-11/C-16, H-9/C-10, H-10/C-13, H-12/C-12 and H-13/C-11. Two overlapping proton signals at 8.34 ppm is evident by the presence of two contour with the same position along the F1 axis but different positions along the F2 axis. The assignment of carbons 10, 11, 12, and 13 were made some what arbitrarily and hence may be interchanged i.e. carbon 10, 11, 12, and 13 may be signals 13, 12, 11, and 10 respectively.

3.1.4.2 IR Spectroscopy: The infrared spectrum of NEP zwitterion (Figure 11) showed several absorption peaks. Some of the absorption peaks were easily assigned: a broad signal at 3374.7 (water of hydration), 3052.5 and 3025.4 (aromatic C-H), 2944.2 and 2879.0 (aliphatic C-H), 1554.9, and 1492.9 (aromatic C-C), and 835.2 and 767.7 cm^{-1} (aromatic C-H).

3.1.4.3 Thermal Analysis:

3.1.4.3.a Thermogravimetric Analysis (TGA): TGA was performed on

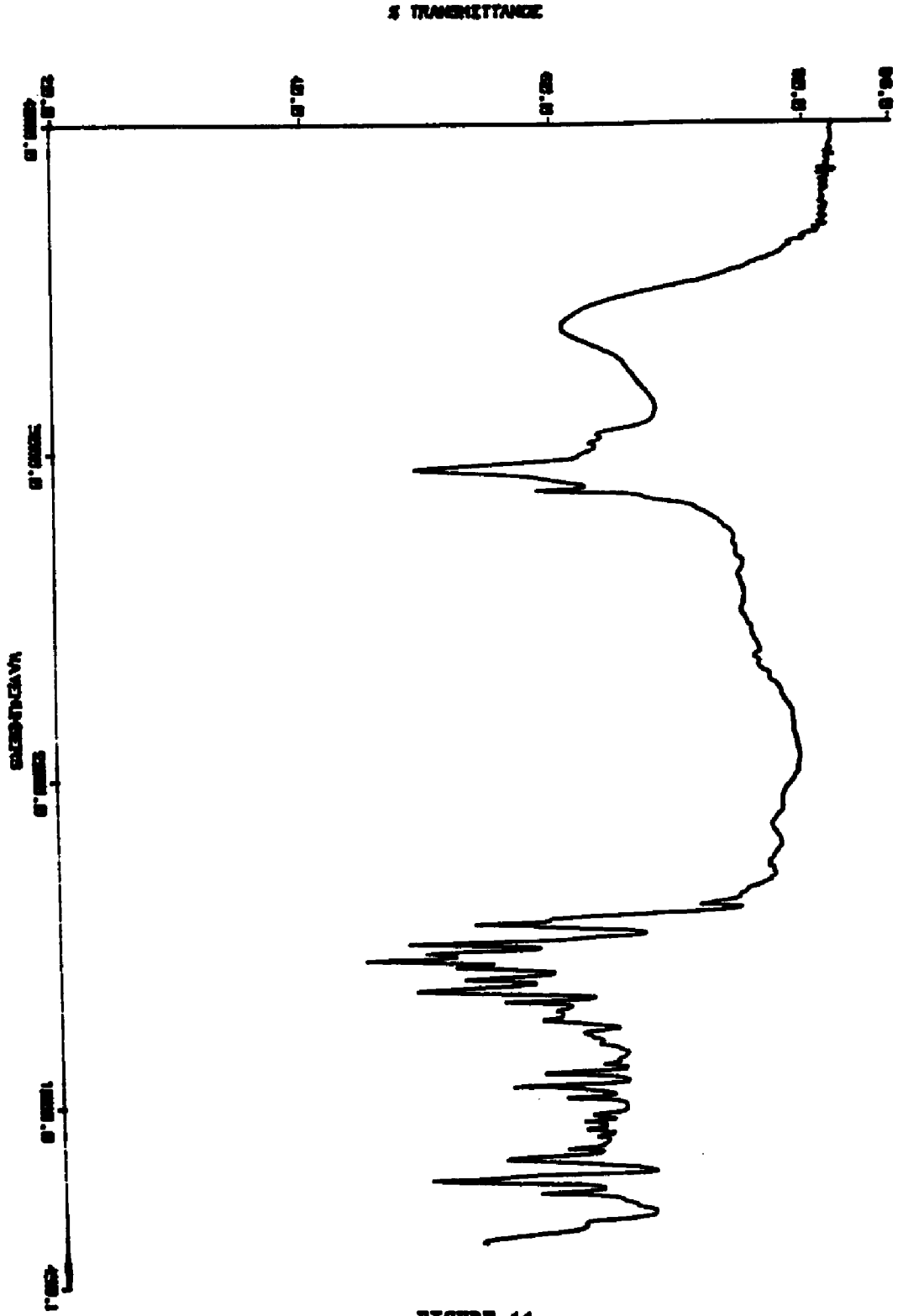


FIGURE 11
IR SPECTRUM OF NEP ZVITTERION

the NEP zwitterion to determine the amount of water present. 1.82 ± 0.04 moles of water per mole of zwitterion was found to be present (Figure 12). The water was lost over the temperature range of 40 to 150°C. The NEP zwitterion did not polymerize on losing its water of hydration, as indicated by its ^1H spectrum, even though the final temperature in the TGA reached 180°C. However a color change to a stronger shade of green occurred.

3.1.4.1.b Differential Scanning Calorimetry (DSC): DSC was carried out on the NEP zwitterion in order to determine its melting point. Figure 13 shows the DSC thermogram of the NEP zwitterion. Two endotherms were evident at 144° and 194°C. Endotherm A (144°C) was assigned to the ΔH_{vap} of water and endotherm B (194°C) to the melting point of the NEP zwitterion. The assignment of endotherm A as ΔH_{vap} of water was confirmed by carrying out DSC on the anhydrous NEP zwitterion which resulted in only one endotherm at 194°C. Visible confirmation of these assignment were made by taking a melting point of the NEP zwitterion where no physical change was apparent in the zwitterion until the temperature was above 190°C. On cooling the NEP zwitterion slowly and reheating it no endotherms were present (Figure 13b) indicating that crystallization did not occur although a slight change in slope of the thermogram occurred at approximately 60°C.

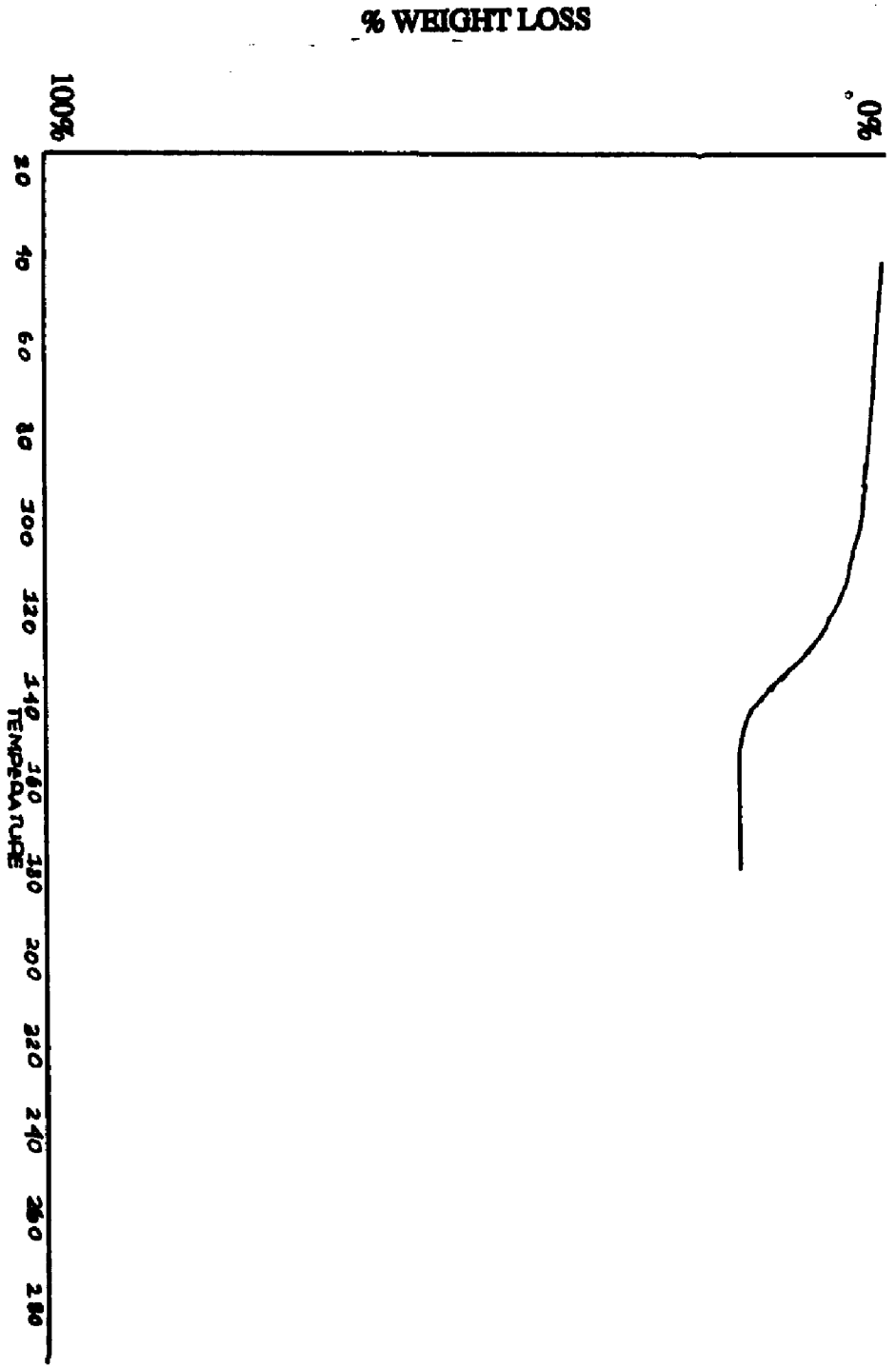


FIGURE 12
TGA OF NEP ZWITTERION

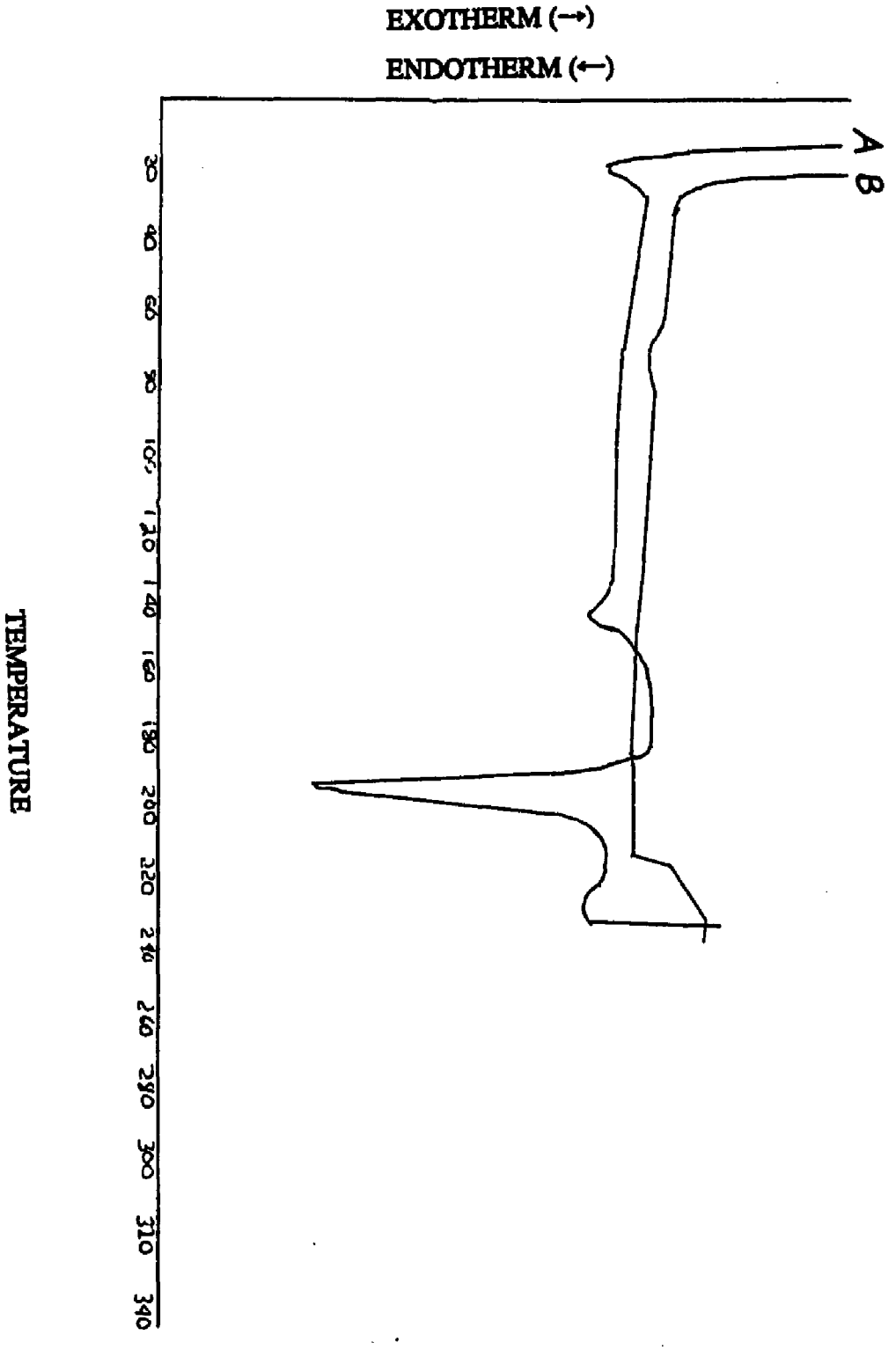


FIGURE 13
DSC OF NEP ZWITTERION

3.1.5 *Polymerization of the NEP Zwitterion*

The polymerization of the NEP zwitterion was investigated in bulk only and not in solution since a suitable solvent for both the NEP monomer and polymer was not found. The polymerization of the NEP zwitterion was studied over a temperature range of 175-225°C under both sealed tube and continuous vacuum conditions (Table 7). On heating the NEP zwitterion at temperatures below 175°C (i.e. 150°C for two days) no evidence of polymerization existed. The reaction mixture

TABLE 7

POLYMERIZATION RESULTS OF NEP ZWITTERION

Sample #	Temp. (oC)	Reaction Time	Molecular Weight by NMR
1[a]	175	20	1.3×10^4
2[b]	175	20	1.1×10^4
3[a]	200	1	1.0×10^4
4[a]	200	2	8.7×10^3
5[b]	200	2	9.1×10^3
6[a]	200	4	8.5×10^3
7[a]	225	0.3	9.8×10^3
8[a]	225	0.67	8.6×10^3
9[a]	225	1	8.7×10^3

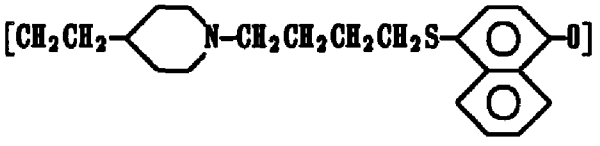
[a]sealed tube; [b]continuous vacuum

was a transparent solid containing a light green tint. The NEP

polymer was isolated by stirring the transparent solid over CH_2Cl_2 followed by precipitation into CH_3OH, all at room temperature. The absence of any CH_2Cl_2 insoluble material was indicative of a quantitative conversion to polymer or oligomer since the NEP zwitterion is insoluble in CH_2Cl_2. In a typical polymerization a yield of 75% polymer (methanol insoluble) and 25% oligomer (methanol soluble) was obtained. This report will discuss the methanol insoluble fraction only.

3.1.6 *Characterization of the NEP Polymer*

The polymer was characterized as structure XVIa by elemental analysis, NMR and IR spectroscopy. The elemental analysis (Found: C, 73.61; H, 7.94; S, 9.56; and N, 3.92) was in good agreement with that calculated for XVIa (Theory: C, 73.84; H, 7.98; S, 9.39; N, 4.10). The DSC thermogram obtained on the NEP zwitterion (Section 3.1.4.3.b) indicated that polymerizations conducted below 190°C occurred in the



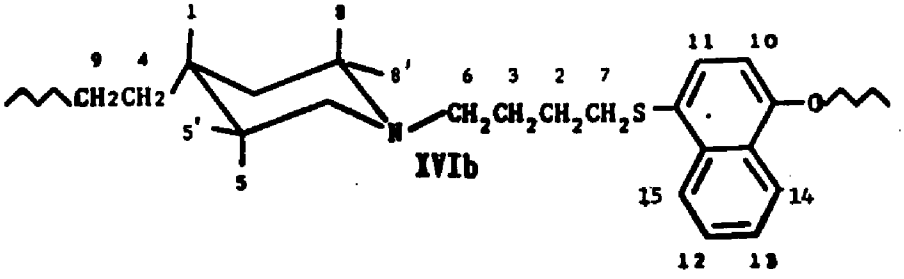
XVIa

solid state while polymerizations exceeding 190°C occurred in the melt. This was deduced since the NEP zwitterion did not melt until the temperature exceeded 194°C. Although the NEP zwitterion polymerized at 175°C on prolong heating, it was found to be unreactive

on heating at this temperature for short intervals of time. The stability of the NEP zwitterion was clearly demonstrated by the ^1H spectrum of the anhydrous NEP zwitterion. The anhydrous NEP zwitterion was prepared by heating the NEP zwitterion to 180°C in a Thermogravimetric Analysis Instrument (see TGA scan, Figure 12). The ^1H spectrum of the anhydrous NEP zwitterion showed no indication of polymerization occurring.

3.1.6.1 NMR Spectroscopy: The NEP polymer was characterized by the use of ^1H and ^{13}C NMR, DEPT, COSY, HCCORR, and IR spectroscopy.

3.1.6.1.a Proton Assignments of the NEP Polymer: Figure 14 and Table 8 show the ^1H spectrum and δ values of the NEP polymer synthesized at 200°C. The signal assignments shown in XVIb, where ∿∿ represents the polymer chain, were based on the observed splitting patterns, signals areas, COSY (Figure 15) and HCCORR experiments (Figure 16a and 16b). The ethylene group was drawn



XVIb

arbitrarily in the equatorial position in XVIb but may exist in the axial position since there was no evidence indicating support of either position. The signals (Figure 14) for protons 1 through 5 (including 5′) and 8 overlap in the region between 1.0 and 2.0 ppm.

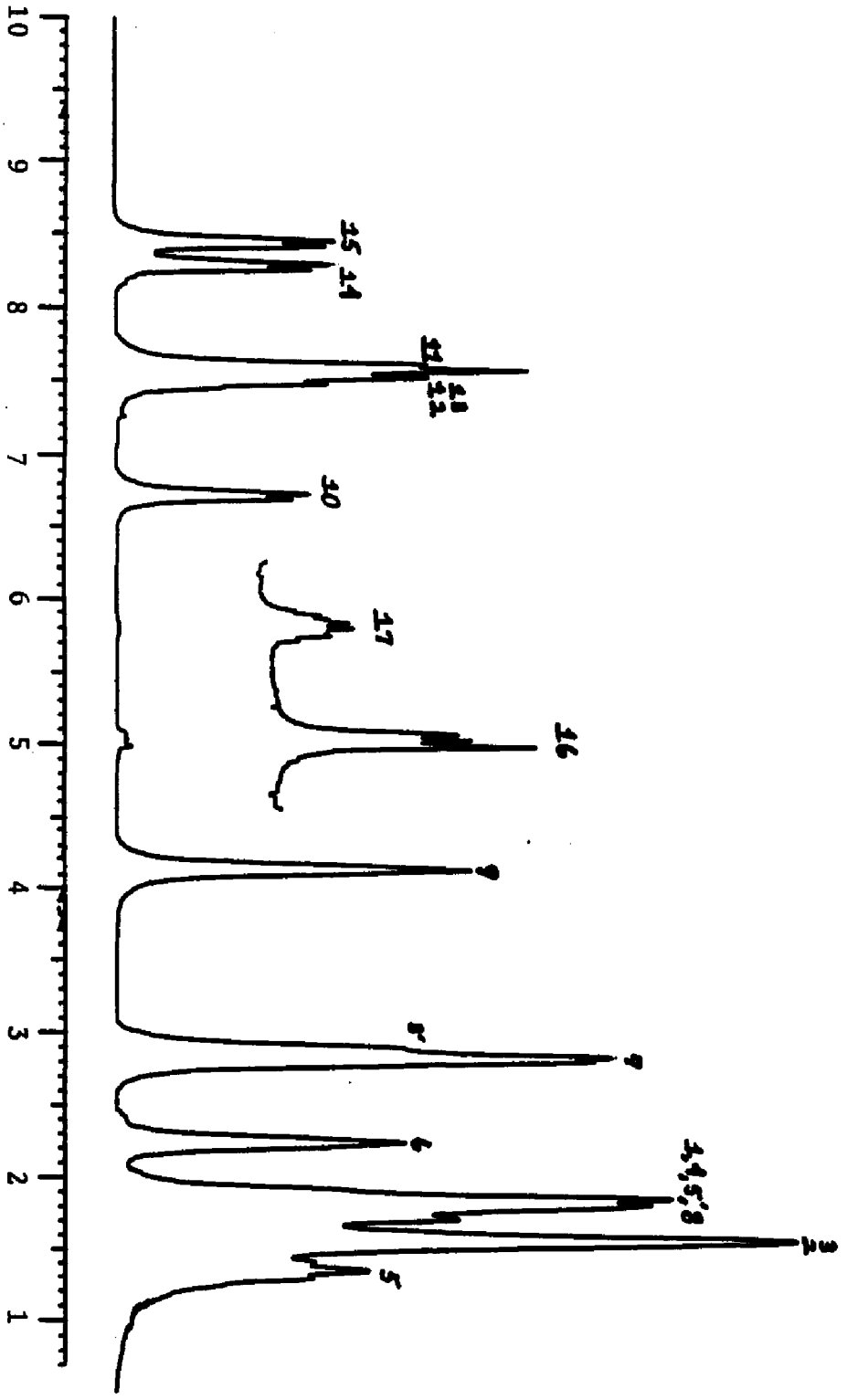


FIGURE 14
^{1}H SPECTRUM OF NEP POLYMER
$CDCl_3$ SOLVENT

TABLE 8

Assignments of the ^{1}H Spectrum of the NEP Polymer

Proton Number	Chemical Shift (ppm)
1	1.83
2	1.56
3	1.56
4	1.83
5	1.37
5	1.82
6	2.25
7	2.83
8	1.86
8	2.90
9	4.13
10	6.71
11	7.60
12, 13	7.50
14	8.30
15	8.46

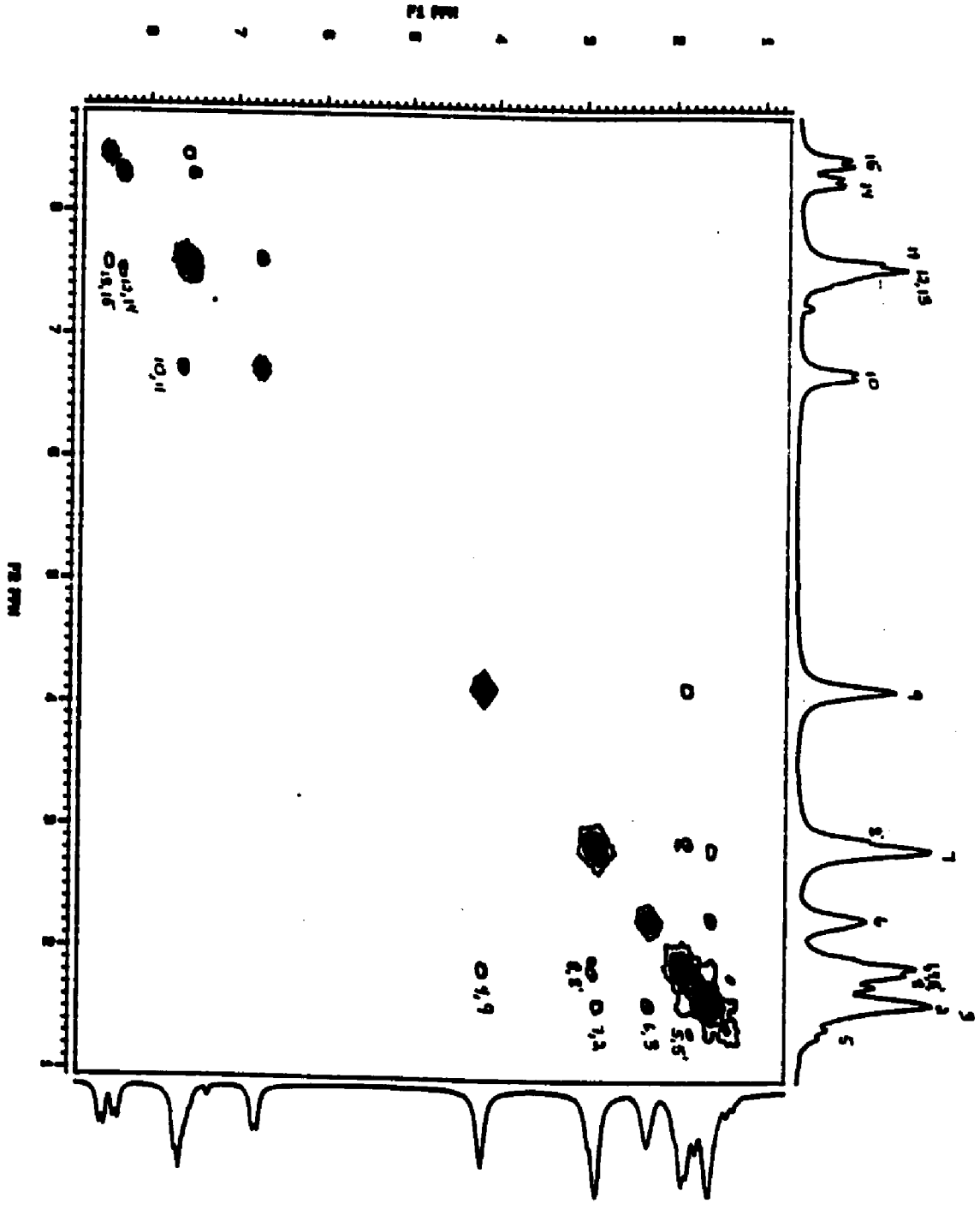


FIGURE 15
COSY SPECTRUM OF NEP POLYMER
$CDCl_3$ SOLVENT

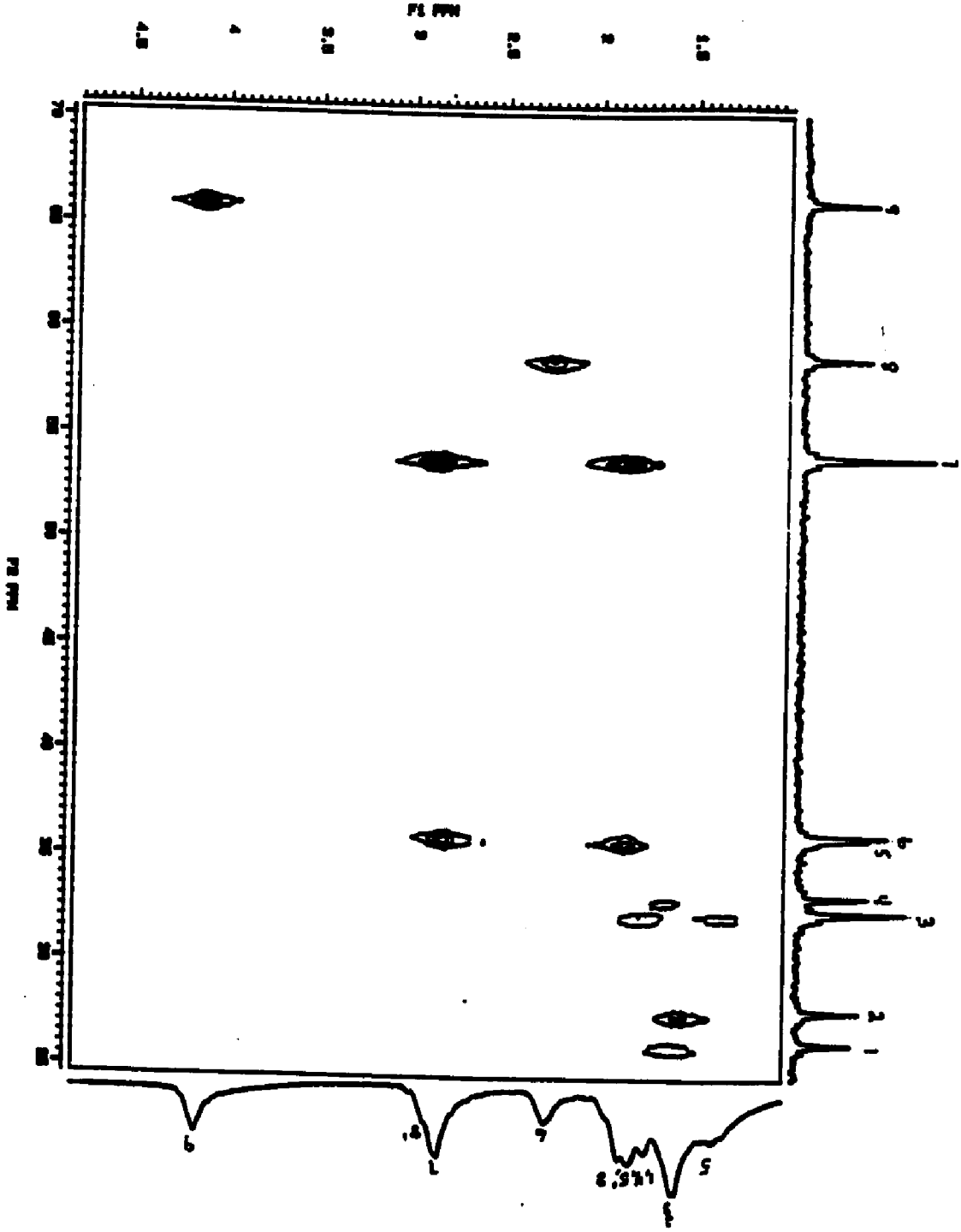


FIGURE 16a
ALIPHATIC REGION OF HCCORR SPECTRUM
OF NEP POLYMER
$CDCl_3$ SOLVENT

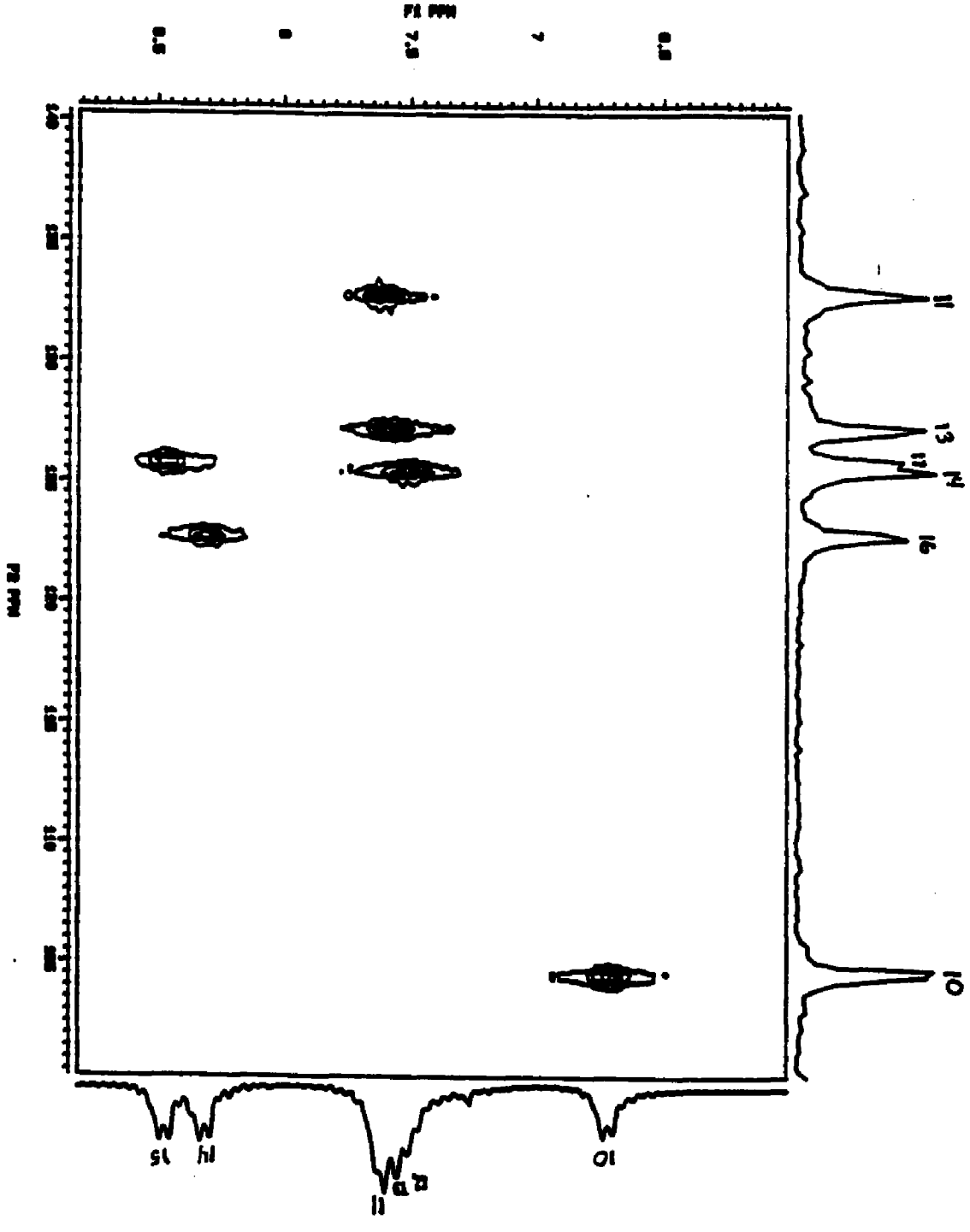


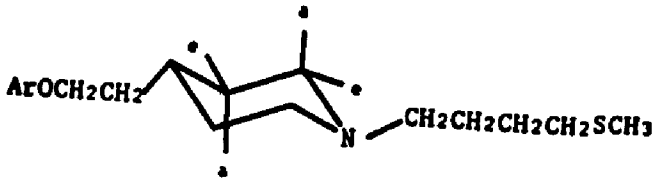
FIGURE 16b
AROMATIC REGION OF HCCORR SPECTRUM
OF NEP POLYMER
$CDCl_3$ SOLVENT

Although several signals occur in this region, it was possible to assign certain proton resonances by the use of the information obtained from the HCCORR spectrum (Figure 16a and 16b). The 1-D computer generated ^{1}H and ^{13}C spectrum are plotted along the F1 and F2 axis respectively in the HCCORR spectrum in order to aid in the interpretation of the spectrum. In interpreting the information concerning the proton assignments from the HCCORR spectrum the carbon assignments of the NEP polymer (Section 3.1.6.1.b) were assumed to be correct. The multiplet centered at 1.37 ppm was assigned to the axial protons, 5, β to the nitrogen atom in the piperidine ring; the corresponding equatorial protons, 5′,were assigned to a signal slightly downfield from the axial protons at approximately 1.82 ppm. The nonequivalence of the ring protons was attributed to the rigidity of the piperidine structure in the polymer backbone. The piperidine structure probably exists exclusively in one chair conformation since both ring inversion and nitrogen inversion are resisted strongly due to the presence of bulky substituent groups in the 1 and 4 position of the piperidine ring. H. Booth and J.H Little showed that for a conformationally biased N-alkyl derivative of piperidine, 1-t-butyl-4-cyclohexyl-piperidine, a difference of 1.05 ppm existed between the ring equatorial and axial protons α to the nitrogen atom with the equatorial protons occurring further downfield.[21] The HCCORR spectrum of the aliphatic region of the NEP polymer (Figure 16a) shows two distinct sets of contours, correlated to one carbon atom at 32.0 ppm, approximately 0.4 ppm apart ascribed to an increased chemical shift difference between axial and equatorial protons caused by the rigidity

of the piperidine ring in the polymer backbone. The chemical shift difference of the distereotopic ring protons, equatorial (8′) and axial (8), was even more pronounced for the ring protons *α* to the nitrogen atom where two sets of contours occurred at approximately 1.0 ppm apart. In general the ring axial protons *α* to the nitrogen atom are shielded to a higher extent than the equatorial protons thus appearing further upfield.[22]

The assignments of the aliphatic protons were as follows: protons 2 and 3 at 1.56, 1, 4 and 5′ at approximately 1.8, 5 at 1.37, 8 at 1.9 and 8′ at 2.90, 6 at 2.25, 7 at 2.83, and 9 at 4.13 ppm. The COSY spectrum (Figure 15) of the NEP polymer was quite complicated; proton pairs 5 and 5′, 3 and 6, 2 and 7, 8 and 8′, and 4 and 9 showed cross peaks indicating coupling. Protons 7 and 8′ are partially overlapping in the proton spectrum (Figure 14) however from the COSY spectrum it is possible to differentiate between the two protons and proton 8′ was assigned as the shoulder adjacent to the signal at 2.8 ppm. For the diastereotopic protons of the piperidine ring only geminal coupling was observed as no cross peaks were present which could be assigned to vicinal axial/axial, axial/equatorial or equatorial/equatorial coupling. The absence of cross peaks for axial/equatorial and equatorial/equatorial coupling may be due to a small coupling constant (normally 0-5 Hz); an increase in the digitial resolution of the experiment or running the experiment at higher field could possible result in the appearance of the cross peaks. However axial/axial coupling (normally 10-15 Hz) is normally only slightly weaker than that for geminal coupling for distereotopic protons in rigid six

membered rings. A possible explanation is that the linewidths of the signals are approximately as large as the coupling constants so the positive and negative lobes of the cross peaks can overlap and begin to cancel each other out. In addition, complex spin coupling patterns result in highly complex cross peaks that are even more likely to cancel as the linewidth becomes large.[23] Coupling constants were calculated for the ring protons of compound XVII to determine the magnitude of the coupling constants for a compound similar in structure to that of XVIb by the use of a computer program entitled PCMODEL[24] and are shown in Table 9 where "e" and "a" stand for equatorial and axial protons respectively and Ar represents a benzene ring. The exact linewidth of the signals were not possible to measure



XVII

TABLE 9

CALCULATED COUPLING CONSTANTS OF 1,4-DISUBSTITUTED PIPERIDINE RING

Type of Coupling	Magnitude of Coupling
H_e/H_a	2.56 Hz
H_e/H_e	2.22 Hz
H_a/H_a	12.84 Hz

since each signal was composed of more than one type of proton. However, linewidths of the order of approximately 10 Hz were measured

for a majority of the aliphatic signals. The absence of vicinal coupling for distereotopic protons were also observed in the COSY spectrum of the NZ zwitterion which showed cross peaks for coupling among the geminal protons only (see Section 5.1.1.1.a). The lack of any cross peaks involving coupling with the ring methine proton, 1, in the NEP polymer is explained by the the fact that the signal overlaps with protons 4, 5′ and 8. The lack of coupling between protons 1' and 5 was attributed to either small coupling constants, low digitial resolution of the experiment, or the linewidth approaching the magnitude of the coupling constant.

The aromatic region of the NEP polymer was assigned as follows: proton 10 at 6.70, 11 at 7.59, and 12 and 13 overlap at approximately 7.48 ppm. Cross peaks for proton pairs 10 and 11, 12 and 14, and 13 and 15 are evident for the aromatic region in the COSY spectrum. No cross peak was present for the proton pair 12 and 13 because there signals were overlapping in the proton spectrum. The assignments of protons 12 and 13, and 14 and 15 were made arbitrary and may be interchanged, i.e 13 may be 12 and 15 may be 14.

3.1.6.1.b Carbon Assignments of the NEP Polymer: The proton decoupled ^{13}C spectrum (Figure 17, Table 10) of NEP polymer also supported structure XVIa. The carbon signals were assigned as shown in XVIc based on the results from DEPT (Figure 18) and HCCORR (Figure 16a and 16b) experiments, and the chemical shift values of similar carbons.[19] From the DEPT spectrum (Figure 18) the ring methine carbon, 4, was assigned at 35.9 ppm and the four quaternary aromatic

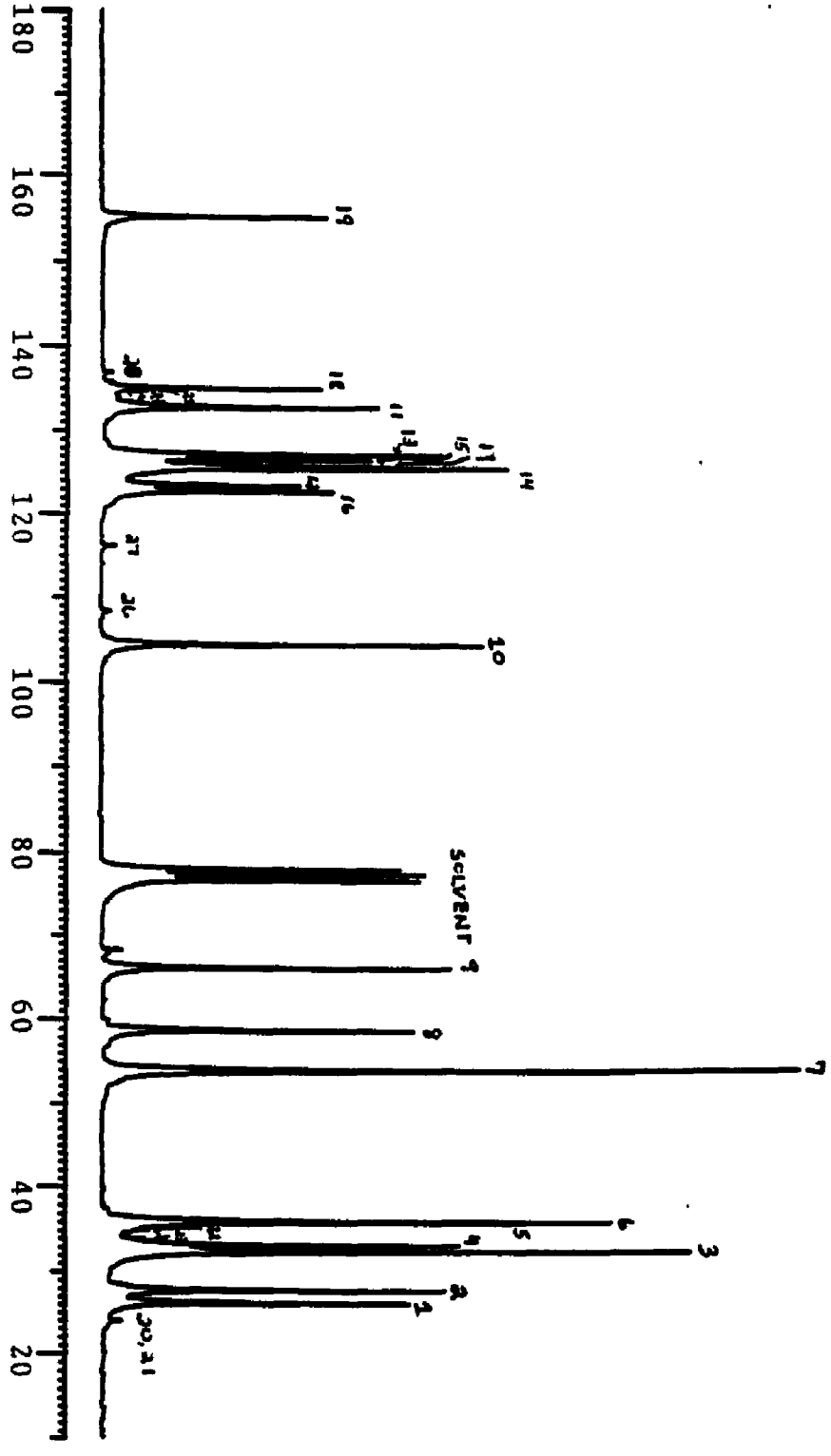


FIGURE 17
^{13}C SPECTRUM OF NEP POLYMER
$CDCl_3$ SOLVENT

TABLE 10

Assignments of the ^{13}C Spectrum of the NEP Polymer

Carbon Number	Chemical Shift (ppm)
1	26.0
2	27.5
3	32.2
4	33.0
5	35.7
6	35.8
7	53.8
8	58.5
9	65.8
10	104.3
11	122.5
12	123.2
13	125.3
14	125.5
15	126.3
16	126.9
17	132.5
18	134.8
19	155.0

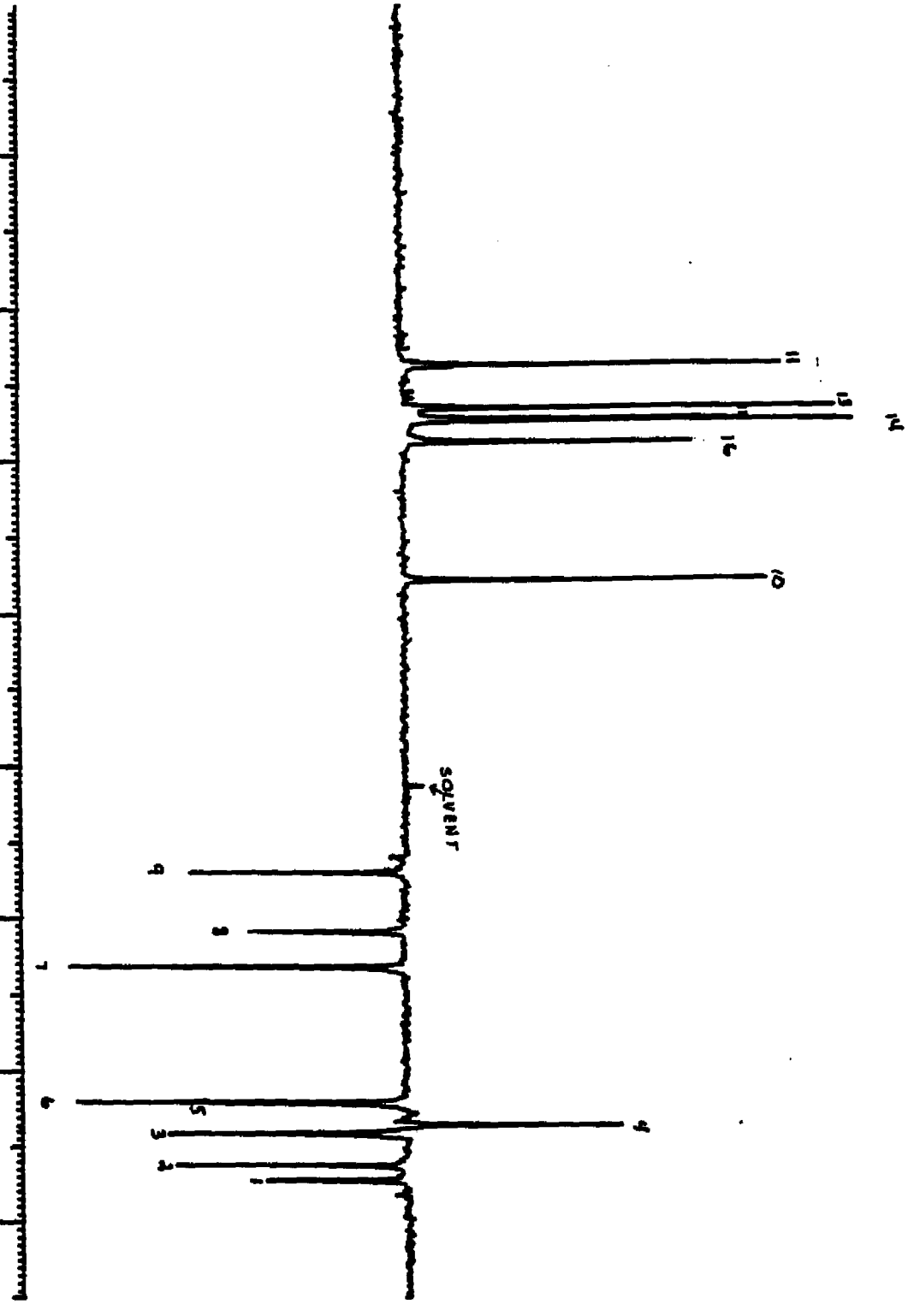
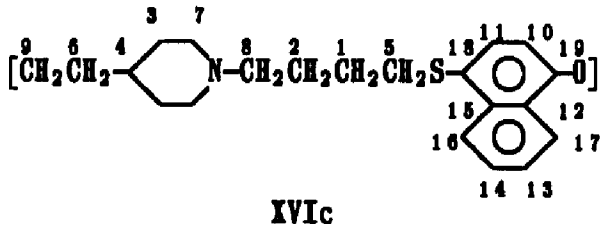


FIGURE 18
DEPT SPECTRUM OF NEP POLYMER
$CDCl_3$ SOLVENT

TABLE 11

Assignments of the DEPT Spectrum of the NEP Polymer

Carbon Number	Chemical Shift (ppm)
1	26.0
2	27.5
3	32.2
4	33.0
5	35.7
6	35.8
7	53.8
8	58.5
9	65.8
10	104.3
11	122.5
13	125.3
14	125.5
16	126.9
17	132.5



XVIc

carbons, 12, 15, 18 and 19, at 123.3, 126.4, 134.8 and 155.1 ppm. Direct calculations for the chemical shift of carbons 18 and 19 could not be made for the NEP polymer since the appropiate substituent chemical shift parameters for the naphthalene ring were not available. However, chemical shifts of 130.3 and 155.8 ppm were calculated for carbons 18 and 19 respectively assuming that the substituent parameters for substituted benzenes were applicable to substituted naphthalenes and the substitutents parameters for S-Me and O-Me simulate those for the CH_2-S and O-CH_2 respectively.[20] The observed chemical shifts for carbons 18 and 19 were 134.8 and 155.1 ppm respectively. The disagreement between the observed and calculated chemical shift for carbon 19 was insignificant; however the calculated value for carbon 18 was intermediate between the assigned value of 18 and that of a second quaternary carbon, 126.4 ppm. The assignment of carbons 12, 15, and 18 hence were made arbitrary and may be interchanged. Figure 16a represents HCCORR spectrum of the aliphatic portion of the NEP polymer. Due to the presence of the distereotopic protons in the piperidine ring, the carbon signals at 32.0 and 53.7 ppm each had two sets of contours correlated to it which appeared at different chemical shift positions along the F1 axes. The ring carbon β to the nitrogen, 3, occurred at 32.0 and the carbon α to the

nitrogen further downfield at 53.7 ppm. Using the labeling shown in structures XVIb and XVIc to represent the proton and carbon atoms respectively the following connectivity were established: H-1/C-4, H-2/C-1, H-3/C-2, H-4/C-6, H-5/C-3, H-5′/C-3, H-6/C-8, H-7/C-5, H-8/C-7, H-8′/C-7, and H-9/C-9. The assignment of carbon signals 5 and 6 may be interchanged since they are quite close together (difference of 0.15 ppm in the carbon spectrum) and not clearly discernible in the HCCORR spectrum due to the digital resolution used in this experiment. The HCCORR spectrum of the aromatic region of the NEP polymer shown in Figure 16b indicates the following connectivities: H-10/C-10, H-12/C-14, H-13/C-13, H-14/C-16, and H-15,/C-17. The four quaternary carbons do not show a cross peak since there are no attached protons and the long range J_{c-h} coupling is much too small to be visible.

3.1.6.2 IR Spectroscopy of the NEP Polymer: The I.R. spectrum (Figure 19) supports structure XVIa as the polymer structure. The IR spectrum was compared to that of poly(oxytetramethylenethio-1,4-naphthylene), herein referred to as naphthyl polymer, for which the I.R. spectrum has previously been assigned (see Section 5.1.4.2).[14] The major difference between the naphthyl polymer and the NEP polymer is the presence of a piperidine ring in the polymer backbone for the NEP polymer therefore any differences in the IR spectrum were attributed to the presence of this ring. The two I.R. spectra were similar with the exception of absorption bands at 2804.5, 2769.8, and 2669.5 cm^{-1} for the NEP polymer spectrum. These three absorption were

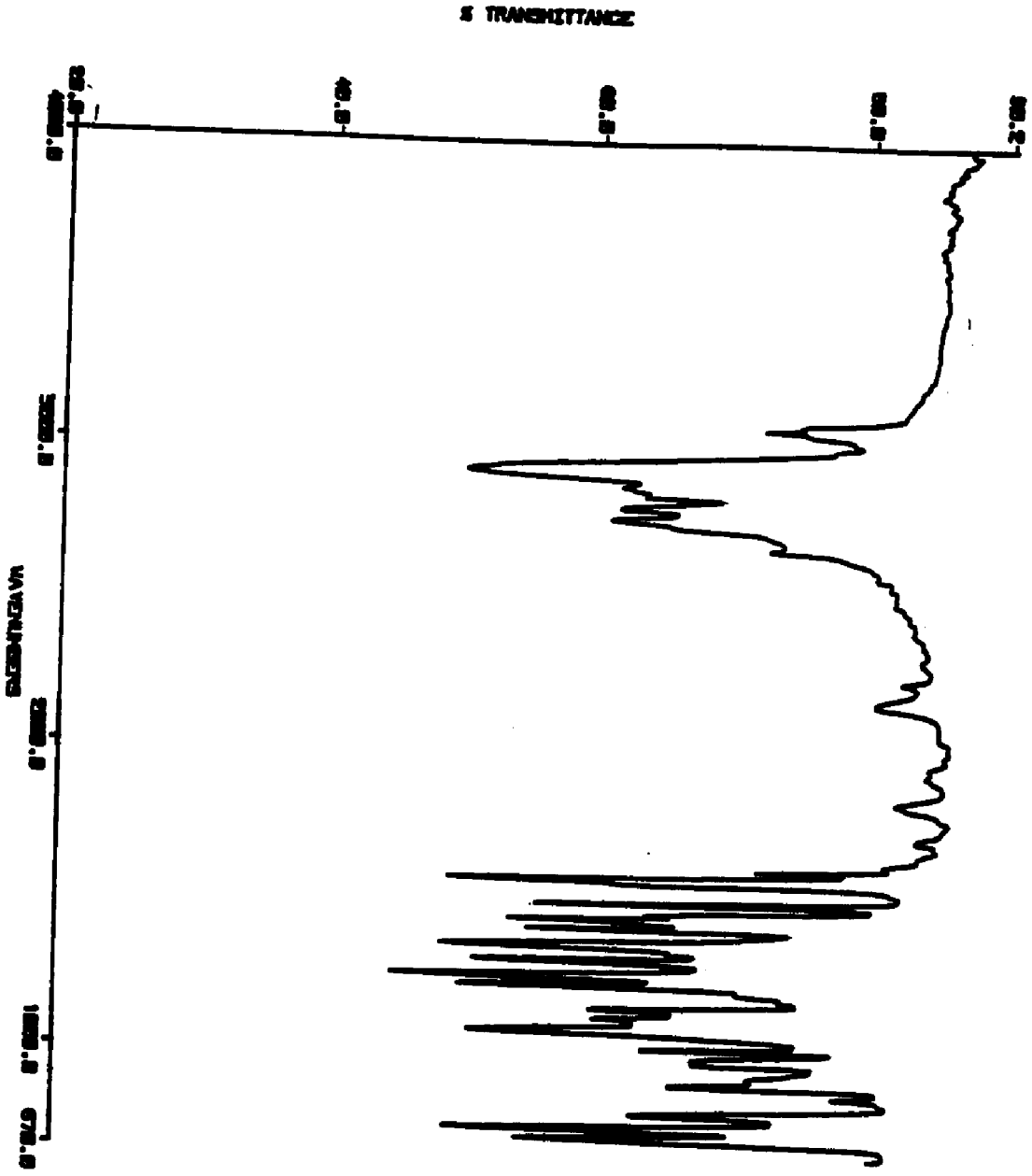


FIGURE 19

IR SPECTRUM OF NEP POLYMER

attributed to N–CH_2 stretching. The remaining absorption were assigned similar to those of the naphthyl polymer: 3030 (aromatic C-H), 2882 (aliphatic C-H), 1585 and 1505 (aromatic C-C), 1254, and 1083 (C-O), and 810 and 760cm^{-1} (aromatic C-H). Several other signals at 1453, 1424, 1365, 1319, and 1235 cm^{-1} are consistent with C-O, CH_2, aromatic C-H, S-CH_2, and other moieties of structure XVIa.

3.1.6.3 Thermal Analysis of the NEP Polymer:

3.1.6.3.a Differential Scanning Calorimetry (DSC): DSC was conducted on the NEP polymer in order to determine the presence of any thermal transitions. The NEP polymer was heated from room temperature to 85°C. The DSC thermogram reveals the presence of only one transition, A, (Figure 20), an endotherm at 56°C. On cooling the NEP polymer slowly and reheating no endotherm occurred but rather a change in slope, B. For samples of the NEP polymer preheated prior to DSC at 40°C for one hour in a vacuum oven no endotherm appeared in the DSC thermogram.

3.1.7 *Polymerization Mechanism of the NEP Zwitterion*

Polymerization is initiated by ring-opening nucleophilic attack of the arene oxide end of one NEP zwitterion (XVII) on the α-carbon of the ammonium ring of a second zwitterion (Scheme XIII), where Ar represents the naphthalene ring to form the dimer, XVIII. Propagation proceeds by the reaction of XVIII with itself and XVII to

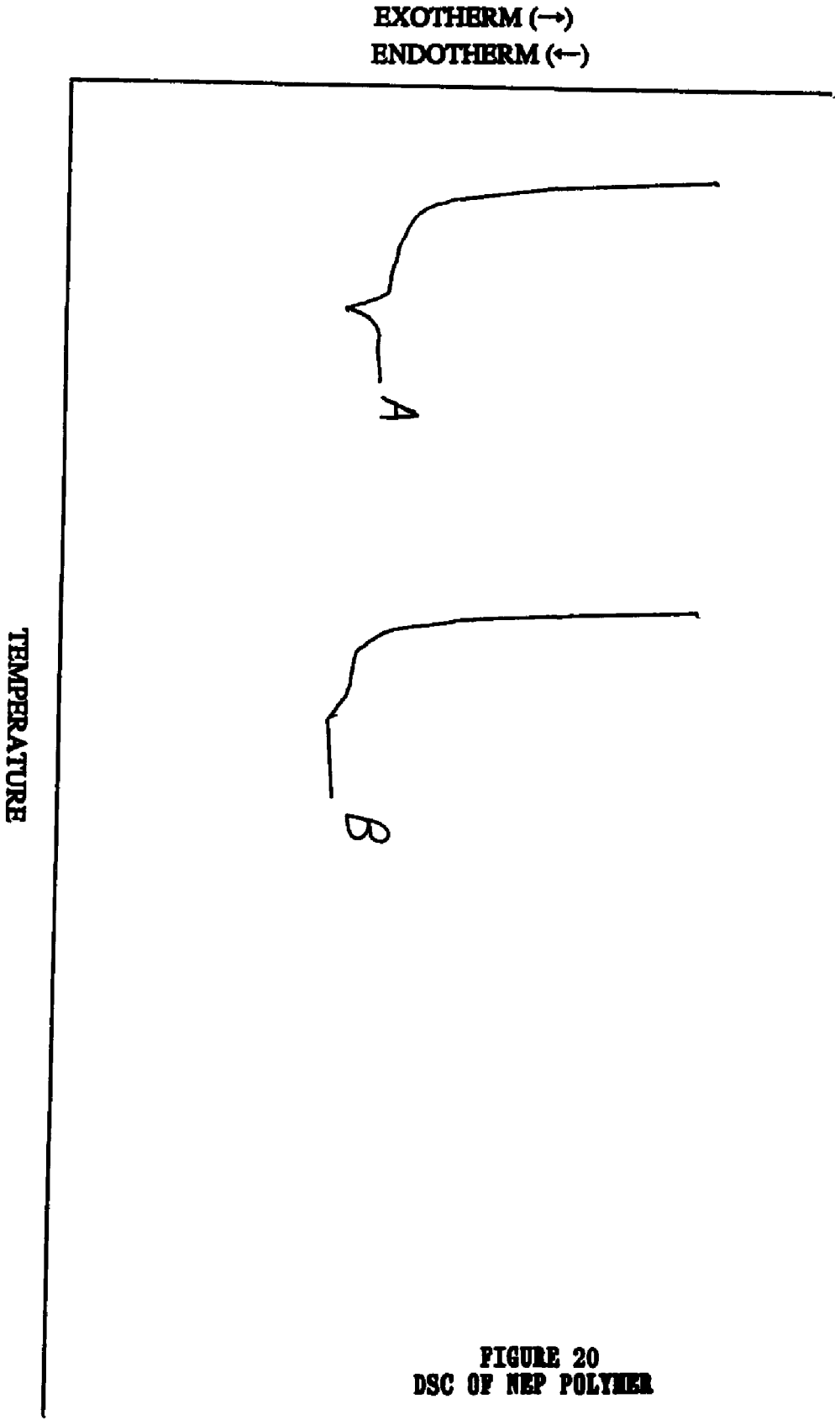
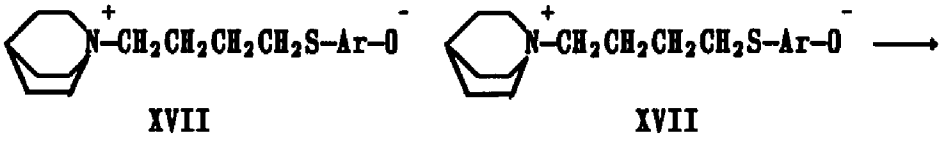


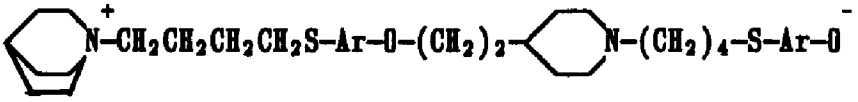
FIGURE 20
DSC OF NEP POLYMER

Scheme XIII:



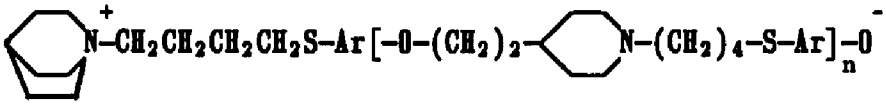
XVII XVII

eq (1)



XVIII

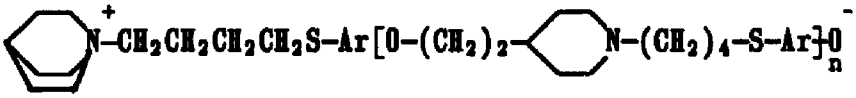
produce linear tetramer and trimer, respectively. The latter can react with themselves, or XVII and XVIII. Growth continues in a step reaction manner with the formation of different-sized macrozwitterions of type XIX. Termination occurs by a β-elimination reaction.



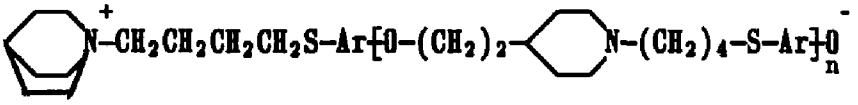
XIX

Termination by β-elimination can potentially occur along two sites of the NEP macrozwitterion XIX as shown in Scheme XIV. One, at the β methylene carbon of the 1,4-ethylenepiperidinium ring to form structure XX and two, at the β carbon of the straight chain alkyl group to form structure XXI and 1,4-ethylenepiperidine. However,

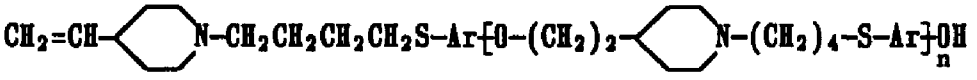
Scheme XIV:



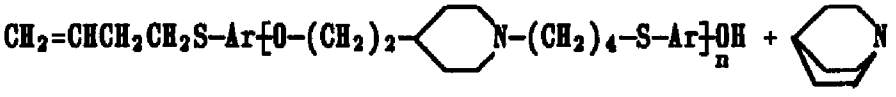
XIX



XIX



XX

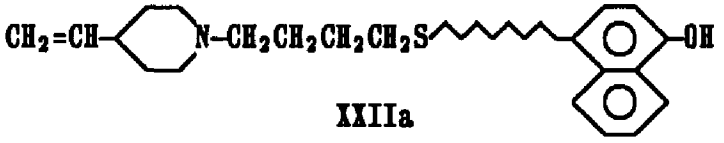


XXI

β-Elimination was found to occur exclusively at the 1,4-ethylene-piperidinium ring by abstraction of a H^+ by the phenoxide center to form structure XX based on NMR analysis for this type of double bond end group (Section 3.1.8). This is in line with studies on simple piperidinium salts. The possibility of β-elimination occurring by abstraction of H^+ from the main chain alkyl group was ruled out by the ease of opening a piperidinium ring in relation to elimination of simple alkyl groups, i.e. β-elimination of N-butyl-N-methyl-piperidinium hydroxide yields approximately a statistical ratio of 2:1 for ring opening versus loss of the alkyl group.[25] The termination process may occur intra- and/or intermolecularly to form the end groups.

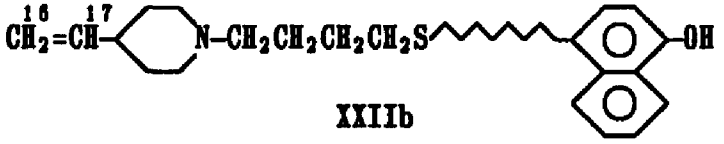
3.1.8 *Polymer End Groups*

3.1.8.1 Characterization by ^{1}H and ^{13}C NMR: The ^{1}H and ^{13}C NMR spectra provided evidence that olefinic and naphtholic groups were the predominant polymer end groups as shown in XXIIa where ⩘ represents the polymer backbone. The expanded region in the proton spectrum of



XXIIa

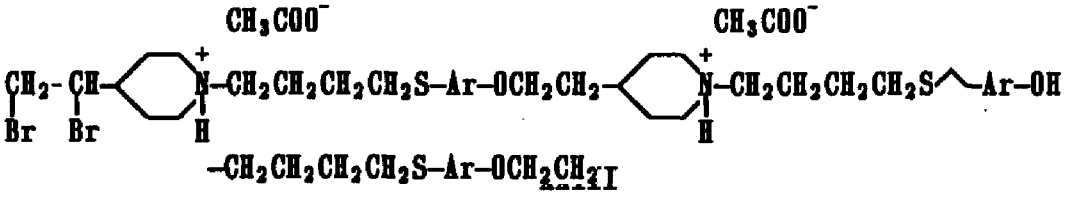
the NEP polymer represents the signals due to the presence of the vinyl end group (see Figure 14 signals 16-17). The existent of signals 16 and 17 in structure XXIIb as belonging to olefinic protons was confirmed by the addition of Br_2 across the double bond of the amine protonated NEP polymer. Attempts to add Br_2 across the double



XXIIb

bond of the nonprotonated NEP polymer resulted in failure since tertiary amines produce N-halo quaternary halides with molecular bromine.[26] The amine was protonated by dissolving the NEP polymer into an acetic acid-d_4/methanol-d_4 solution. On the addition of Br_2 a precipitate formed; the precipitate was isolated. Attempts to

dissolve the precipitate into $CDCl_3$ (a good solvent for the NEP polymer) were unsuccessful; however, the precipitate dissolved readily into DMSO-d_6 (a poor solvent for the nonprotonated NEP polymer) and ^1H NMR was taken on the solution. Figure 21 shows the ^1H spectrum of the protonated NEP polymer to which Br_2 was added (structure XXIII). The signals for protons 16 (4.97, 5.02, and 5.05 ppm) and 17 (multiplet from 5.65 to 6.00 ppm) were clearly missing. Several new signals appeared in the aromatic region which were attributed to the bromination of the naphthalene ring. Analysis of the olefin



splitting pattern was supportive of termination occurring by path 1 only and not path 2, as shown in Scheme XIV in Section 3.1.7. The observed multiplicity in the splitting pattern of the olefinic region in Figure 14 is not indicative of an olefin with structure XXI. This was confirmed by observing the splitting pattern of the olefinic protons of 1-pentene which should have a splitting pattern similar to structure XXI. The single olefinic proton appears as four sets of triplet and the terminal methylene protons appear as an overlapped multiplet.

Although there was no evidence of naphtholic end groups in the ^1H spectrum of the NEP polymer, the ^{13}C spectra of the NEP polymer

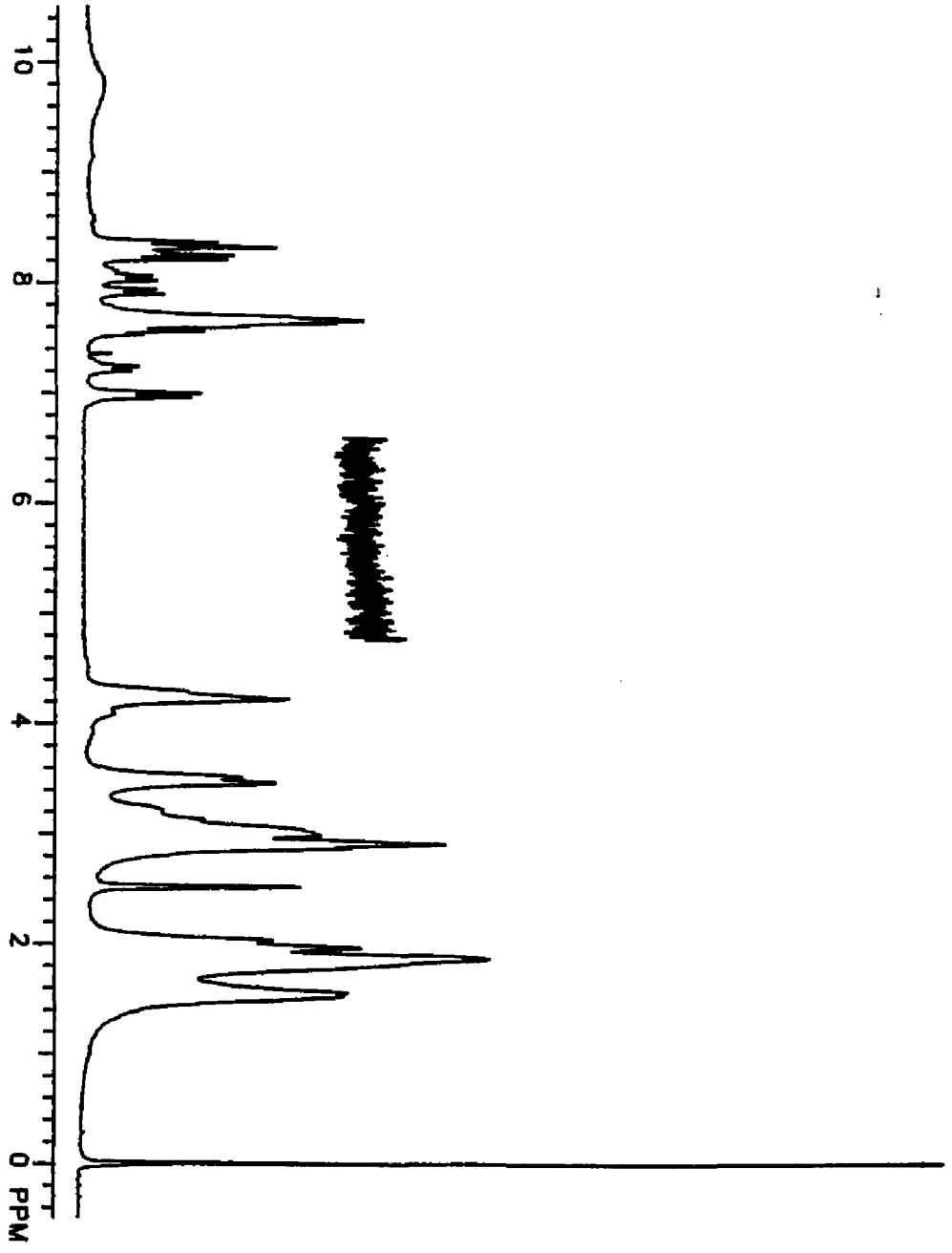
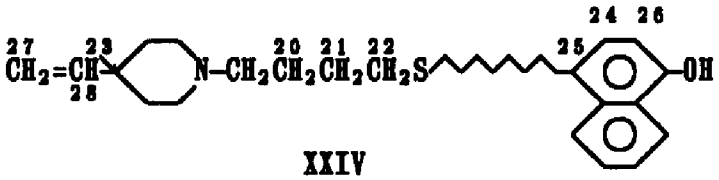


FIGURE 21

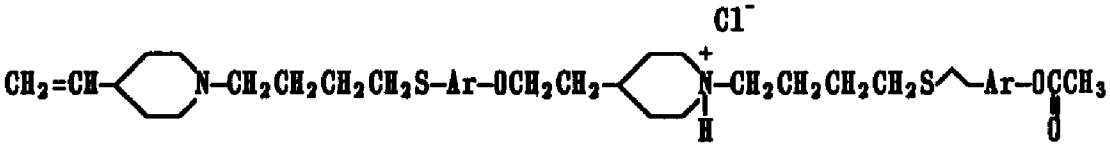
^{1}H SPECTRUM OF THE BROMINATED PROTONATED NEP POLYMER DMSO SOLVENT

indicated the presence of a naphtholic end group. The ^{13}C spectrum of the NEP polymer (Figure 17) showed several signals (20-28) which were assigned to both olefinic and naphtholic end groups; the assignments of the end group signals are shown in XXIV. Signal 26 at 108.1 ppm was in agreement for a carbon *a* to a naphthol, and signals 27 and 28 at 115.9 and 136.6 ppm respectively were assigned as the olefinic carbons. Several other signals present in the spectrum were assigned to carbons of the end group: 23.8 (20, 21), 34.7 (22), 33.6 (23), 133.6 (24), 135.5 ppm (25). No assignment was made for the signal at 67.9 ppm.



XXIV

3.1.8.2 Acetylation of the NEP Polymer: The NEP polymer was acetylated as shown in structure XXV (Ar represents the naphthalene ring and ^ the polymer backbone). Acetylation of the NEP polymer



XXV

resulted in formation of a random copolymer containing units of piperidinium hydrochloride salt in the polymer backbone. The formation of the piperidinium hydrochloride salt in the polymer

backbone resulted from the release of HCL which is a by-product of the acetylation reaction. Although triethyl amine was added to the acetylation reaction mixture to react with the released HCl by formation of the amine·HCl salt, the ring nitrogen of piperidine competes favorably with the triethyl amine for the released HCl hence the nitrogen in piperidine becomes protonated. No basicity constant was found for a 1,4-disubstituted piperidine hence no comparison could be made between its basicity relative to triethyl amine. If a weak base, i.e. pyridine, was used, the NEP polymer would precipitate out during the acetylation reaction due to the extent of the protonation of the nitrogen atom. The proton spectrum of the acetylated polymer showed no differences from that of the unacetylated polymer. The methyl protons from the acetyl group would be expected to show a proton signal at approximately 2.4 ppm but this is in a congested area in the proton spectrum of the NEP polymer. However evidence for acetylation and the protonation of the nitrogen atom was seen in both the IR spectrum (Figure 22) and the ^{13}C spectrum (Figure 23) of the NEP polymer. Due to the molecular weight of the NEP polymer the presence of the naphtholic end group (3300 cm^{-1}) was not observed in the IR spectrum of the NEP polymer (Figure 19). However, the IR spectrum of the acetylated polymer (Figure 22) contained two signals which was attributed to the acetylated end group: 1761.91 cm^{-1}, carbonyl stretching vibration, and 1194.68 cm^{-1}, C–O stretching vibration. A small broad signal was observed between 2559.45 and 2194.34 cm^{-1} which was assigned to the presence of a tertiary amine salt.

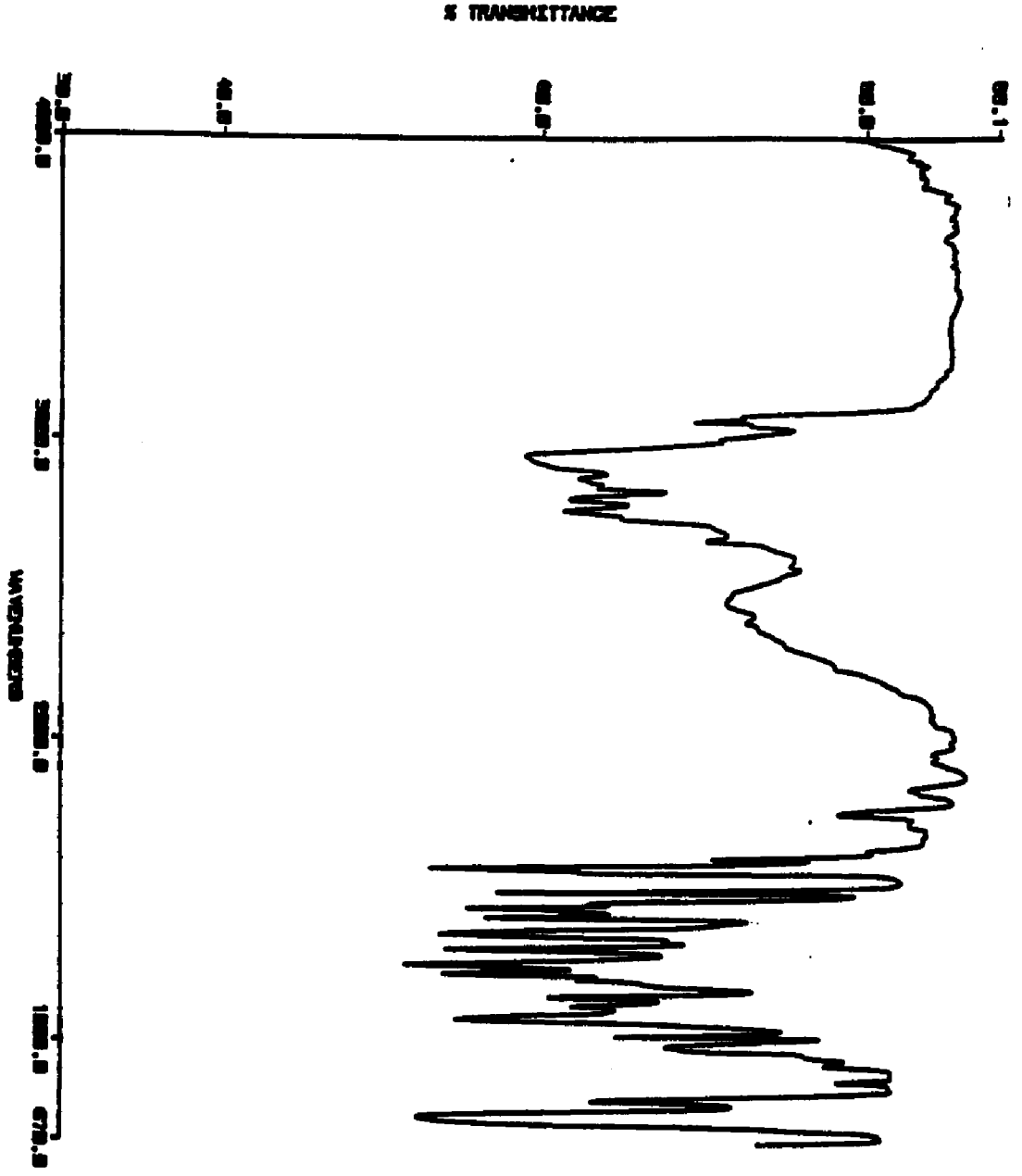
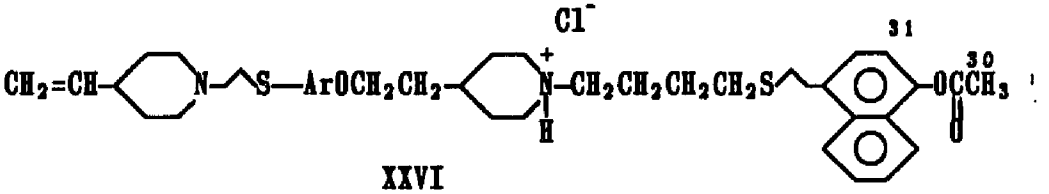


FIGURE 22
IR SPECTRUM OF THE ACETYLATED NEP POLYMER

The ^{13}C NMR spectra (30% w/v in $CDCl_3$) of the acetylated NEP polymer (XXV), Figure 23, revealed several signals which were attributed to the presence of an acetylated end group of which only two were assigned as shown in structure XXVI: 20.63 (carbon 30), and 117.57 (carbon 31).



XXVI

3.1.9 *Effect of Temperature on Polymerization*

Table 9 in Section 3.1.5 shows the number average molecular weight of the NEP polymer prepared by the sealed-tube and vacuum methods as determined by ^1H NMR. The degree of polymerization (DP) was determined by comparison of the sum of the integral values of the olefinic signal to that of the methylene protons adjacent to an aryl ether. The DP was then multiplied by the molecular weight of one repeat unit to give the molecular weight of the polymer. The molecular weight of the NEP polymer showed no significant variation dependent on the polymerization route, sealed tube or continuous vacuum. The absence of any significant variations suggests that the water of hydration present in the NEP zwitterion is not a determining factor in limiting the molecular weight, i.e. water is not involved in termination. This fact is substantiated by the absence of any signals in the ^1H and ^{13}C spectra which could be due to the presence of an aliphatic hydroxy group. This observation has been previously seen in

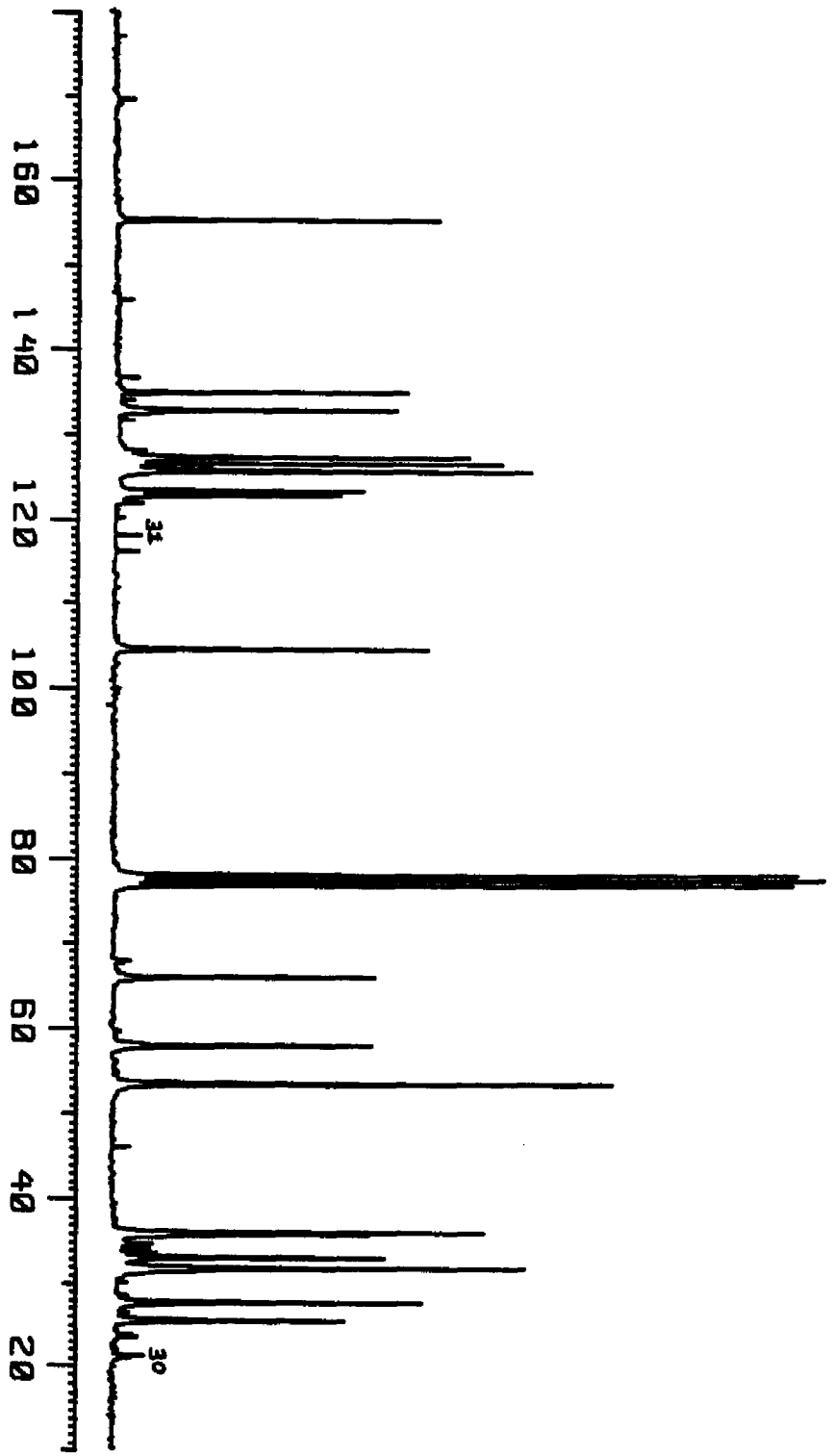


Figure 23
^{13}C SPECTRUM OF THE ACETYLATED NEP POLYMER
$CDCl_3$ SOLVENT

the polymerization of the NZ zwitterion where the molecular weight is independent of the polymerization route above 100°C but is strongly dependent below 100°C.[14] Above 100°C water is rapidly expelled from the reaction mixture (and condenses at the top of the polymerization tube) and termination by water is non-existent.

The maximum molecular weight was achieved at 175°C. The decrease in the molecular weight of the NEP polymer obtained at temperatures exceeding 175°C under both sealed-tubed and vacuum conditions is ascribed to the increased extent of β-elimination. Since β-elimination reactions generally have high activation energies as the temperature increases so does the rate of termination. At 200°C the molecular weight shows no significant change as the reaction time increases from one to four hours. However, at 225°C the molecular weight reaches its maximum value after only 0.3 hour and shows a large drop in the molecular weight on heating for periods exceeding 1 hour. Heating a polymer sample previously prepared at 175°C for 2 hours at 225°C in a sealed tube also resulted in a significant decrease in the molecular weight. The molecular weight decreased from 1.3×10^4 to 5.3×10^3. This drop in molecular weight with time could be do to the decomposition of the NEP polymer. Elemental analysis of a NEP polymer sample which was prepared at 175°C and heat at 225°C for two hours showed no significant difference in comparison to a sample which was not heated at 225°C after polymerization.

4.0 CONCLUSION I

A new isolable zwitterion, 4-(4-[1,4-ethylenepiperidinium]-butanethio)-1-naphthol inner salt (NEP zwitterion), was prepared by the ring opening reaction between tetrahydro-1-(4-hydroxy-1-naphthyl)-thiophenium hydroxide hydrochloride salt (NZ·HCl salt) and 1,4-ethylenepiperidine to form 4-(4-[1,4-ethylenepiperidinium]-butanethio)-1-naphthol hydrochloride salt which was treated with anion exchange resin to give the NEP zwitterion. The NEP zwitterion was not prepared directly by modification of tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt (NZ zwitterion) by 1,4-ethylenepiperidine in order to avoid competition between the phenoxide end of the NZ zwitterion and 1,4-ethylenepiperidine for the thiophenium center. The NEP zwitterion was isolated as a hydrate containing 1.8 moles of water as demonstrated by TGA; however, it is also stable in its anhydrous form. The structure of the NEP zwitterion was deduced by the use of 1-D ^{1}H and ^{13}C NMR, 2-D NMR (COSY and HCCORR), Spectral Editing Techniques (DEPT), and IR spectroscopy.

Polymerization of the NEP zwitterion was investigated over the temperature range of 175-225°C under both sealed tube and continuous vacuum conditions. DSC showed that polymerizations conducted below 190°C occurred in the solid state and polymerizations exceeding 190°C occurred in the melt. Polymerization of the NEP zwitterion occurs by a ring opening mechanism whereby the phenoxide end of one molecule attacks the ring methylene carbon *α* to the ammonium atom to form a dimer. The dimer may react with either a second molecule of dimer or

the NEP zwitterion to form tetramer and trimer, respectively, Polymerization proceeds in this manner to form an alternating copolymer containing a piperidine ring in the polymer backbone. Termination of the polymeriztion reaction occurs by a β-elimination mechanism. The phenoxide anion of one macrozwitterion abstracts a H^+ from the β carbon of the 1,4-ethylenepiperidinium ring to form olefinic end groups on one end and naphtholic end groups at the other end.

The structure of the NEP polymer was confirmed by elemental analysis, 1-D (^1H and ^{13}C) NMR, 2-D (COSY and HCCORR) NMR, Spectral Editing Techniques (DEPT), and IR spectroscopy. The piperidine ring in the polymer backbone was shown to be rigid by the results from the 2-D NMR experiments; hence, it did not undergo either chair-chair or nitrogen inversion. Evidence of polymer end groups (olefin and naphthol) was seen in the ^1H and ^{13}C spectra. The presence of olefinic end groups was confirmed by the addition of bromine across the double bond of the protonated NEP polymer; the assignment of the olefin end groups were also based on their chemical shift in both the proton and carbon spectra . The presence of the naphthol end group was confirmed by an acylation reaction. Acylation of the NEP polymer resulted in the formation of a random copolymer containing piperidinium hydrogen chloride units. The IR spectrum of the acylated NEP polymer was identical to the NEP polymer with two exceptions. One, it contained a small sharp absorption at 1761.91 cm^{-1} which was assigned to the C-O stretching vibration due to the carbonyl group and, two, a small broad absorption band between 2559.45 and 2194.34

cm^{-1} which was assigned to a tertiary amine salt.

The number average molecular weight of the polymer was determined by ^1H NMR by comparing the sum of the integrals of the olefinic signals with the integral for the methylene protons adjacent to the aryl ether linkage. The presence of water was determined not to be a deciding factor in the termination reaction since the molecular weight did not vary significantly if the polymerization occurred in a sealed tube or under continuous vacuum. The highest molecular weight, 1.3×10^4, was achieved for the sample polymerized at the lowest temperature, 175°C, indicating that termination became more favored at higher temperatures.

It was thought that by isolating the zwitterion, polymers of high molecular weight could be obtained since the zwitterionic intermediate could not undergo termination by reaction with excess reactants or by-products. The failure of this system to achieve higher molecular weight polymer than 1.3×10^4, even though the zwitterion was isolable, can partially be blamed on the stability of the bicyclic ammonium ring. The ring was exceptionally stable to polymerizations below 175°C and on increasing the temperature the rate of termination increased faster than that of propagation. It is thought that other starting bicyclic amine monomers, i.e. conidine, which form more highly strained ammonium compounds offer promise in obtaining higher molecular weight polymers.

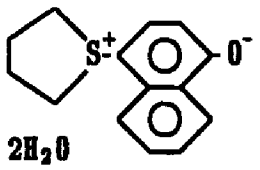
5.0 RESULTS and DISCUSSION II

5.1 Results and Discussion for the Copolymerization of Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt and β-Butyrolactone

Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt, herein referred to as the NZ monomer or NZ zwitterion, was chosen as the nucleophilic monomer and β-butyrolactone as the electrophilic monomer for this system. Previously the NZ zwitterion has been characterized by ^{1}H and ^{13}C NMR spectra, chemical shift values for similar carbons, single-frequency off-resonance decoupling (SFOR) experiments, and data for several other tetrahydrothiophenium-arene oxide systems.[14] The NZ zwitterion was further characterized by the use of 2-D NMR techniques (COSY and HCCORR) in order to confirm the assignments made previously. The assignments of the ^{1}H and ^{13}C spectra of β-butyrolactone have been well documented so no further experiments will be done in order to elucidate the structure.[27]

5.1.1 *Characterization of the NZ zwitterion*

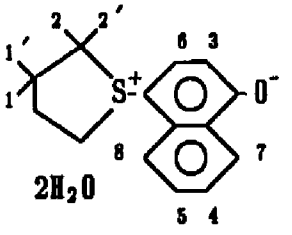
The NZ zwitterion was prepared as described in Section 2.1.1.1 and isolated as a dihydrate as shown in structure XXVIIa.



XXVIIa

5.1.1.1 NMR Spectroscopy of the NZ Zwitterion: The NZ zwitterion was characterized by the combination of 1-D NMR (^{1}H and ^{13}C) and 2-D NMR (COSY and HCCORR) experiments.

5.1.1.1.a Proton Assignment of the NZ Zwitterion: Figure 24 and Table 12 show the proton spectrum and δ values of the NZ zwitterion. The signal assignment shown in structure XXVIIb was based on the observed splitting pattern, signal areas, and results from the COSY



XXVIIb

experiment (Figure 25). The sharp signal at 3.48 ppm belongs to the water of hydration of the NZ zwitterion. The solvent signal for DMSO is hidden under the signal for proton 1. The signal assignment of protons 1 and 1′, and 2 and 2′ were made arbitrarily and may be interchanged. The COSY spectrum of the NZ zwitterion contains a high resolution 1-D spectrum along the F1 and F2 axes in order to aid in the interpretation of the spectrum. The ring protons on the carbons α and β to the sulphonium atom are distereotopic. Coupling between the geminal proton is clearly shown by the presence of cross peaks for the proton pairs 1/1′ and 2/2′; however there is no indication of coupling among the vicinal protons. The lack of cross peaks for coupling among vicinal protons was also observed for the distereotopic protons in the

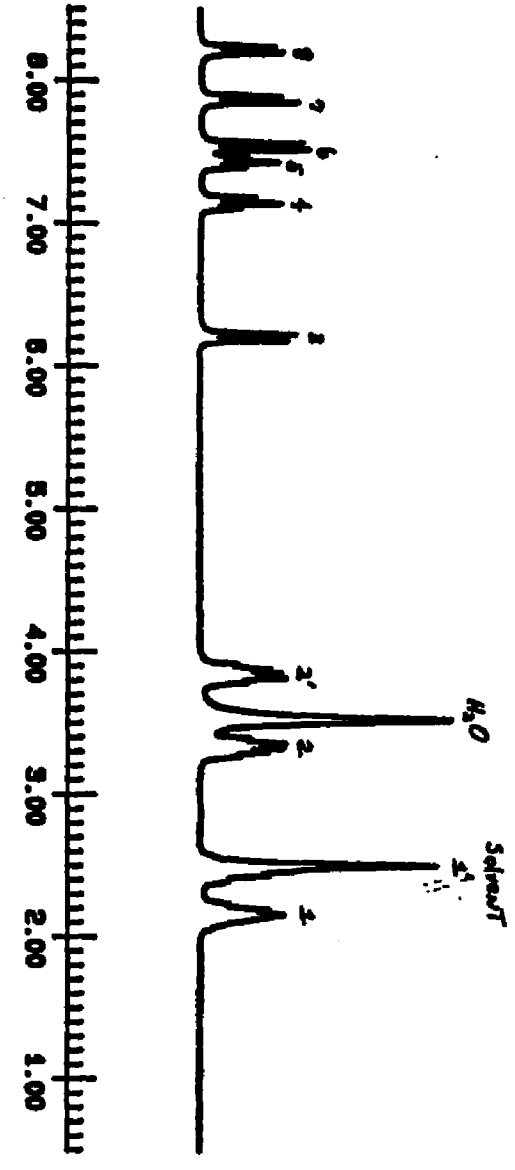


FIGURE 24
^{1}H SPECTRUM OF THE NZ ZWITTERION
DMSO SOLVENT

TABLE 12

Assignments of the ^{1}H Spectrum of the NZ Monomer

Proton Number	Chemical Shift (ppm)
1, 1'	2.22, 2.43
2, 2'	3.36, 3.84
3	6.20
4	7.14
5	7.43
6	7.54
7	7.87
8	8.22

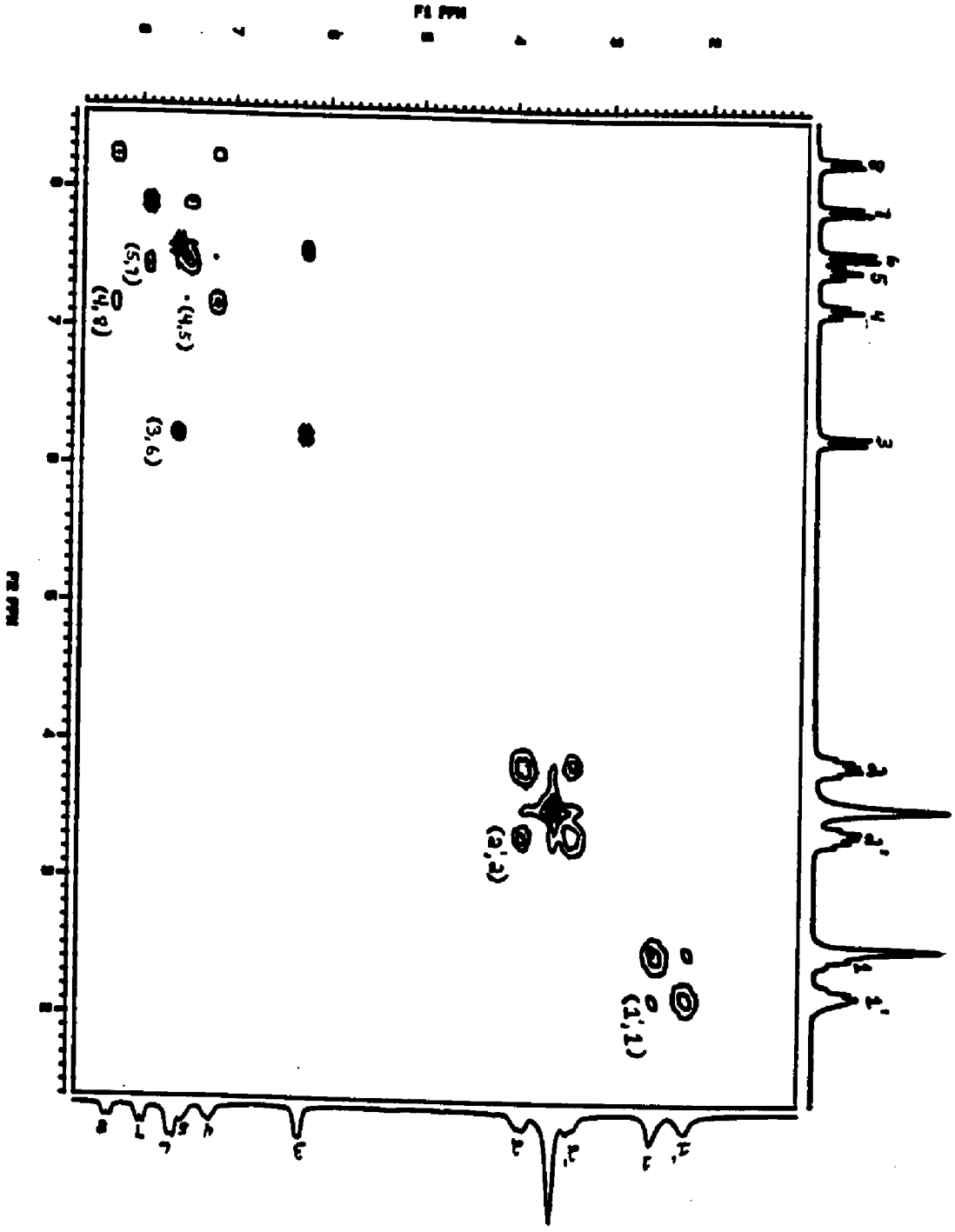
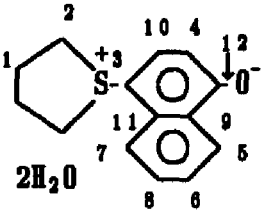


FIGURE 25
COSY SPECTRUM OF THE NZ ZWITTERION
DMSO SOLVENT

NEP polymer system (see Section 3.1.6.1.a). The absence of cross peaks for vicinal coupling may be due to a small coupling constant; an increase in digitial resolution of the experiment or running the experiment at higher field could possible result in the appearance of the cross peaks. Cross peaks were also present in the aromatic region for the proton pairs 3/6, 4/5, 4/8, and 5/7. Although the assignments of proton pairs 4/5 and 7/8 were made arbitrary, hence may be interchanged, i.e. protons 4, 5, 7 and 8 may correspond to signals 5, 4, 8, and 7 respectively, from the COSY spectrum it is clear that protons 4 and 7, and 5 and 8 are adjacent to each other. Previously it was thought that protons 4 and 5 was adjacent to protons 8 and 7, respectively.[14]

5.1.1.1.b Carbon Assignments of the NZ Zwitterion: The proton-decoupled ^{13}C spectrum (Figure 26 and Table 13) of the NZ zwitterion supports structure XXVIIa. The carbon signals were assigned as shown in XXVIIc based on the chemical shift of similar carbons and the results from the HCCORR experiment.[19] The HCCORR spectrum was divided



XXVIIc

into two parts, the aliphatic region (Figure 27a) and the aromatic

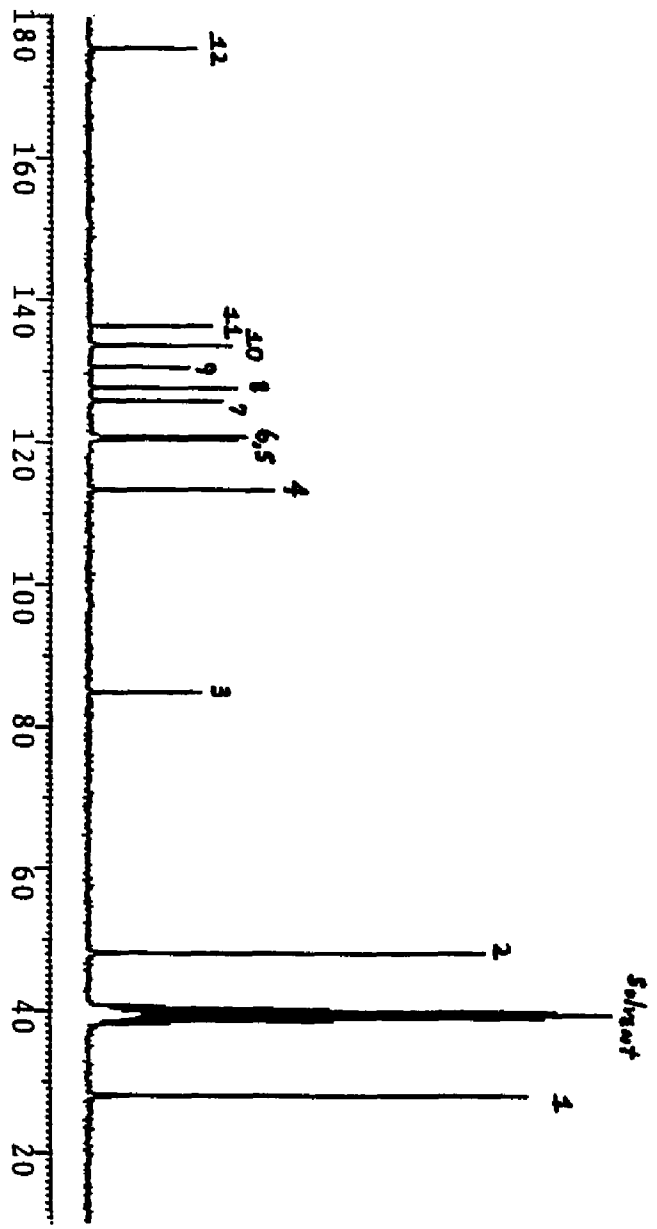


FIGURE 26
^{13}C SPECTRUM OF THE NZ ZWITTERION
DMSO SOLVENT

TABLE 13

Assignments of the ^{13}C Spectrum of the NZ Monomer

Carbon Number	Chemical Shift (ppm)
1	28.0
2	48.0
3	84.7
4	113.3
5	120.5
6	120.8
7	125.8
8	127.6
9	130.5
10	133.6
11	136.3
12	175.2

region (Figure 27b). High resolution carbon and proton 1-D spectrum of the NZ zwitterion appear along the F2 and F1 axes in order to aid in the interpretation. The following proton/carbon connectivities were deduced for the aliphatic region by using the labelling of the structure of XXVIIb for the proton and XXVIIc for the carbon assignments: H-1/C-1, H-1′/C-1, H-2/C-2, and H-2′/C-2. The HCCORR spectrum clearly shows the presence of distereotopic protons in the thiophenium ring by the presence of two sets of distinct proton signals correlated to the carbons at 28.0 and 48.0 ppm. Using the protocol established previously, the following proton/carbon connectivities were established for the aromatic region from Figure 27b: H-3/C-4, H-4/C-6, H-5/C-8, H-6/C-10, H-7/C-5, and H-8/C-7. Previously the following connectivities were thought to be correct: H-3/C-10, H-4/C-5, H-5/C-6, H-6/C-4, H-7/C-7 and H-8/C-8.[14] The carbon assignments of 5, 6, 7, and 8 were made somewhat arbitrarily hence may be interchanged i.e. carbons 5, 6, 7, and 8 may be 7, 8, 5, and 6 respectively. The four quaternary ring carbons were assigned on the basis of no correlating peak along the proton axes. Direct calculations for the chemical shift of carbons 3 and 12 could not be made for the NZ zwitterion since the appropriate substituent chemical shift parameters for the naphthalene ring were not available. However, chemical shifts of 113.5 and 174.0 were calculated for carbons 3 and 12 respectively, assuming that the substituent parameters for substituted benzenes were applicable to substituted naphthalenes and the substitutents parameters for $\overset{+}{S}$-CH_3 and Ar-O^-Na

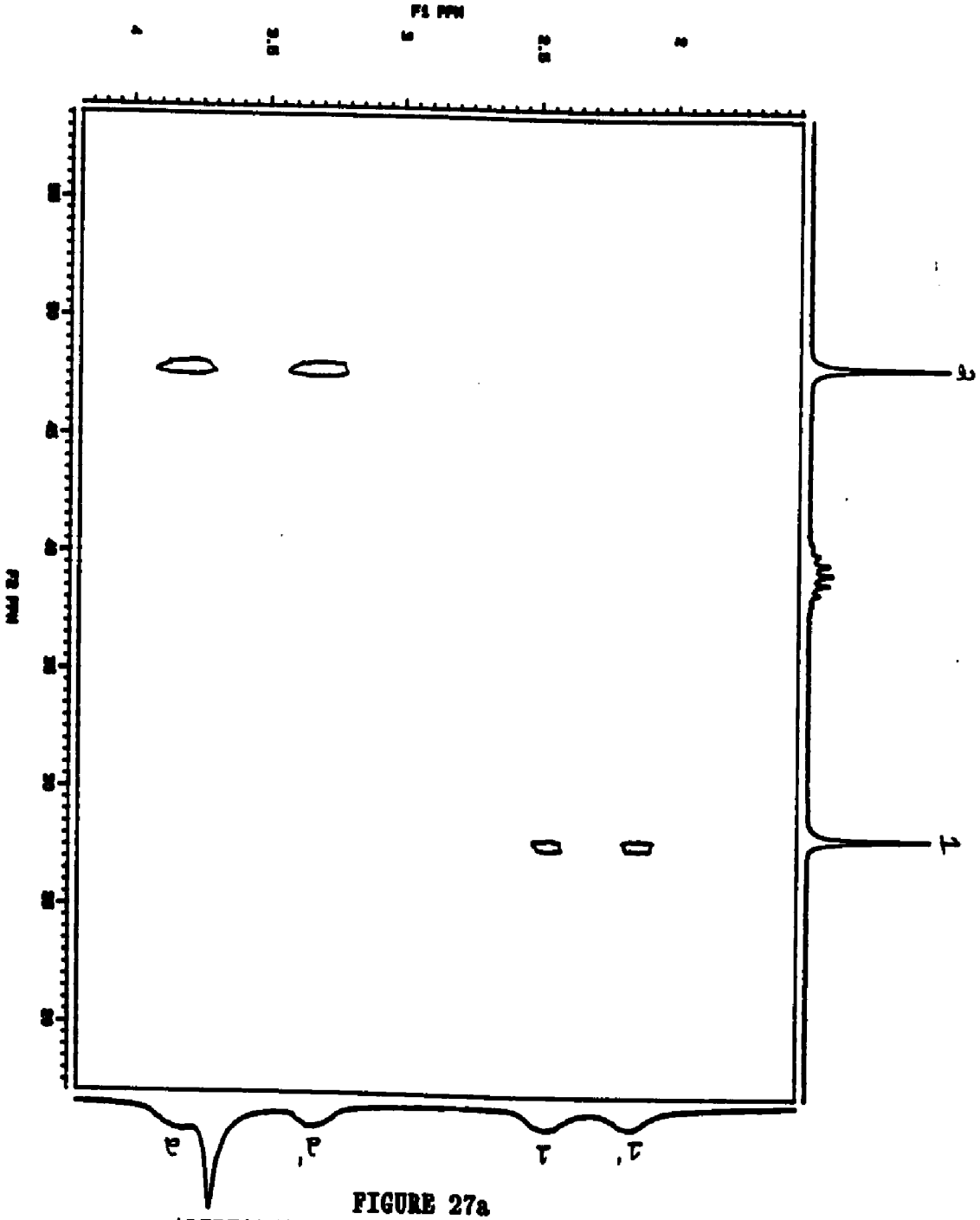


FIGURE 27a
ALIPHATIC REGION OF HCCORR SPECTRUM
OF THE NZ ZWITTERION
DMSO SOLVENT

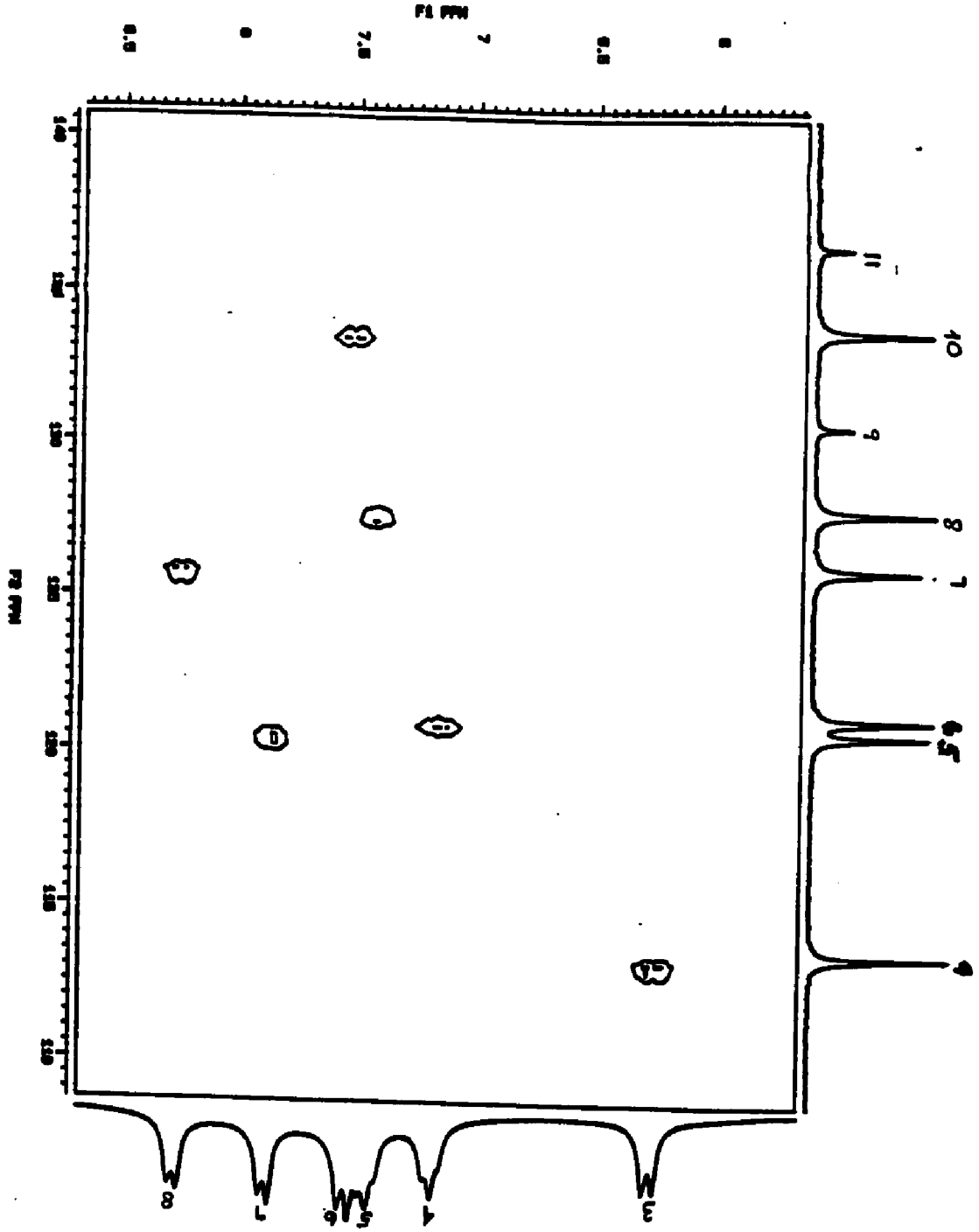


FIGURE 27b
AROMATIC REGION OF HCCORR SPECTRUM
OF THE NZ ZWITTERION
DMSO SOLVENT

simulate those of $\overset{+}{S}\text{-}CH_2$ and $Ar'\text{-}O^-$ where Ar represents benzene and Ar' naphthalene.[20] The observed chemical shift of carbons 3 and 12 were 84.6 and 175.3 ppm. There is no significant different between the observed and calculated chemical shift for carbon 12. However for carbon 3 there is a difference of 28.9 ppm between the observed and calculated value. This large difference between the observed and calculated chemical shift was attributed to the formation of a quinoid-type resonance. Carbons 9 and 11 were assigned arbitrarily hence may be interchanged.

5.1.2 *Characterization of the NZ and β-BL Monomer System*

5.1.2.1 NMR Spectroscopy: An equal molar mixture of NZ and β-BL was characterized by the use of the ^1H and ^{13}C NMR assignments of the individual monomers. The characterization of the monomers was essential to ensure that no starting material remained in the reaction mixture and to determine if the monomers reacted immediately upon mixing.

5.1.2.1.a Proton Assignment of the NZ and β-BL Monomer System: Figure 28 is a ^1H spectrum of an equal molar mixture of the NZ zwitterion and β-BL. The signal assignments shown in structures XXVIIb and XVIIIa (δ values listed in Table 14) were based upon signal area, splitting patterns, and the proton spectrum of the individual monomers. The assignments of the proton spectrum of the NZ

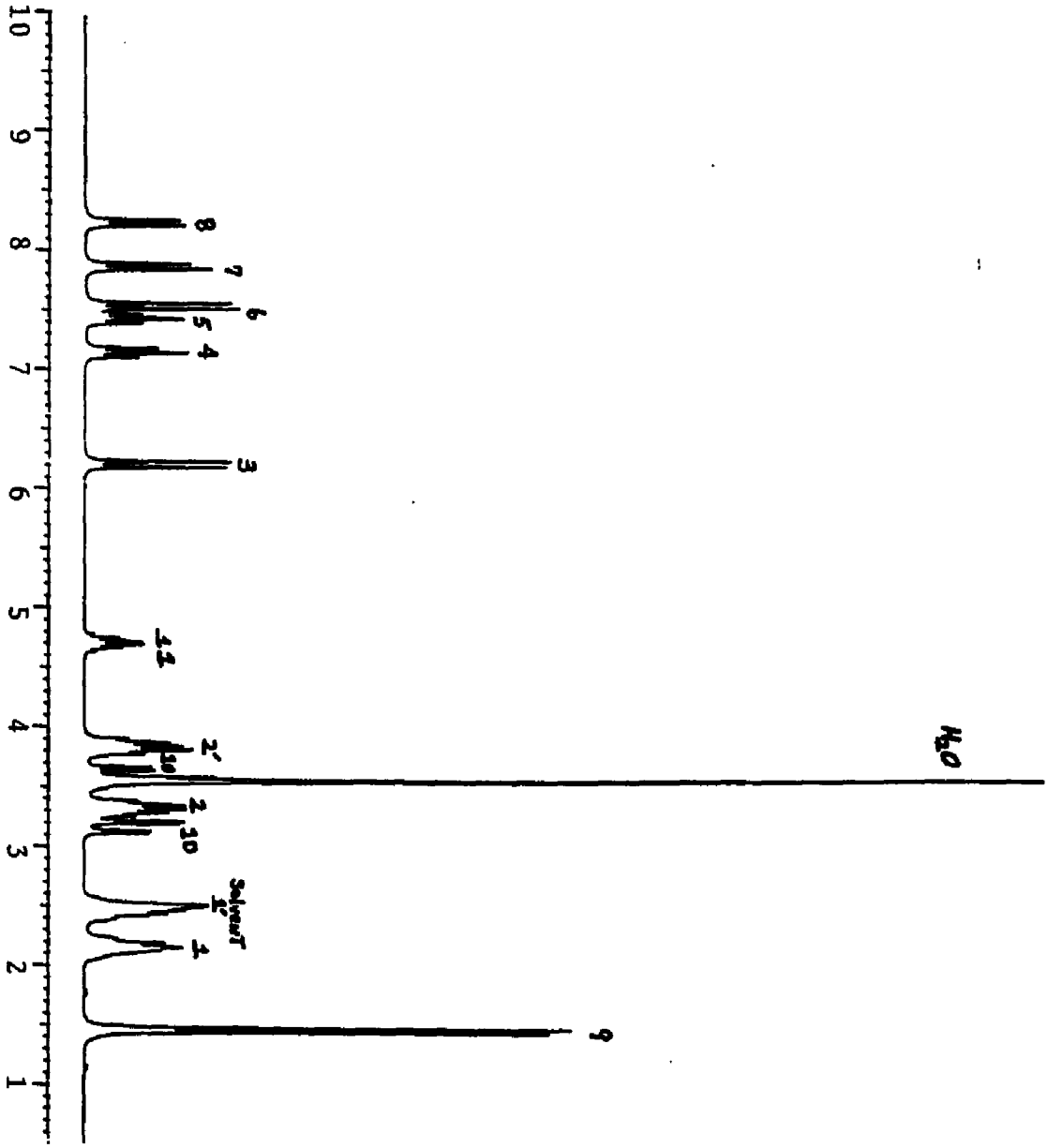
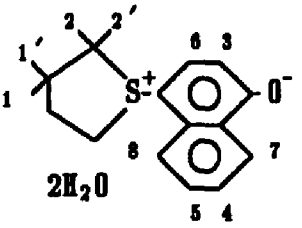


FIGURE 28
^{1}H SPECTRUM OF THE NZ/β-BL SYSTEM
DMSO SOLVENT

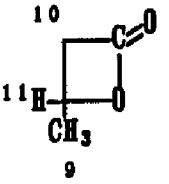
TABLE 14

Assignments of the ^{1}H Spectrum of the NZ/β -BL System

Carbon Number	Chemical Shift (ppm)
1, 1'	2.14, 2.49
2, 2'	3.34, 3.57
3	6.19
4	7.13
5	7.42
6	7.53
7	7.85
8	8.22
9	1.45
10	2.43, 3.32
11	4.69



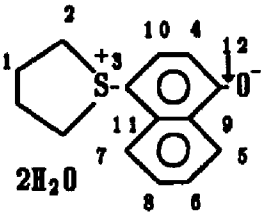
XXVIIb



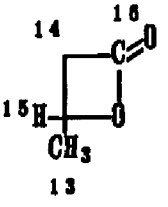
XVIIIa

zwitterion was discussed in Section 5.1.1.1.a.

5.1.2.1.b Carbon Assignments of the NZ and β-BL Monomer System: The proton-decoupled ^{13}C spectrum of the NZ and β-BL monomer system is shown in Figure 29. The carbon signals were assigned as shown in structures XVIIc and XVIIIb (δ values listed in Table 15). The assignments were based on the ^{13}C spectrum of the individual monomers.



XVIIc



XVIIIb

The assignment of the ^{13}C spectrum of the NZ zwitterion was discussed in Section 5.1.1.1.b.

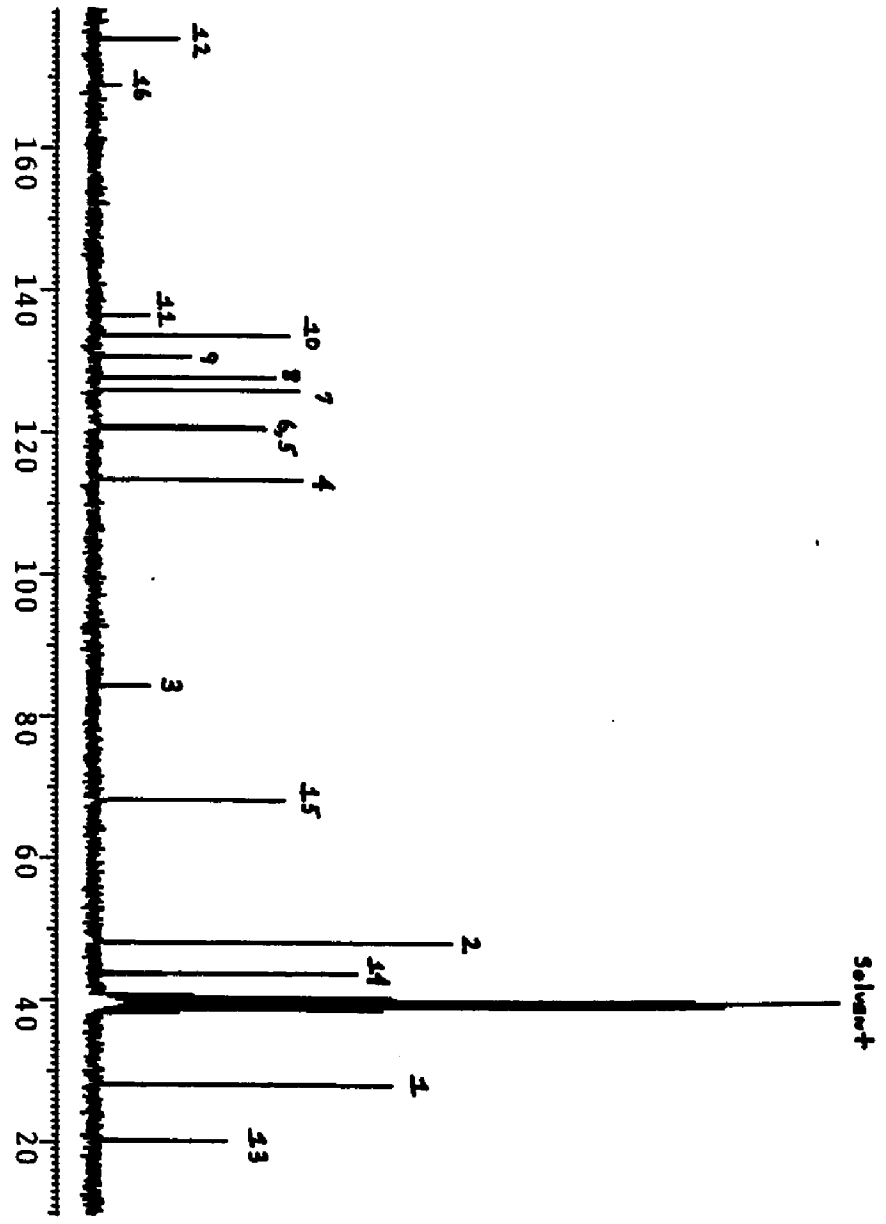


FIGURE 29
^{13}C SPECTRUM OF THE NZ/β-BL SYSTEM
DMSO SOLVENT

TABLE 15

Assignments of the ^{13}C Spectrum of the NZ/β-BL System

Carbon Number	Chemical Shift (ppm)
1	28.0
2	48.0
3	84.3
4	113.3
5	120.4
6	120.7
7	125.8
8	127.6
9	130.6
10	133.6
11	136.4
12	175.1
13	20.1
14	43.7
15	68.0
16	168.8

5.1.3 *Copolymerization of NZ and β-BL*

The solution copolymerization of NZ and β-BL was investigated in an aprotic dipolar solvent, DMF, over a temperature range of 35-100°C in sealed tubes (Table 2). The reaction mixture was a clear lime green

TABLE 16

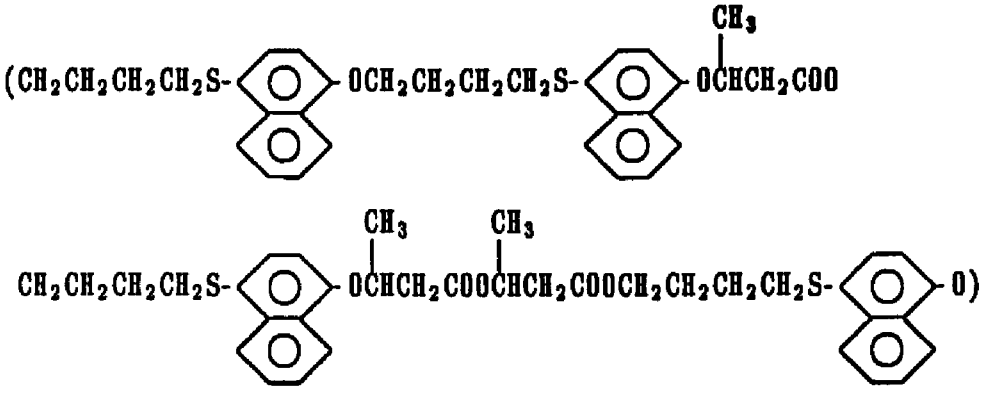
NZ/β-BL COPOLYMER RESULTS

Sample #	Temp. (oC)	Reaction Time (hrs)	Copolymer Composition NZ:β-BL	Homoβ-BL:Copolymer	Molecular Weight (M_n)
1	35	168	1.5:1.0	43:57	3.1×10^3
2	50	20	1.4:1.0	42:58	3.5×10^3
3	50	72	1.5:1.0	46:54	1.9×10^3
4	100	20	1.4:1.0	45:55	3.4×10^3
5	100	72	1.6:1.0	41:59	4.0×10^3

color. The copolymer was isolated from the reaction mixture by precipitating into diethyl ether. Following centrifugation of the reaction mixture the diethyl ether/DMF mixture was decanted off leaving a beige film. The beige film was redissolved into CH_2Cl_2 and reprecipitated into CH_3OH. After centrifuging, the CH_2Cl_2/CH_3OH solution mixture was decanted off leaving a beige film. The absence of any starting monomer was confirmed by the use of ^1H NMR on the original reaction mixture. In a typical polymerization a yield of 31% copolymer (CH_3OH insoluble) was obtained. The remaining 69% was mostly oligomer. The copolymer was soluble in common organic

solvents, i.e. CH_2Cl_2, acetone, DMF, and DMSO, and insoluble in most alcohols and diethyl ether.

The copolymer was characterized as structure XXIXa based on the results of ^1H and ^{13}C NMR Spectroscopy, spectral editing techniques

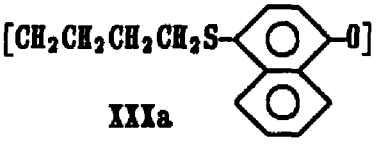


XXIXa

(DEPT), IR Spectroscopy, and preparation and characterization of the comonomers homopolymers. A discussion of the characterization of the homopolymers will be offered first before that of the copolymer.

5.1.4 *Characterization of Poly-NZ*

Poly-NZ was prepared by the polymerization of the NZ zwitterion at 135°C in a sealed tube. The NZ polymer has been previously characterized as structure XXXa by ^1H and ^{13}C NMR, Single Frequency Off-Resonance Decoupling (SFOR) experiments, and IR spectroscopy.[14]

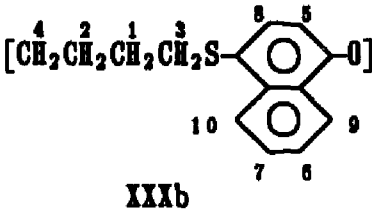


XXIa

The naphthalene ring in the polymer backbone caused the aromatic region in both the ^{1}H and ^{13}C spectra to be complicated thus preventing the assignment of certain signals without ambiguity. 2-D NMR experiments (COSY and HCCORR) were performed on the NZ-polymer in order to substantiate the assignments and to clarify any existing ambiguities.

5.1.4.1 NMR Spectroscopy of Poly-NZ: Poly-NZ was characterized by the use of 1-D (^{1}H and ^{13}C) NMR, 2-D (COSY and HCCORR) NMR and IR spectroscopy.

5.1.4.1.a Proton Assignment of Poly-NZ: Figure 30 and Table 17 show the ^{1}H spectrum and δ values of poly-NZ with various signals for the repeat unit as shown in XXIb based on the results from the COSY experiment, chemical shift values, splitting patterns, and signal



XXIb

areas. The COSY spectrum (Figure 31) of poly-NZ has a computer

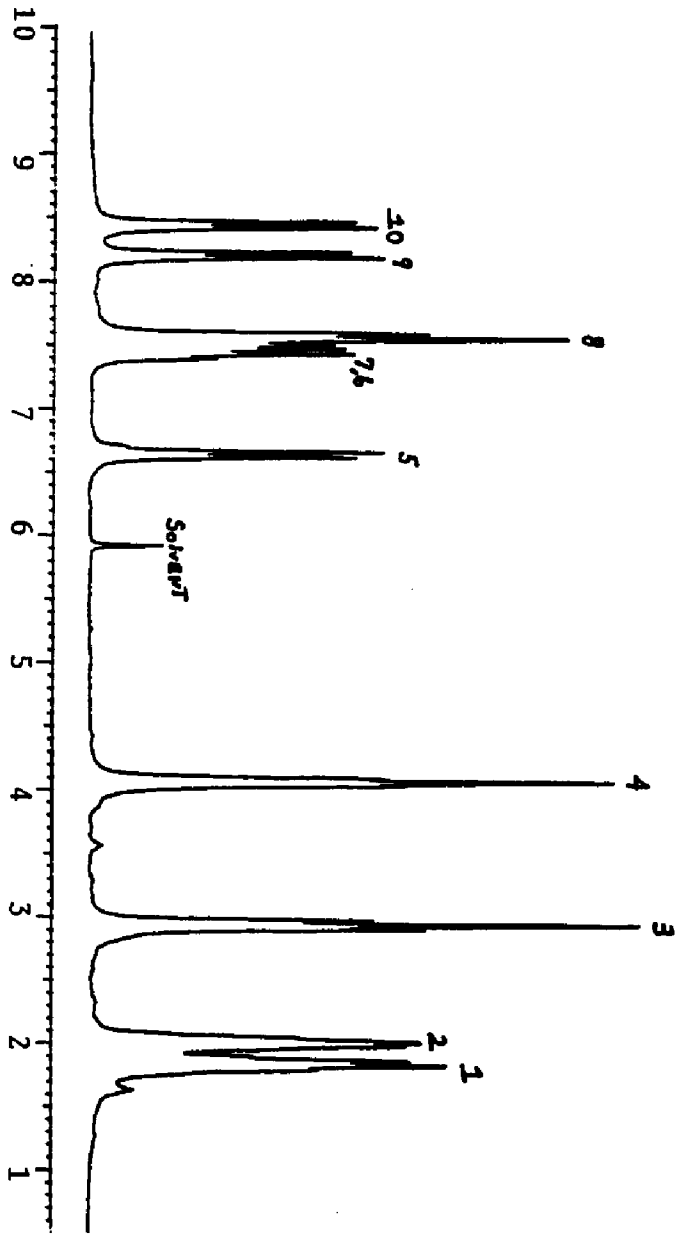


FIGURE 30
^{1}H SPECTRUM OF POLY-NZ
1, 1, 2, 2,-TETRACHLOROETHANE SOLVENT

TABLE 17

Assignments of the ^{1}H Spectrum of the Poly-NZ

Proton Number	Chemical Shift (ppm)
1	1.88
2	1.98
3	2.93
4	4.05
5	6.62
6, 7	7.48
8	7.55
9	8.18
10	8.42

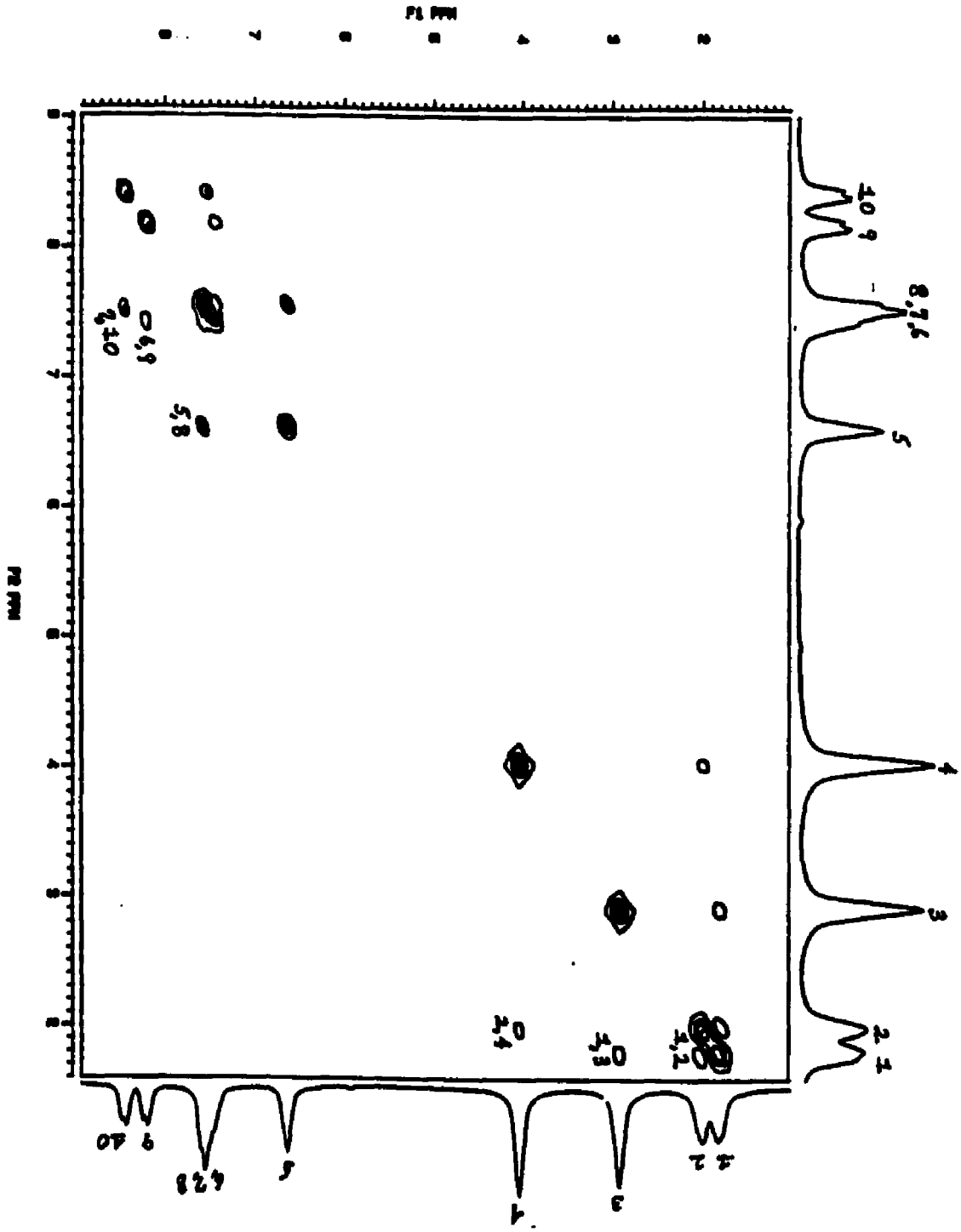
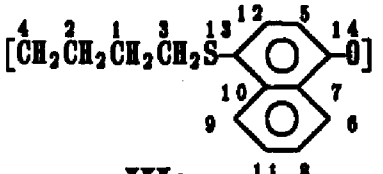


FIGURE 31
COSY SPECTRUM OF POLY-NZ
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

generated 1-D spectrum along both the F1 and F2 axes in order to aid in the interpretation. The COSY spectrum clearly shows that coupling exists between proton pairs H1/H2, H1/H3, H2/H4, H5/H8, H6/H9, and H7/H10. A small contour is also observed for the proton pair H6/H7. From the ^{1}H 1-D spectrum (Figure 30) of poly-NZ, protons H6 and H7 are indistinguishable from each other due to overlapping of the signals to give a multiplet. By distinguishing protons H6 and H7 coupling to H9 and H10 is determined. Although the assignments of protons H6 and H7, and H9 and H10 are made some what arbitrary and may be interchanged, the proton pairs H6/H9 and H7/H10 must remain adjacent to each other in order for the correct coupling patterns as determined by the COSY experiment to exist.

5.1.4.1.b Carbon Assignments of Poly-NZ: The proton-decoupled ^{13}C spectrum (Figure 32, Table 18) of poly-NZ supports structure XXXc. The carbon signals were assigned as shown in XXXc based on the results from the HCCORR experiments (Figure 33a and 33b), and chemical shift values of similar carbons.[19] The HCCORR spectrum is shown in Figures



XXXc

33a and 33b with computer generated 1-D spectrum for proton and carbon along the F1 and F2 axes, respectively, to aid in the interpretation

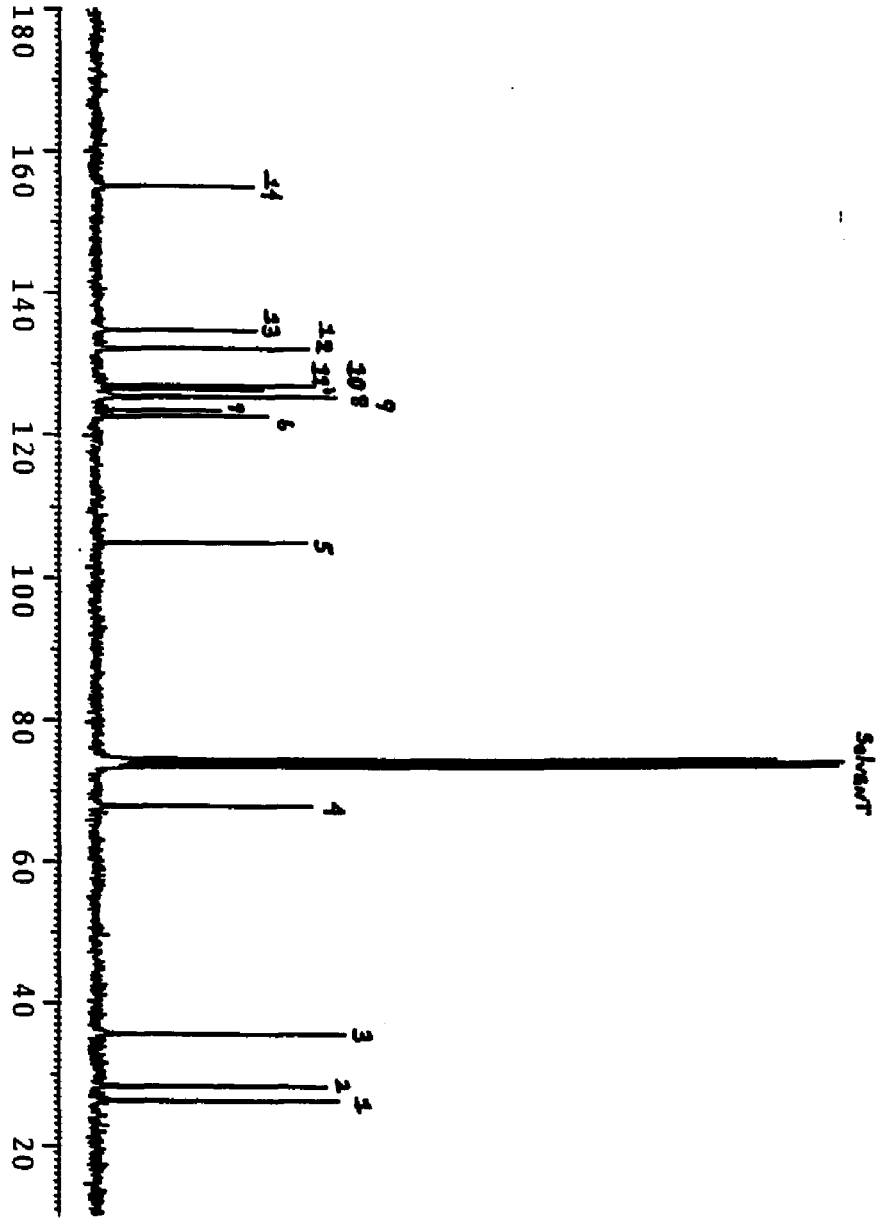


FIGURE 32
^{13}C SPECTRUM OF POLY-NZ
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

TABLE 18

Assignments of the ^{13}C Spectrum of the Poly-NZ

Carbon Number	Chemical Shift (ppm)
1	26.2
2	28.3
3	35.7
4	67.8
5	104.8
6	122.6
7	123.5
8	125.4
9	125.5
10	126.5
11	127.0
12	132.2
13	134.7
14	154.9

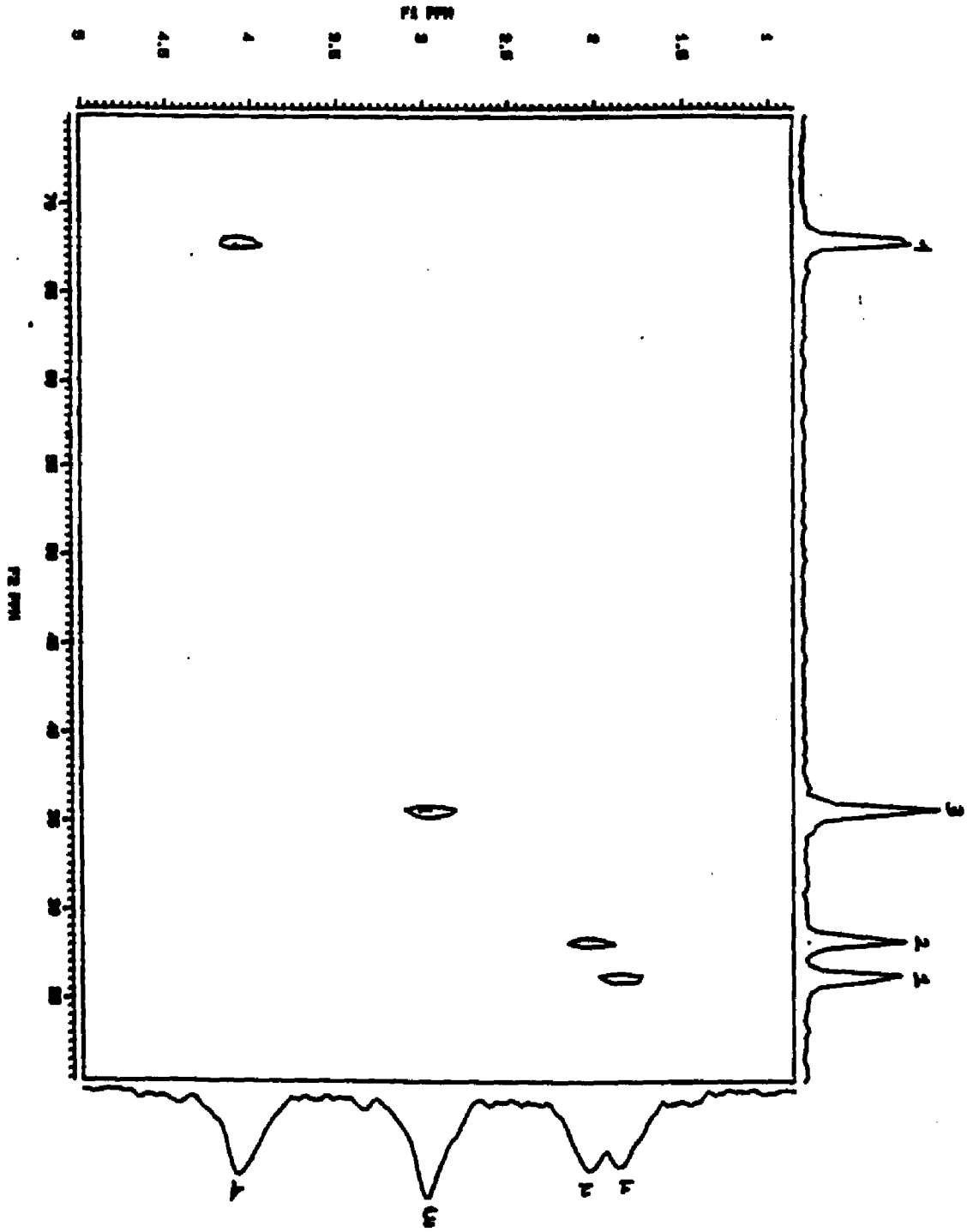


FIGURE 33a
ALIPHATIC REGION OF HCCORR SPECTRUM OF POLY-NZ
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

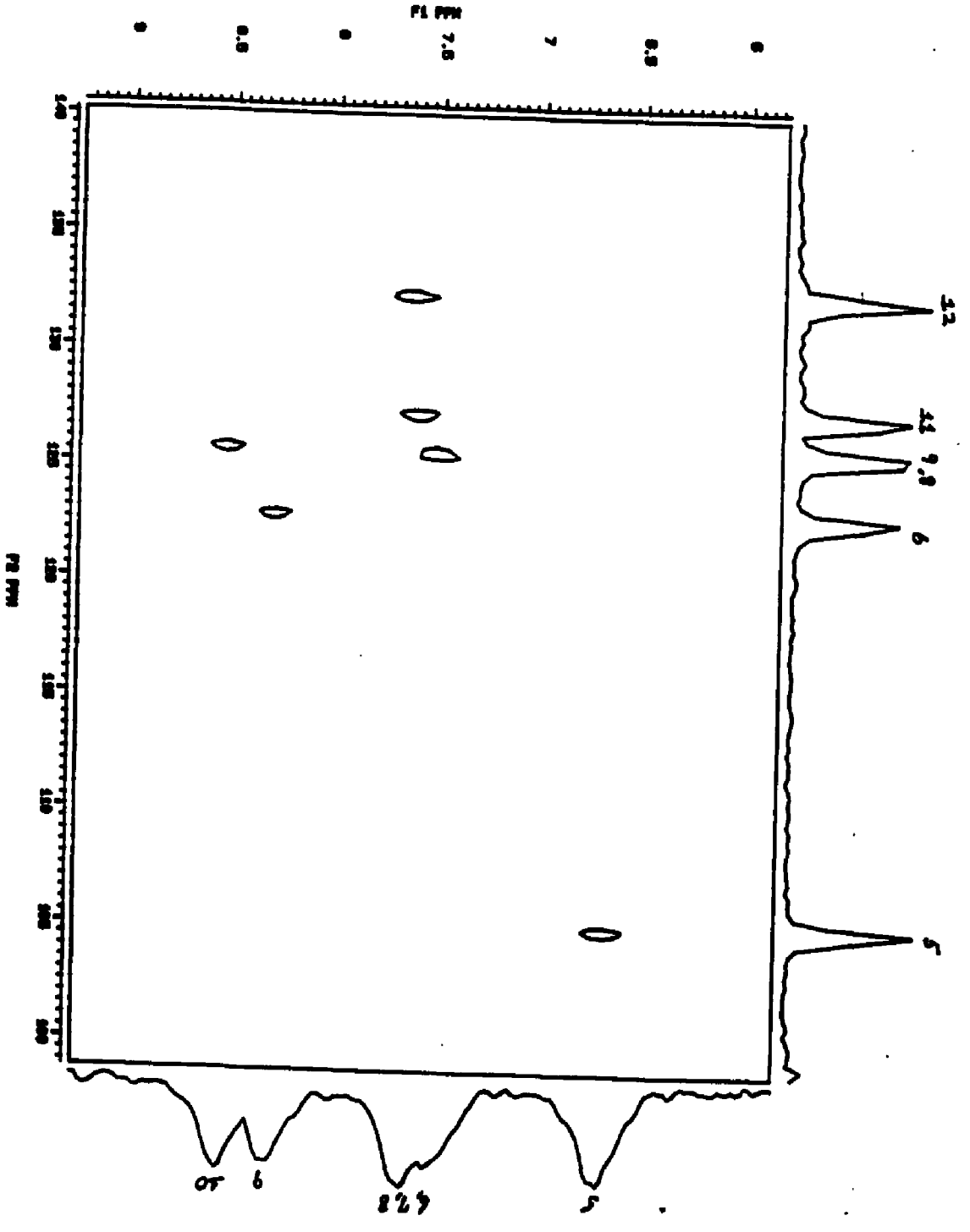


FIGURE 33b
AROMATIC REGION OF HCCORR SPECTRUM OF POLY-NZ
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

of the spectrum. The following proton/carbon connectivities were deduced by using the labelling of the diagram XXXb for the proton and XXXc for the carbon assignments: H1/C1, H2/C2, H3/C3, H4/C4, H5/C5, H6/C8, H7/C11, H8/C12, H9/C6, and H10/C9. Carbons 7, 10, 13, and 14 show no correlating peaks since they lack any directly attached protons and long range ^{1}H-^{13}C J coupling are too weak to be observed. Discrepancies existed between the proton/carbon connectivity derived from the COSY and HCCORR experiments and that previously assigned. Only the correlation of H5/C5 was in agreement in both assignments. Previously H8, H9, and H10 were correlated to C6, C12, and C11, respectively. No correlations were previously made for H6 and H7 since they were indistinguishable in the 1-D spectrum. Direct calculations of the chemical shift of carbons 13 and 14 could not be made for poly-NZ since the appropriate subsstituent chemical shift parameters for the naphthalene ring were not available. However, chemical shifts of 130.2 and 156.8 ppm were calculated for carbons 13 and 14 , respectively, assuming that the substituent parameters for substituted benzenes were applicable to substituted naphthalenes and the substitutents parameters for S-CH_3 and Ar-OCH_3 simulate those of S-CH_2 and Ar′-OCH_2 where Ar represents benzene and Ar′ represents naphthalene.[20] The observed chemical shift of carbons 13 and 14 were 134.7 and 154.9 ppm. There existed no significant difference between the observed and calculated chemical shift of carbon 14. Although the difference between the observed and calculated chemical shift for carbon 13 was only 4.5 ppm, the value calculated was intermediate between the assigned value of carbon 13 and a second quaternary carbon

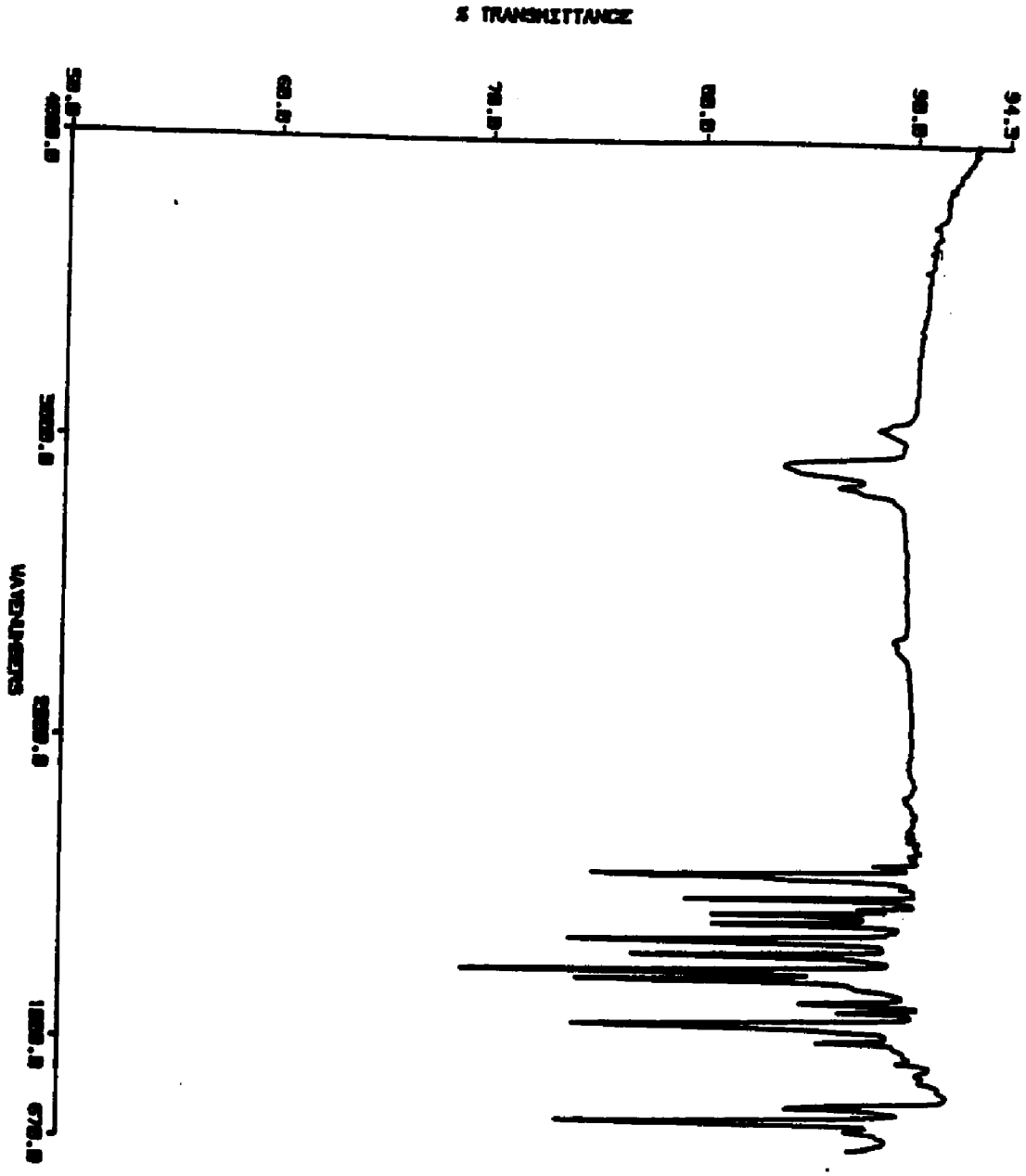


FIGURE 34
IR SPECTRUM OF POLY-NZ

at 126.5 ppm. The assignment of carbons 7, 10 and 13 were made arbitrarily and hence may be interchanged.

5.1.4.2 IR Spectroscopy of Poly-NZ: The IR spectrum of poly-NZ is shown in Figure 34. The assignments were in good agreement with the assignments made previously: 3060 (aromatic C-H), 2940, 2865 (aliphatic C-H), 1585, 1505 (aromatic C-C), 1265, 1080 (C-O-C), 810, 765 cm^{-1} (aromatic C-H). Additional absorption at 1454, 1424, 1365, 1319, and 1234 cm^{-1} were consistent with, CH_2, aromatic C-H, S-CH_2, and other moieties of structure XXIa.

5.1.5 *Characterization of Poly-β-BL*

Poly-β-BL was prepared by the cationic polymerization of β-butyrolactone at 60°C using boron trifluoride etherate as the initiator. The polymer structure of poly-β-BL has previously been characterized by several authors so no attempt was made to further characterized the structure.[28,29]

The spectra of poly-β-BL are shown as an equimolar mixture with poly-NZ in order that they may be compared with the spectra of the NZ/β-BL copolymer.

5.1.5.1 NMR Spectroscopy of a Equimolar Mixture of Poly-NZ/Poly-β BL: The mixture of poly-NZ/poly-β-BL was characterized by the use of ^1H and ^{13}C NMR, IR spectroscopy, and preparation and characterization of the respective homopolymers.

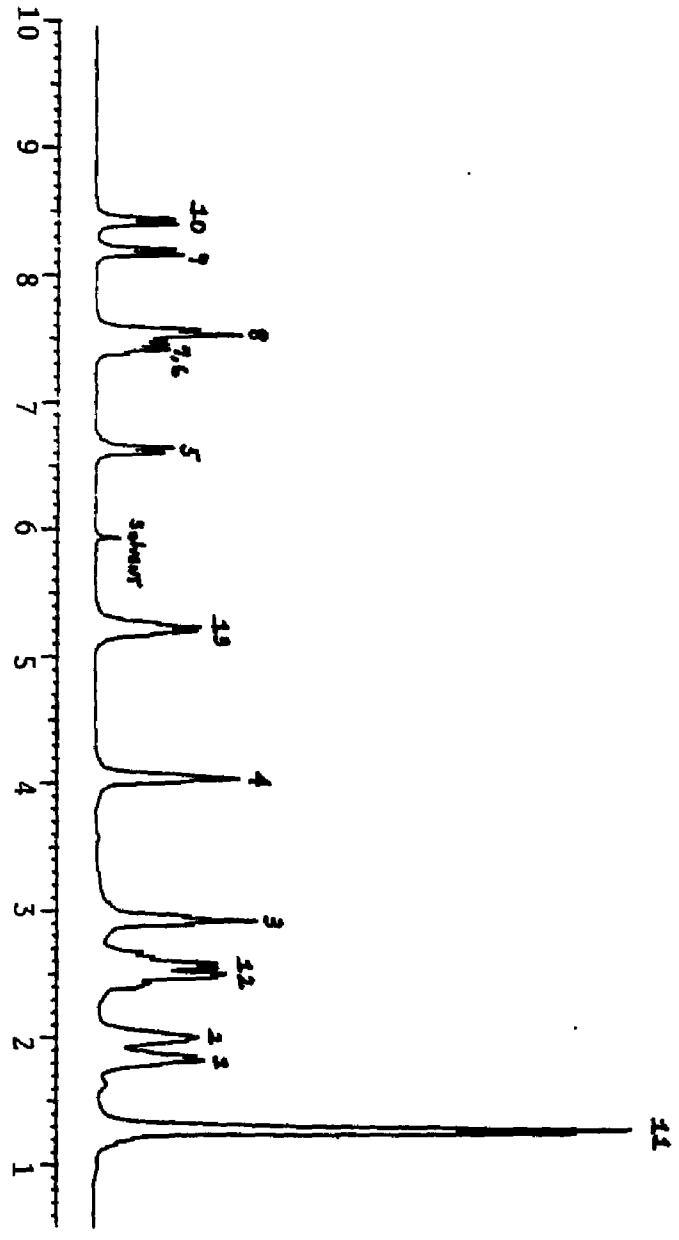


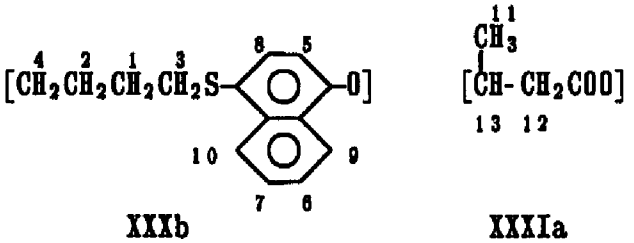
FIGURE 35
^{1}H SPECTRUM OF POLY-NZ/POLY-β-BL SYSTEM
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

TABLE 19

Assignments of the ^{1}H Spectrum of the Poly-NZ/Poly-β-BL System

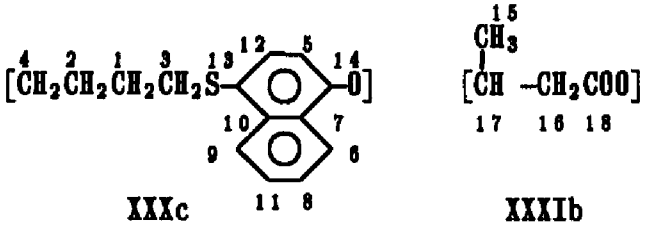
Proton Number	Chemical Shift (ppm)
1	1.86
2	1.99
3	2.93
4	4.05
5	6.62
6, 7	7.45
8	7.55
9	8.18
10	8.42
11	1.28
12	2.51
13	5.23

5.1.5.1.a Proton Assignments of Poly-NZ/Poly-β-BL: Figure 35 and Table 19 show the ^{1}H spectrum and δ values of a equimolar mixture of poly-NZ/poly-β-BL with the assignments listed in structures XXXb and XXXIa. The assignments of poly-NZ was based on the results obtained from Section 5.1.4.1.a and poly-β-BL from splitting patterns and signal areas.



XXXb XXXIa

5.1.5.1.b Carbon Assignments of Poly-NZ/Poly-β-BL: Figure 36 and Table 20 show the proton-decoupled ^{13}C spectrum and δ values of an equimola mixture of poly-NZ/poly-β-BL with the assignments listed in structures XXXc and XXXIb. The carbon assignments for poly-NZ was



XXXc XXXIb

discussed in Section 5.1.4.1.b and for poly-β-BL the assignments was based on the chemical shift of similar carbons.

5.1.5.2 IR Spectroscopy of Poly-NZ/Poly-β-BL Equimola Mixture:

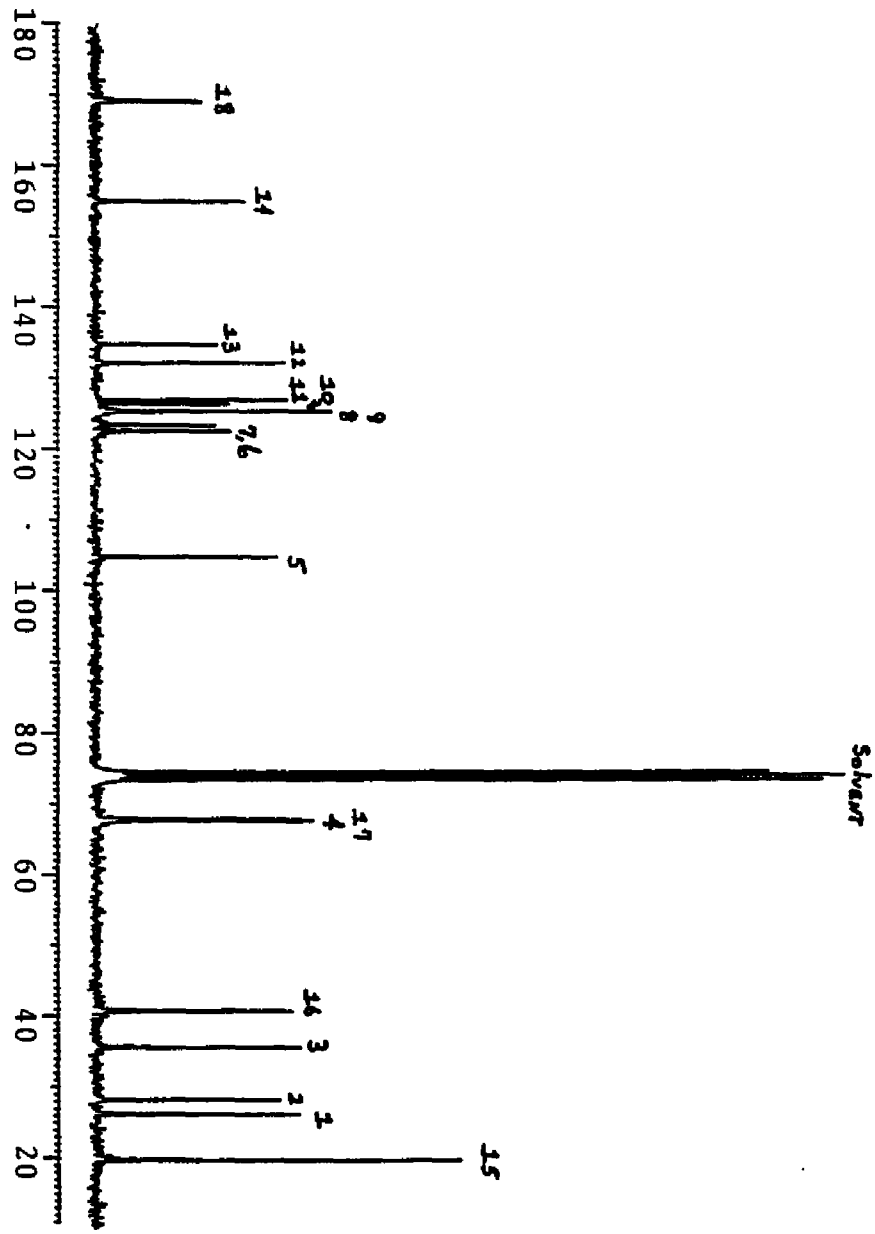


FIGURE 36
^{13}C SPECTRUM OF POLY-NZ/POLY-β-BL SYSTEM
1, 1, 2, 2-TETRACHLOROETHANE SOLVENT

TABLE 20

Assignments of the ^{13}C Spectrum of the Poly-NZ/Poly-β-BL System

Carbon Number	Chemical Shift (ppm)
1	26.2
2	28.2
3	35.6
4	67.6
5	104.8
6	122.6
7	123.5
8	125.3
9	125.4
10	126.4
11	127.0
12	132.1
13	134.7
14	154.9
15	19.7
16	40.8
17	67.8
18	169.0, 169.2

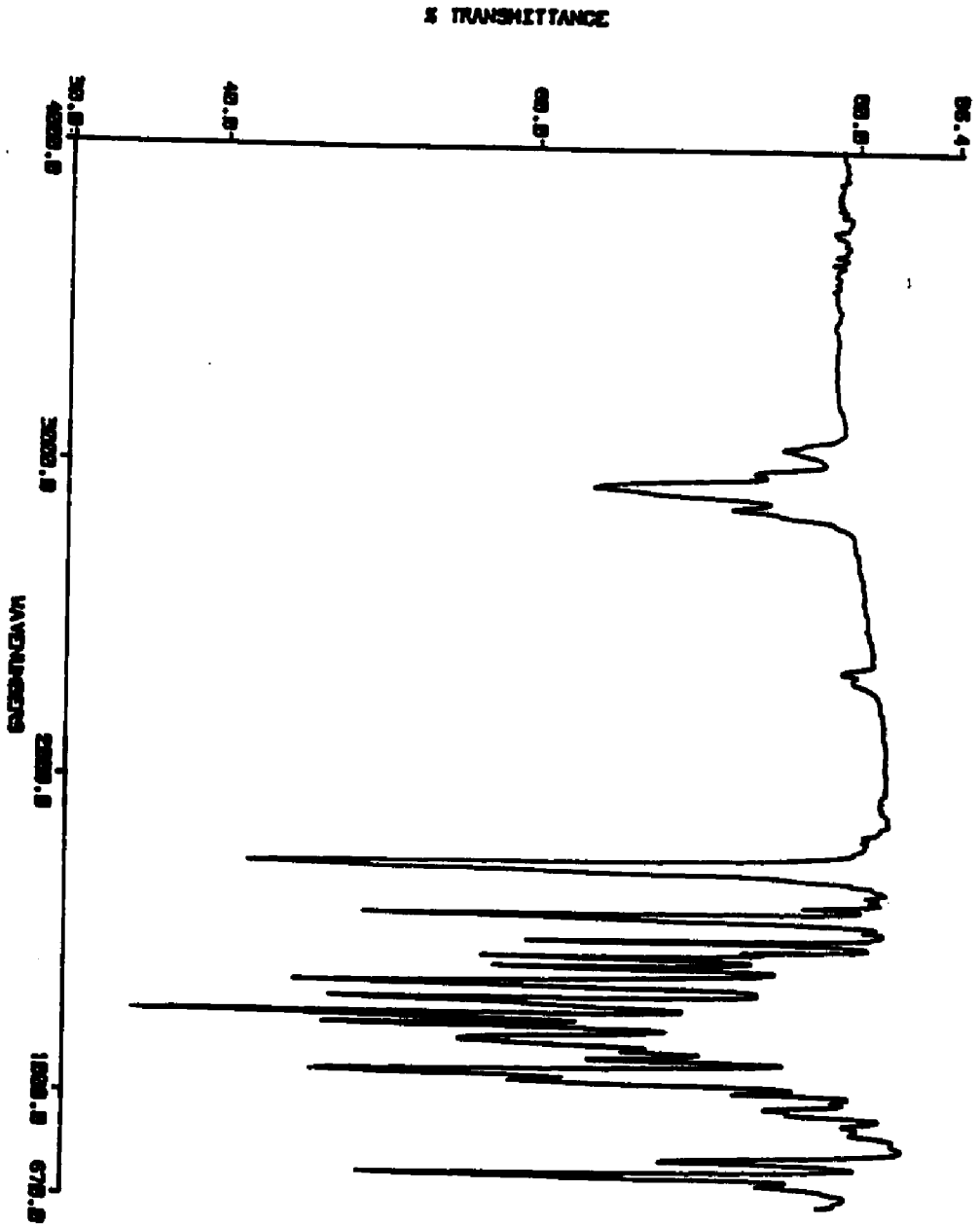
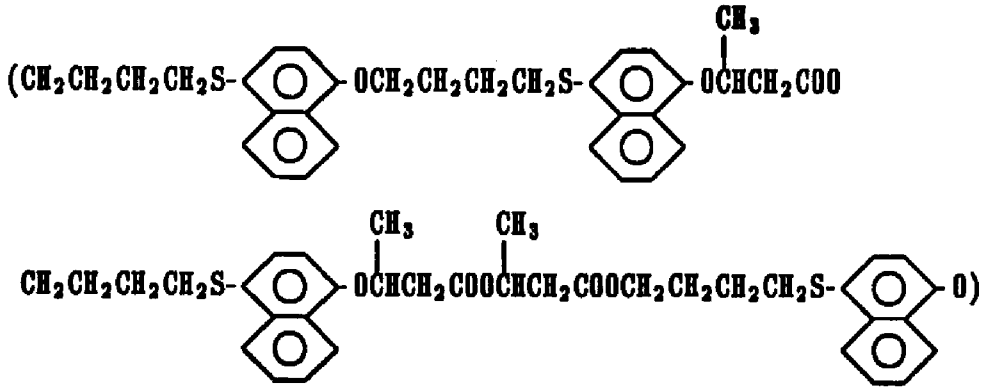


FIGURE 37
IR SPECTRUM OF POLY-NZ/POLY-β-BL SYSTEM

Figure 37 shows the IR spectrum of a molar mixture of poly-NZ/poly-β-BL. The assignment of the IR spectrum of poly-NZ was discussed in Section 5.1.4.2. The following assignments were made for this mixture: 3060 (aromatic C-H), 2962, 2940, 2922, 2862 (aliphatic C-H), 1730 (C=O), 1585, 1505 (aromatic C-C), 1265, 1080 (C-O-C), 1180 cm^{-1} (C-O), and 810 and 760 cm^{-1} (aromatic C-H). Additional absorptions at 1453, 1424, 1365, 1319, and 1235 cm^{-1} are consistent with CH_2, aromatic C-H, S-CH_2, and other moieties of the structures.

5.1.6. *Characterization of NZ/β-BL Copolymer*

The NZ/β-BL copolymer was characterized as structure XXIXa by ^1H and ^{13}C NMR, DEPT, and IR spectroscopy. The copolymer was found



XXIXa

to possess a random structure which was rich in NZ units.

5.1.6.1 NMR Spectroscopy of NZ/β-BL Copolymer:

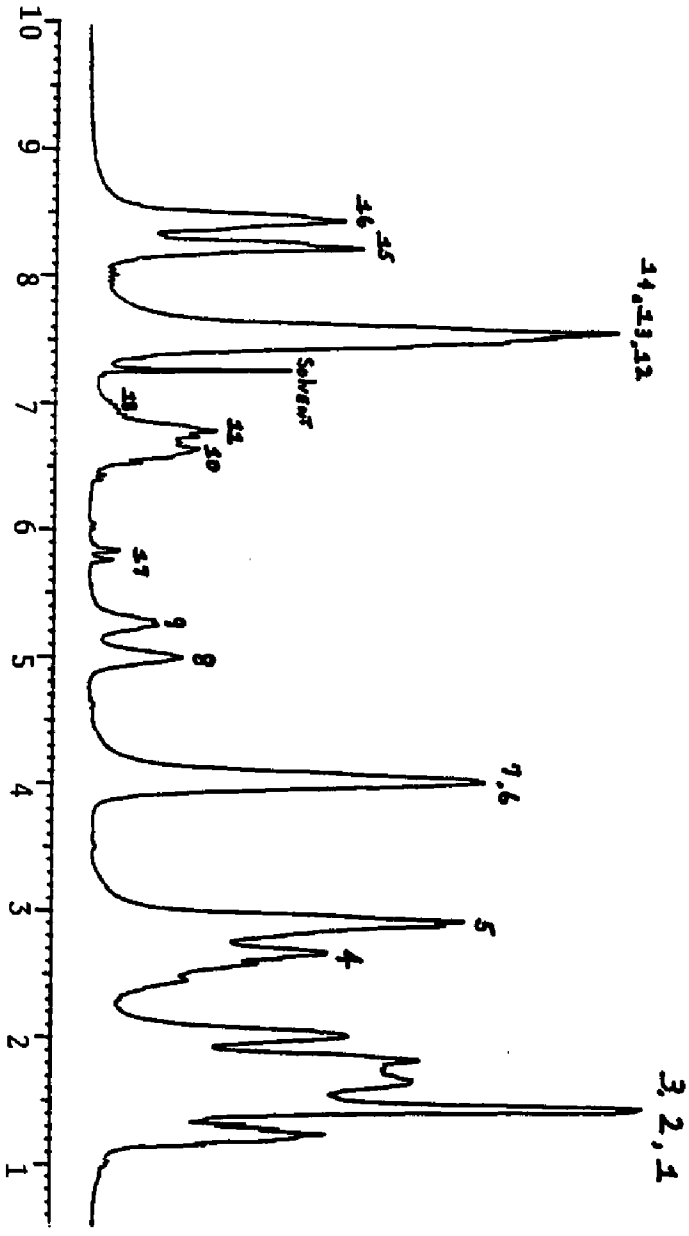


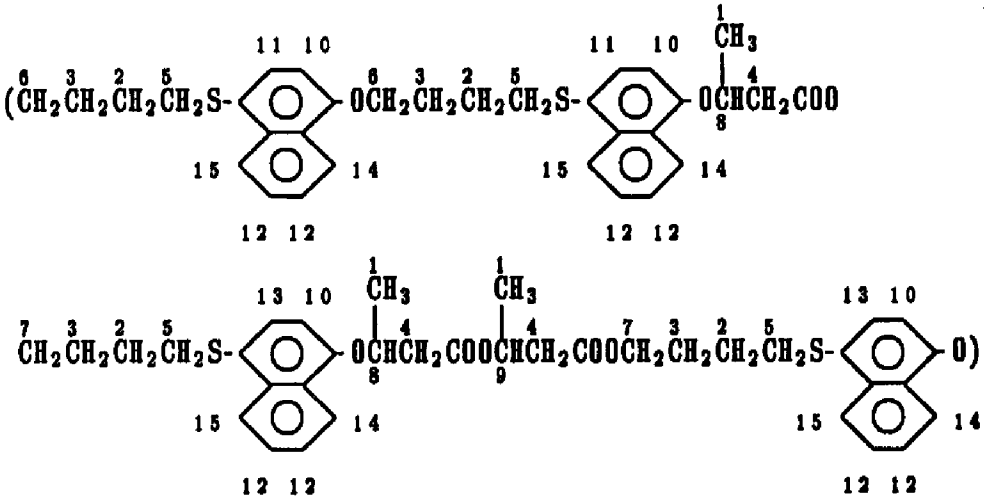
FIGURE 38
^{1}H SPECTRUM OF THE NZ/β-BL COPOLYMER
$CDCl_3$ SOLVENT

TABLE 21

Assignments of the ^{1}H Spectrum of the NZ/$\hat{\beta}$-BL Copolymer

Proton Number	Chemical Shift (ppm)
1, 2, 3	1.19, 1.30, 1.43 1.67, 1.80, 1.99
4	2.58
5	2.90
6, 7	4.00
8	4.97
9	5.23
10	6.60
11	6.77
12, 13	7.54
14	8.21
15	8.43

5.1.6.1.a Proton Assignments of the NZ/β-BL Copolymer: Figure 38 and Table 21 show the ^{1}H spectrum and δ values of the copolymer prepared at 100°C with the assignments listed in structure XXIXb. The copolymer was found to be random based upon comparison of the ^{1}H spectrum (Figure 35) of the molar mixture of poly-NZ/poly-β-BL. Due to the random nature of the copolymer the ^{1}H spectrum was quite



XXIXb

complicated in comparison to the ^{1}H spectrum of the mixture of the two homopolymers. The most obvious indication of the formation of a random copolymer was the presence of two signals, 8 and 9, between the region of 4.5 to 5.5 ppm. If the copolymer was indeed alternating then only one signal at 4.97 ppm (signal 8 from structure XXIXb) should be present. Signal 8 represents a methine proton adjacent to an aryl ether linkage, which is a copolymer linkage. The presence of a second siganl at 5.22 ppm (signal 9 from structure XXIXb) was assigned as a methine proton adjacent to an ester linkage, which is a

homopolymer linkage from poly-β-BL. The assignment of signal 9 was confirmed by comparison with the ^{1}H spectrum of poly-NZ/poly-β-BL (Figure 35) which shows the corresponding proton signal, 13, to occur at 5.23 ppm. Although signals 6 and 7 which represents the methylene protons adjacent to an aryl ether and ester linkage, respectively, were overlapping in Figure 38, a ^{1}H spectrum taken at 50°C in DMSO (d_6) shows a clear separation of the signals. Signals 10 and 11 were assigned as the naphthalene ring proton α to the phenoxide group. Signal 10 was γ to the methylene protons for the NZ homopolymer linkage and signal 11 was γ to the methine proton for a copolymer linkage. The assignment of 10 was based on the chemical shift of the corresponding proton in poly-NZ (proton 5) which appeared at 6.60 ppm in Figure 35. The region between 1.0 and 2.3 ppm was quite complicated (Figure 38) so no correlation was deduced between chemical shift and proton type. The formation of a block copolymer was ruled out due to the intensity of the junction signals. The most obvious junction signal belong to the methine proton adjacent to the aryl ether linkage (4.97 ppm). The intensity of this signal was on the same order of magnitude as the signal corresponding to the methine proton of successive β-BL moieties (5.32 ppm).

5.1.6.1.b Carbon Assignments of the NZ/β-BL Copolymer: The proton-decoupled ^{13}C spectrum (Figure 39, Table 22) of the NZ/β-BL copolymer supported structure XXIXa. The carbon signals were assigned as shown in structure XXIXc based on the results from DEPT (Figure 40, Table 23), chemical shift values of similar carbons, and the ^{13}C

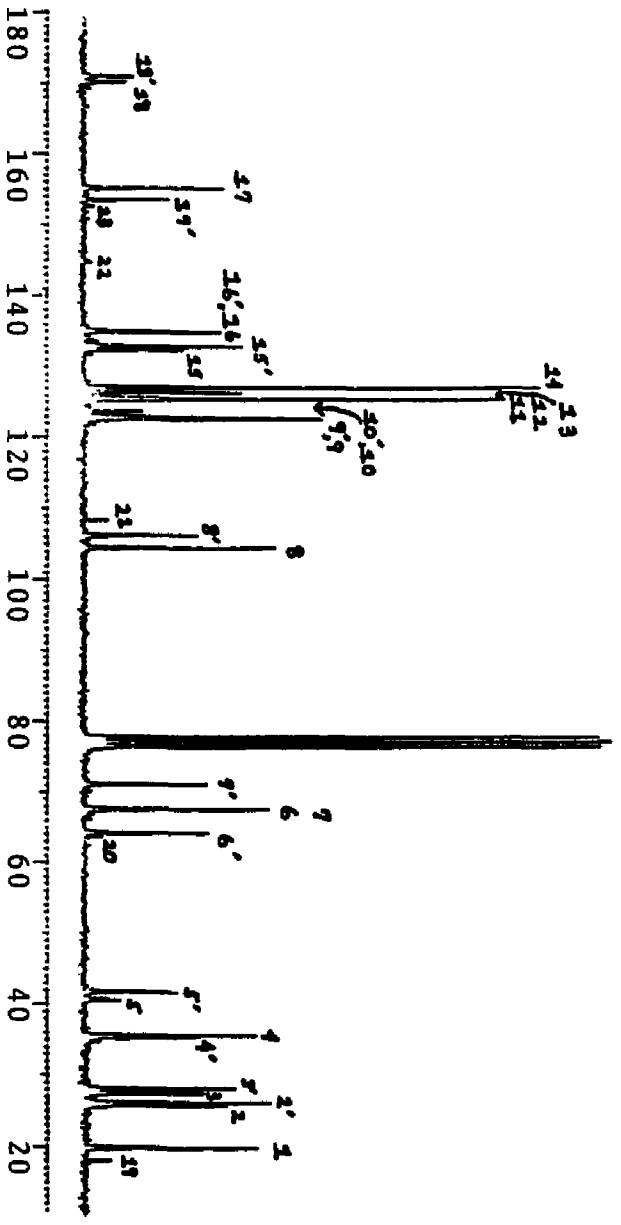


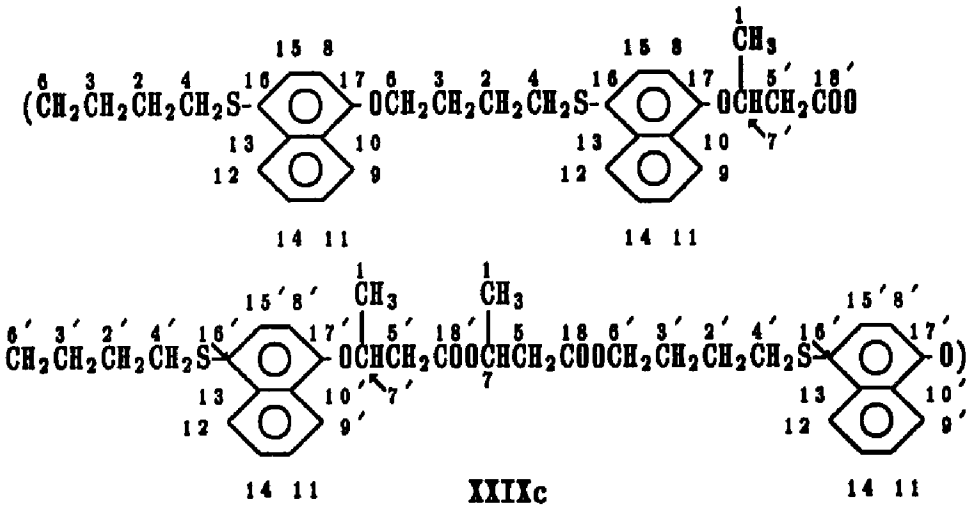
FIGURE 39
^{13}C SPECTRUM OF THE NZ/β-BL COPOLYMER
$CDCl_3$ SOLVENT

TABLE 22

Assignments of the ^{13}C Spectrum of the NZ/β-BL Copolymer

Carbon Number	Chemical Shift (ppm)
1	19.7
2, 2	25.7, 26.1
3, 3	27.4, 28.1
4, 4	35.3, 35.6
5, 5	40.6, 41.7
6	67.5
6	64.2
7	67.5
7	71.0
8	104.4
8	106.1
9, 9	122.6, 122.7
10, 10	122.9, 123.6
11	125.4
12	125.4
13	126.3
14	127.0
15, 15	132.2, 132.7
16, 16	134.8, 134.9
17, 17	153.4, 155.0
18, 18	170.0, 170.8

assignments of the poly-NZ/poly-β-BL mixture (Figure 36). The randomness of the copolymer was even more pronounced in the ^{13}C. There existed a multitude of signals in the ^{13}C spectrum of the copolymer. If the copolymer was alternating, only 18 signals should



XXIXc

appear; however there is in excess of 30 major signals present in the actual ^{13}C spectrum. A majority of the carbon signals showed some degree of splitting in response to the sensitivity of the carbons to different enviroments. The only carbons which showed no sensitivity to their environment were 1, 11, 12, 13, and 14. A case could be made for the lack of sensitivity of carbons 11 through 14 due to their distance in separation between different units. However the lack of sensitivity to its enviroment of carbon 1 was surprising since its enviroment is entirely different if it is proceeded by a NZ or β-BL unit.

The random copolymer is composed of four junction carbons: (1) methylene carbon adjacent to an aryl ether, 6, (successive NZ

moities), (2) methine carbon adjacent to an ester, 7, (successive β-BL moities), (3) methylene carbon adjacent to an ester, 6′, (copolymer linkage) and (4) methine carbon adjacent to an aryl ether, 7′, (copolymer linkage). The signals for these four junction linkages occur between 60 to 73 ppm in Figure 39. The possibility of a block copolymer was ruled out based on the signal intensities of the block junction linkages which would be the methylene carbon adjacent to an ester at 64.2 ppm (signal 6′ from structure XXIXc), and the methine carbon adjacent to an aryl ether at 71.1 ppm (signal 7′ from structure XXIXc). Signal 6′ was assigned by comparison of the chemical shift of the methylene carbon adjacent to an ester linkage in poly-β-propiolactone, which was at 60.4 ppm. Signal 7′ was assigned by the process of elimination since the assignment of the methine carbon adjacent to an ester, 7, and a methylene carbon adjacent to an aryl ether, 6, were readily assigned by comparison of the carbon assignments in the spectrum of the mixture of the two homopolymers (Figure 36). The overlapping of signals 6 and 7 was evident in the DEPT spectrum (Figure 40) of the copolymer in which the methine carbon, 7, gives a signal of positive intensity and the methylene carbon, 6, gives a signal of negative intensity at 67.7 and 67.5 ppm respectively. Also from the DEPT spectrum the assignment of the methyl carbon, 1, at 19.7 ppm, the four quaternary ring carbons, 10, 10′, 13, 16, 16′ and 17, 17′, at 122.9, 123.6, 126.3, 134.8, 134.9, 155.0, and 153.4 ppm, respectively, and the carbonyl carbon 18 and 18′ at 170.0 and 170.8 ppm. For certain aromatic carbon signals it was easy to differentiate between successive NZ units and a NZ moiety

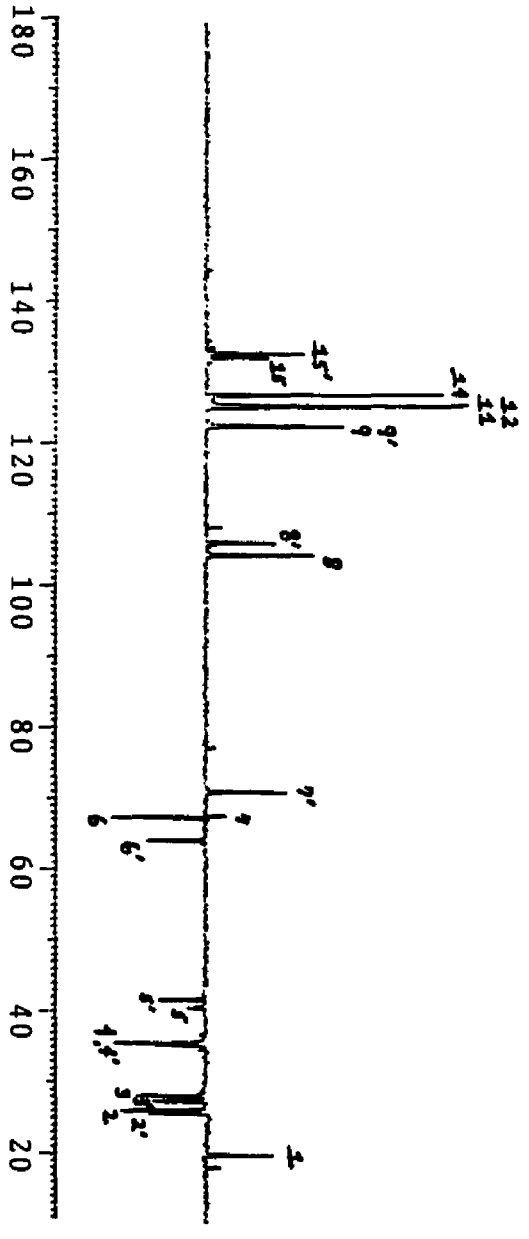


FIGURE 40
DEPT SPECTRUM OF THE NZ/β-BL COPOLYMER
CDCl₃ SOLVENT

TABLE 23

Assignments of the DEPT Spectrum of the NZ/β-BL Copolymer

Carbon Number	Chemical Shift (ppm)
1	19.7
2, 2	25.7, 26.1
3, 3	27.4, 28.1
4, 4	35.3, 35.6
5, 5	40.8, 41.7
6	64.2
6	67.5
7	67.7
7	71.0
8	104.4
8	106.1
9, 9	122.6, 122.7
11	125.5
12	125.7
14	127.1
15, 15	132.3, 132.8

followed by a β-BL moiety by comparison with the ^{13}C of the homopolymer mixture (Figure 36) The most obvious signals corresponding to successive NZ moieties occurred at 104.4, and 155.0 ppm for carbons 8 and 17 which indicates that the signals at 106.1 and 153.4, 8′ and 17′ respectively, corresponds to a NZ unit followed by a β-BL moiety. Signal 5 at 40.6 ppm was assigned to the methylene carbon from the β-BL moiety based upon the chemical shift of the corresponding carbon from poly-β-BL, carbon 16, in Figure 36 which was 40.8 ppm. The assignment of the remaining carbons were based on the chemical shifts of the corresponding homopolymers. The number assignments of each carbon and its prime were made arbitrarily and may be interchanged unless other wise stated.

5.1.6.2 IR Spectroscopy of the NZ/β-BL Copolymer: There existed some obvious differences between the IR spectrum of poly-NZ/poly-β-BL (Figure 37) and that of the copolymer (Figure 41); there were new signals at 3300 which was due to the phenol end group, and 1678 and 1663 cm^{-1} which were assigned to the olefinic bond in conjugation with a carbonyl group. The absorptions in the 1660 to 1680 cm^{-1} region was also seen for ethyl crotonate which has a similar structure. The remaining assignments were based on the assignments made for the IR spectrum of poly-NZ/poly-β-BL (Section 5.1.5.3): 3056 (aromatic C-H), 2933, 2872 (aliphatic C-H), 1732 (C=O), 1585, and 1505 (aromatic C-C) 1184 (C-O), and 814 and 765 cm^{-1} (aromatic C-H).

5.1.7 *Polymerization Mechanism of the NZ/β-BL Copolymer*

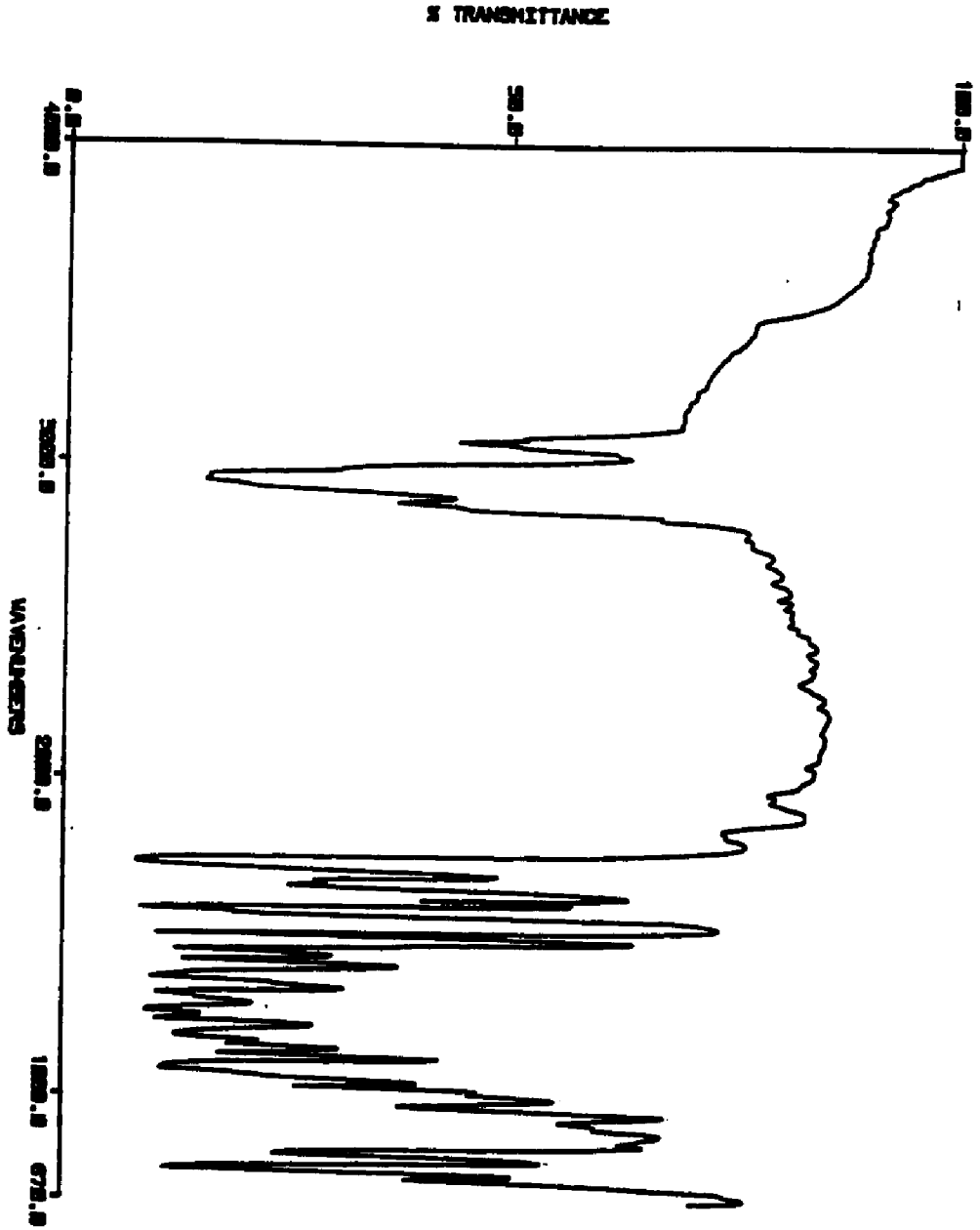
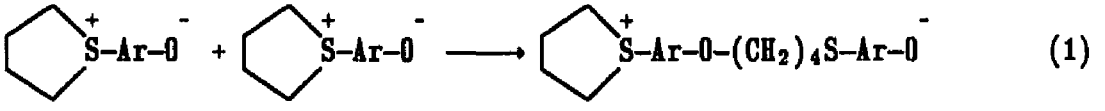
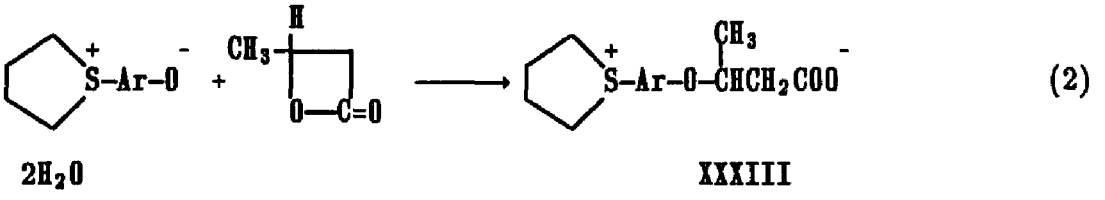


FIGURE 41
IR SPECTRUM OF THE NZ/β-BL COPOLYMER

NZ and β-BL polymerizes thermally by means of zwitterion formation to form a random copolymer somewhat richer in the NZ monomer than β-BL. Polymerization is initiated by a ring-opening nucleophilic attack of the arene oxide end of one NZ zwitterion, where Ar represents a naphthalene group, on either the α-carbon of the tetrahydrothiophenium ring of a second molecule of the NZ zwitterion to form the NZ homo-dimer (Eq (1) structure XXXII) or on the β-carbon of the β-BL to form a co-dimer (Eq (2) structure XXXIII). Both path ways are demonstrated in Scheme XV. Polymerization proceeds either by

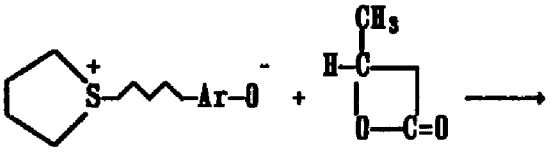
Scheme XV:



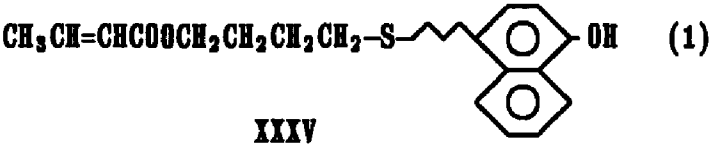


the NZ homo-dimer reacting with a second molecule of NZ homo-dimer, a co-dimer, a NZ zwitterion, or β-BL monomer or the co-dimer reacting with a second molecule of co-dimer, NZ homo-dimer, a NZ zwitterion, or β-BL monomer to form a random copolymer. The nucleophilic end of both the homo- and co-dimer favor reaction with the tetrahydrothiophenium end of either the propagating specie or the NZ monomer over the β-BL monomer as evident by formation of a copolymer structure rich in NZ

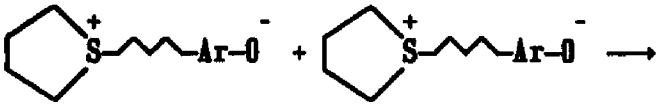
units. Termination occurs by a chain transfer mechanism. The possibility exists for the termination reaction to occur by four different routes: 1) the phenoxide end of the macrozwitterion (XXXIV) abstracts a H^+ from either the α-carbon of the β-BL monomer (Eq 1 Scheme XVI) or 2) from the β carbon of the tetrahydrothiophenium ring (Eq 2 Scheme XVI) to form olefinic and naphtholic end groups of structures XXXV and XXXVI, respectively; 3) the carboxylic end of the macrozwitterion (XXXVII), abstracts a H^+ from either the α-carbon of the β-BL monomer (Eq 3 Scheme XVI) or 4) from the β carbon of the tetrahydrothiophenium ring (Eq 4 Scheme XVI) to form olefinic and acid end groups structures XXXVIII and XXXIX, respectively where ~~ represents the polymer backbone and Ar represents the naphthalene ring, as shown in Scheme XVI. For eq 2 and 4 termination occurs Scheme XVI:



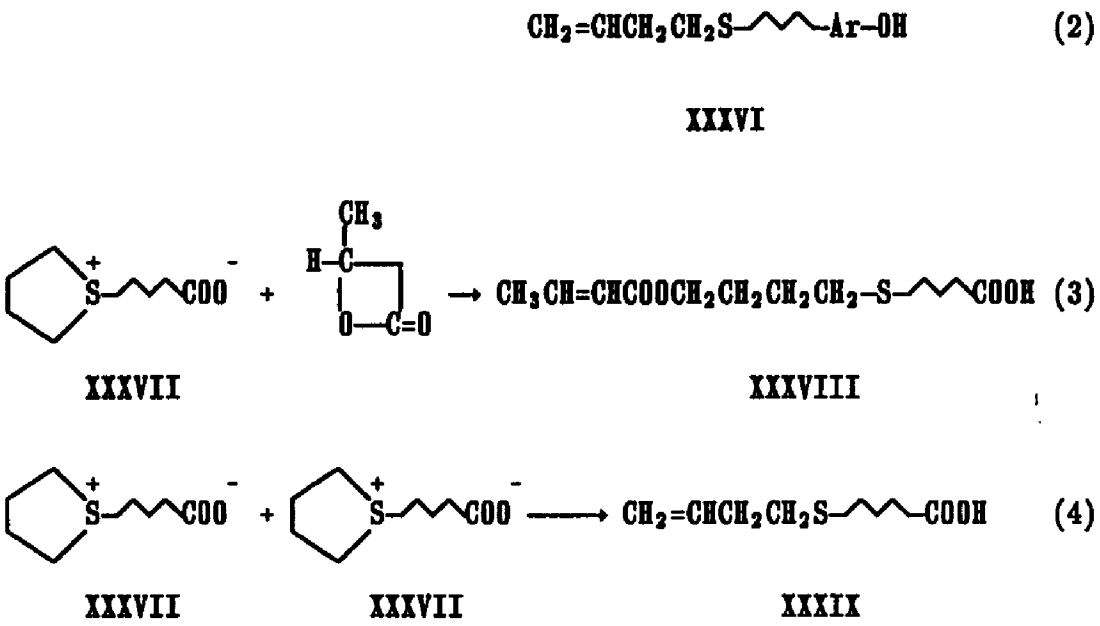
XXXIV



XXXV (1)



XXXIV XXXIV



independently of the nucleophilic group on the macrozwitterion so one molecule of structure XXXVII may be substituted into Eq 1 and one molecule of structure XXXIV into Eq 4. For reaction temperatures below 100°C termination by routes 2 and 4 are believed to be insignificant since for the homopolymerization of the NZ monomer termination by elimination is not present until the reaction exceeds 100°C.[14]

5.1.8 *Polymer End Groups*

The copolymer end groups were determined by the use of ^{1}H and ^{13}C NMR, IR spectroscopy, and the preparation and characterization of a model compound, 1-(tetramethylenethio)-4-naphthol β-methyl acrylate.

5.1.8.1 Preparation of 1-(tetramethylenethio)-4-naphthol β-methyl acrylate: The vinyl naphthol model compound was prepared in order to

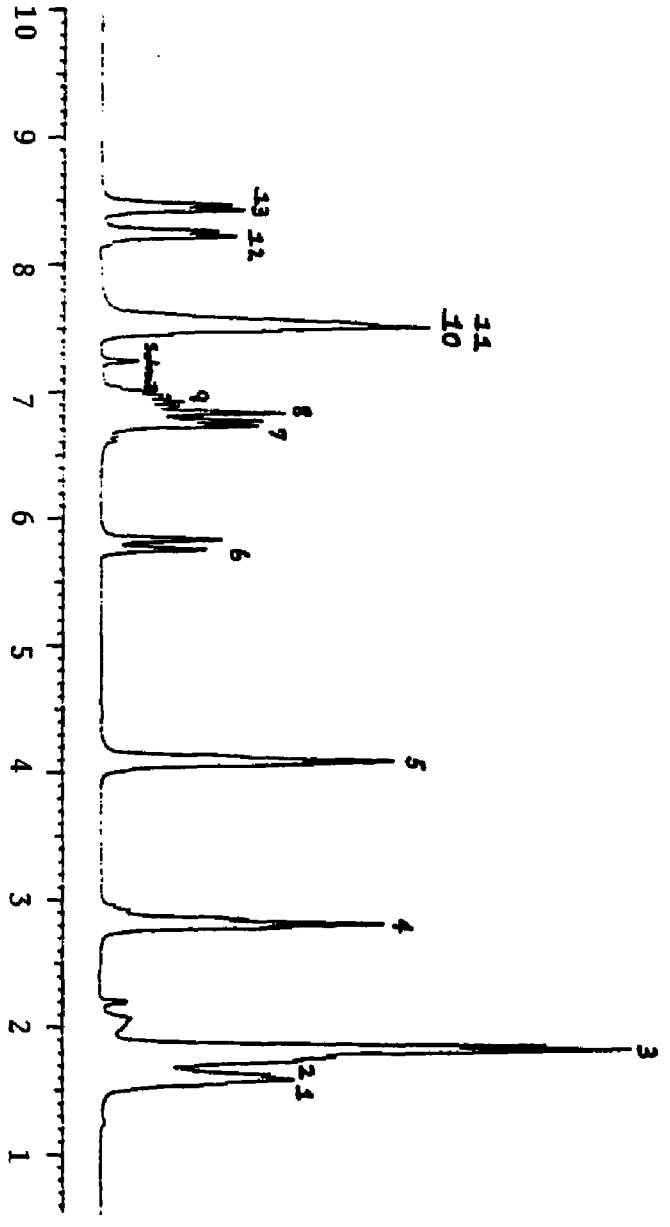


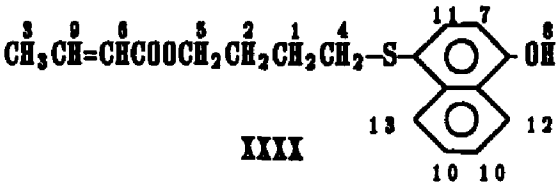
FIGURE 42
^{1}H SPECTRUM OF VINYL NAPHTHOL COMPOUND
$CDCL_3$ SOLVENT

TABLE 24

Assignments of the ^{1}H Spectrum of the Vinyl Naphthol Compound

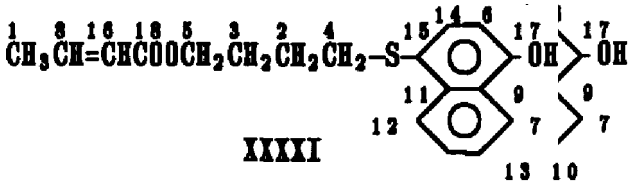
Proton Number	Chemical Shift (ppm)
1	1.61
2	1.75
3	1.83
4	2.82
5	4.10
6	5.80
7	6.75
8	6.85
9	6.95
10	7.46
11	7.54
12	8.25
13	8.46

aid in the assignment of the end group signals. The ^1H spectrum (Figure 42, Table 24) of the vinyl naphthol compound supported structure XXXI with the proton assignments listed in the structure.



XXXI

The purification of the vinyl naphthol compound was not 100% effective as can be seen in the ^1H NMR spectrum (Figure 42). A trace of possibly cyclic NZ is present. The purity is greater than 85%, however, and the effect of the vinyl group is seen in signals centered at 5.80 and 6.95 ppm. The naphtholic proton is seen as a singlet at 6.85 ppm. The ^{13}C spectrum (Figure 43, Table 25) of the vinyl naphthol compound is also consistent with the expected structure and the assignments are shown in structure XXXXI.



XXXXI

5.1.8.2 Bromination of 1-(tetramethylenethio)-4-naphthol β-methyl acrylate: The vinyl naphthol was treated with bromine in order to determine the chemical shift of the formed vicinal dibromide protons. Bromine was added until the solution retained the red color. The ^1H spectrum of this sampled revealed that the proton α to the aryl ether

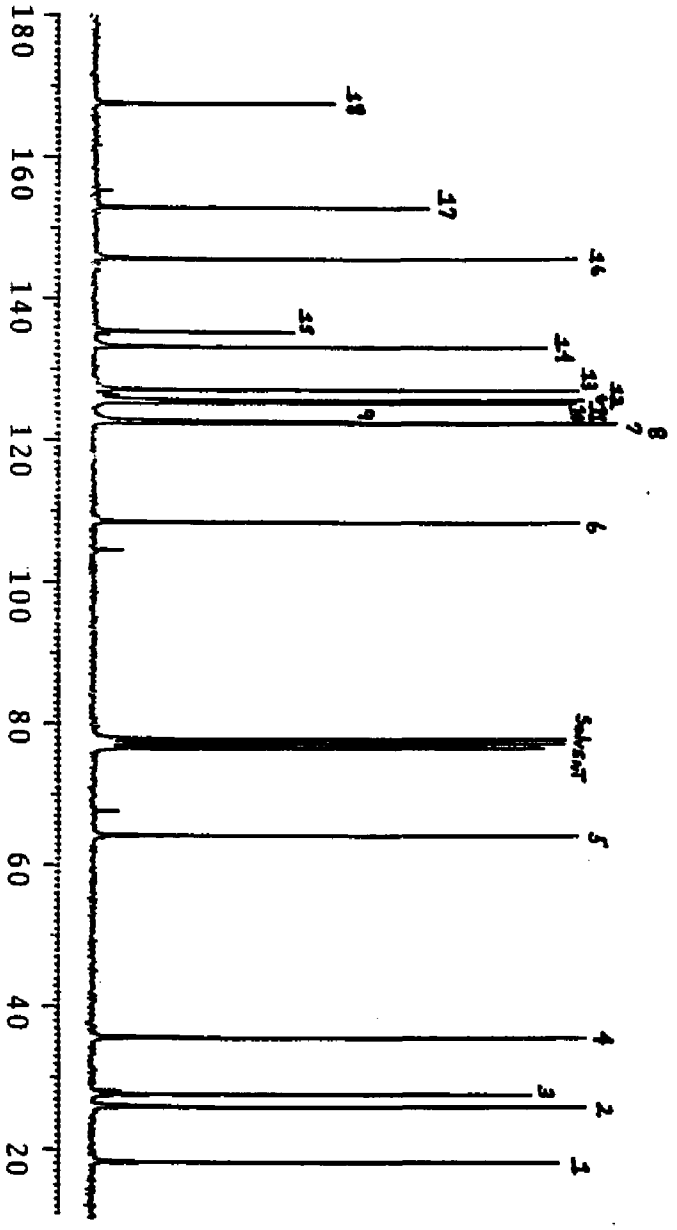


FIGURE 43
^{13}C SPECTRUM OF VINYL NAPHTHOL COMPOUND
$CDCL_3$ SOLVENT

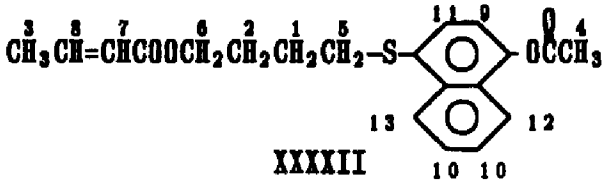
TABLE 25

Assignments of the ^{13}C Spectrum of the Vinyl Naphthol Compound

Carbon Number	Chemical Shift (ppm)
1	18.0
2	25.8
3	27.5
4	35.5
5	64.0
6	108.3
7	122.4
8	122.5
9	122.7
10	125.2
11	125.3
12	125.6
13	127.0
14	133.0
15	135.2
16	145.4
17	152.6
18	167.3

in the naphthalene ring underwent complete substitution with the bromine as indicated by the disappearance of its corresponding proton signal (proton 7 in structure XXXX) and the presence of a singlet for proton 11 in structure XXXX.

5.1.8.3 Acetylation of 1-(tetramethylenethio)-4-naphthol β-methyl acrylate: The vinyl naphthol compound was acetylated in order to confirm the presence of a naphthol end group. The acetylated vinyl naphthol compound was not purified 100% effectively as can be seen in the ^{1}H NMR spectrum (Figure 44, Table 26), however, the effect of the acetyl group is clearly evident. The ^{1}H spectrum of the acetylated vinyl naphthol compound supports structure XXXXII. The methyl protons from the acetyl group appears as a singlet at 2.46 ppm. The



XXXXII

naphthalene proton *a* to the acetyl group (9) shift further downfield to 7.19 ppm and proton 12 shifted further upfield to 7.89 ppm in comparison to the analogous protons in the vinyl naphthol model compound (Figure 42). The naphthol proton signal at 6.85 ppm in the vinyl naphthol model compound is absent in the acetylated vinyl naphthol compound ^{1}H spectrum. The ^{13}C spectrum and δ values of the acetylated vinyl naphthol compound, shown in Figure 45 and Table 27, is supportive of structure XXXXIII with the carbon assignments listed

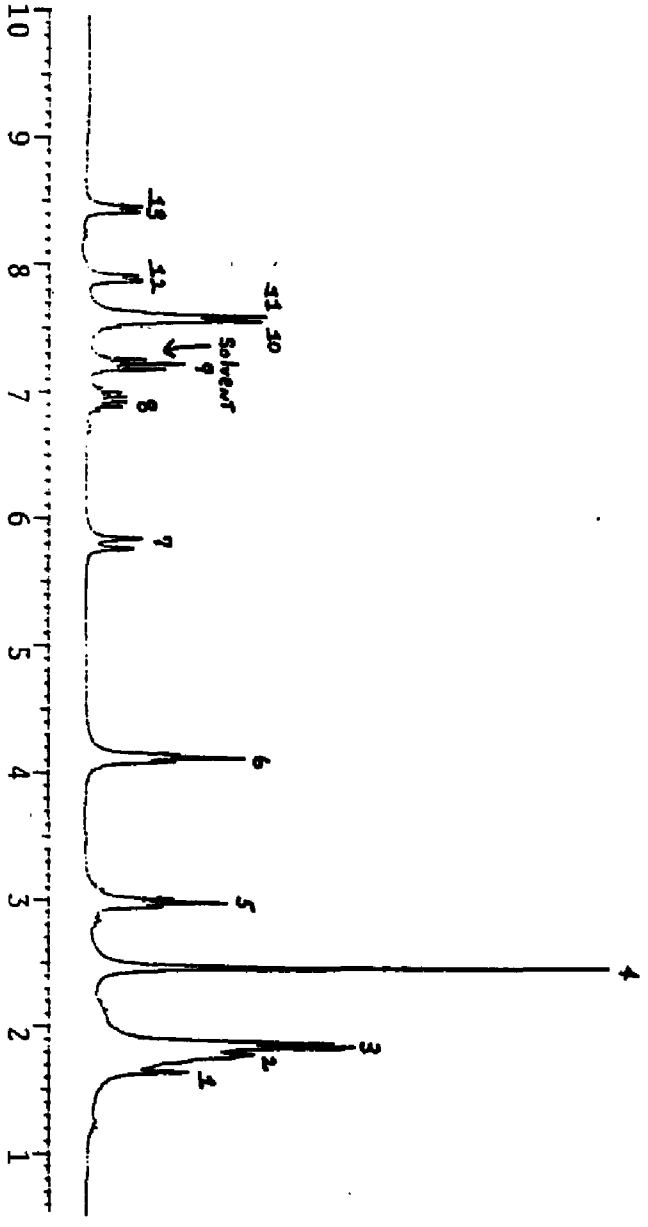


FIGURE 44
^{1}H SPECTRUM OF ACETYLATED VINYL NAPHTHOL COMPOUND
$CDCL_3$ SOLVENT

TABLE 26

Assignments of the ^{1}H Spectrum of the Acetylated Vinyl Naphthol Compound

Proton Number	Chemical Shift (ppm)
1, 2	1.78
3	1.84
4	2.46
5	2.87
6	4.12
7	5.80
8	6.91
9	7.19
10	7.56
11	7.58
12	7.89
13	8.44

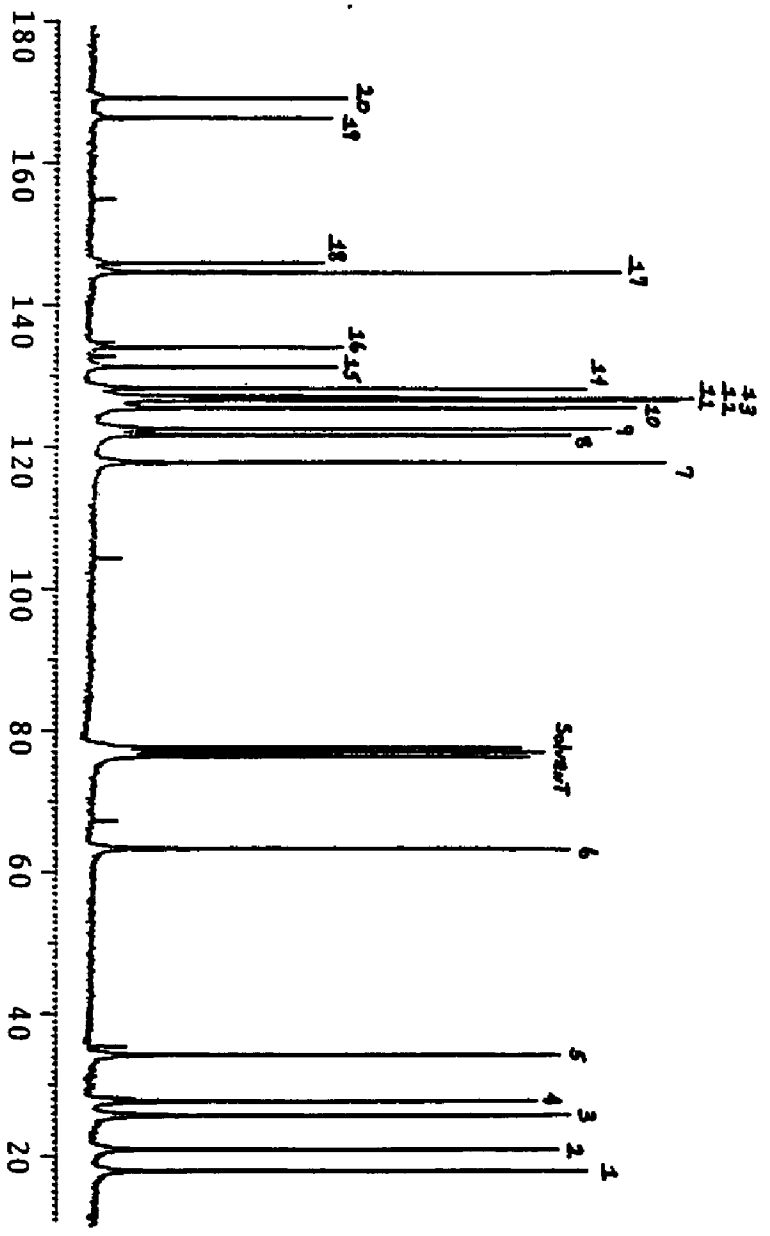


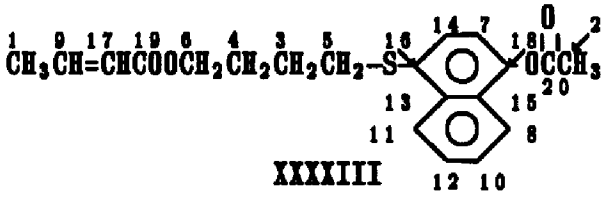
FIGURE 45
^{13}C SPECTRUM OF ACETYLATED VINYL NAPHTHOL COMPOUND
$CDCL_3$ SOLVENT

TABLE 27

Assignments of the ^{13}C Spectrum of the Acetylated Vinyl Naphthol Compound

Carbon Number	Chemical Shift (ppm)
1	17.7
2	20.8
3	25.5
4	27.6
5	34.1
6	63.3
7	117.7
8	121.6
9	122.4
10	125.4
11	126.5
12	126.7
13	127.1
14	128.1
15	131.1
16	133.9
17	144.5
18	145.8
19	166.3
20	169.1

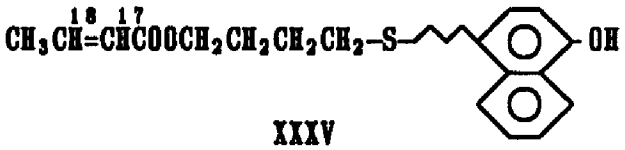
on the structure. The signal at 20.8 ppm belongs to the methyl



XXXIII

carbon, 1, of the acetyl group and the acetyl carbonyl, 20, appears at 169.1 ppm.

5.1.8.4 Characterization of the Copolymer End Groups by NMR Spectroscopy: Both the ^{1}H and ^{13}C NMR spectra provided evidence that the predominant termination mechanism was route 1 (see Section 5.1.7 Scheme XVI) to form a polymer with olefinic and naphtholic end groups as shown in structure XXXV. The olefinic end group signals were



XXXV

clearly visible in the ^{1}H spectrum of the copolymer (Figure 38) as a doublet at 5.75 and 5.83 ppm and a multiplet seen as a shoulder centered at approximately 6.95 ppm. No signal for the naphtholic proton was visible in the ^{1}H spectrum of the copolymer. It is believed that the naphtholic proton is hidden under the signals at approximately 6.7 ppm. Termination by routes 2 and 4 to form structures XXXVI and XXXIX is difficult to prove since their corresponding olefinic protons occur in the region of 5.0 ppm where

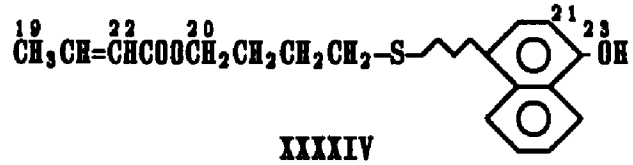
the proton signals for a methine adjacent to an ester and methine adjacent to an aryl ether occurs. No evidence existed in either the ^{1}H, ^{13}C, or IR spectrum for the presence of carboxylic

XXXVI XXXIX

acid end groups either. The assignment of the doublet at 5.75 and 5.83 ppm and the multiplet at 6.95 ppm as olefinic protons, as shown in structure XXXV, was confirmed by the addition of bromine to the sample. Initially the naphthalene ring underwent bromination at a rate substantially quicker than the addition to the double bond. The bromination reaction occurred to a large extent at the position α to the aryl ether. The slow addition of bromine to the double bond is not surprising since the presence of the carbonyl group lowers the reactivity of the carbon-carbon double bond toward electrophilic addition.[30] There was a large decrease in the intensity of the doublet at 5.75 and 5.83 ppm. No new signals were detected for the vicinal dibromide protons in the ^{1}H spectrum. Normally vicinal dibromide protons occur in the region between 4.1 and 4.4 ppm so it may be hidden under a signal for the copolymer in this region. The chemical shift of the olefinic protons in the copolymer is in good agreement with the assigned value of the analogous protons in the vinyl naphthol model compound (Section 5.1.8.3).

The ^{13}C spectrum of the copolymer (Figure 39) contains several

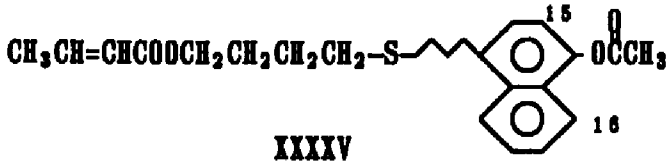
small signals which were attributed to the presence of olefinic and naphtholic end groups as shown in structure XXXXIV. Carbon signals at



XXXXIV

17.9, 63.7, 108.3, 144.6 and 152.6 ppm were assigned to carbons 19, 20, 21, 22, and 23 respectively.

The presence of naphtholic end groups were confirmed by acetylation of the copolymer. The ^{1}H spectrum of the acetylated copolymer (Figure 46) showed new signals centered at 7.16 and 7.87 ppm; the signals were assigned to protons 15 and 16, respectively, in structure XXXXV based on the chemical shift of the analogous protons of the acetylated vinyl naphthol compound (Section 5.1.8.3). The ^{13}C spectrum of the



XXXXV

acetylated copolymer (Figure 47) contained several new signals at 21.0, 117.8, 121.7, 126.7, and 128.4, ppm which were assigned to carbons 24, 25, 26, 27, and 28, respectively, as shown in structure XXXXVI based on the chemical shifts of the analogous carbons in the acetylated vinyl naphthol model compound (Section 5.1.8.3).

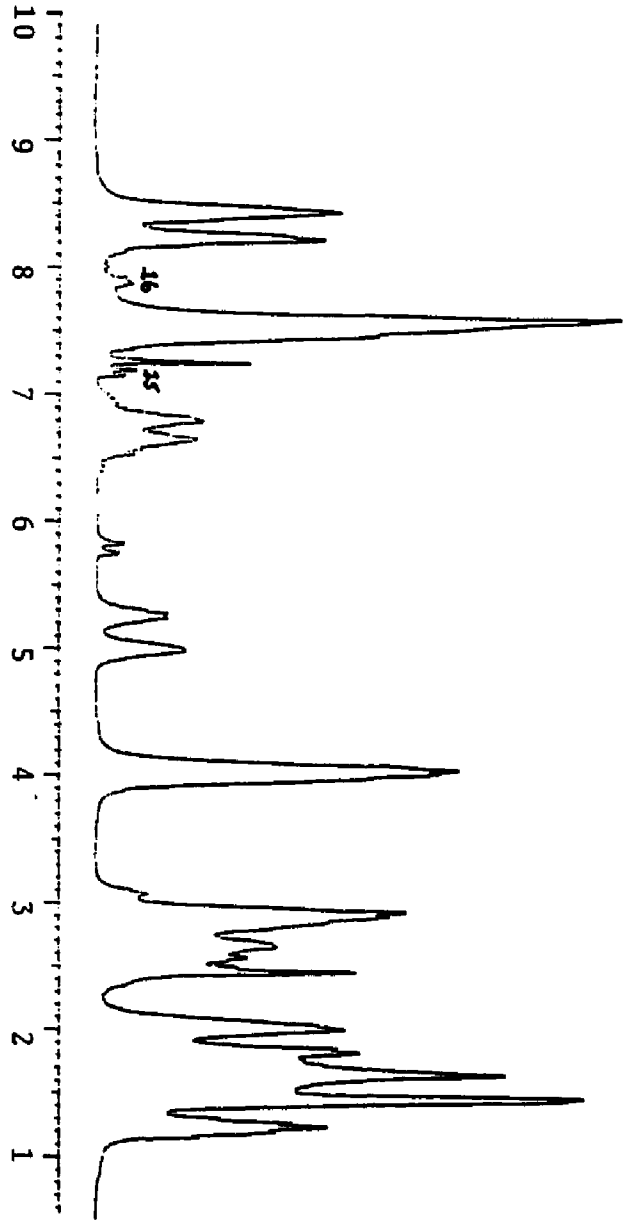


FIGURE 46
^{1}H SPECTRUM OF ACETYLATED NZ/β-BL COPOLYMER
$CDCL_3$ SOLVENT

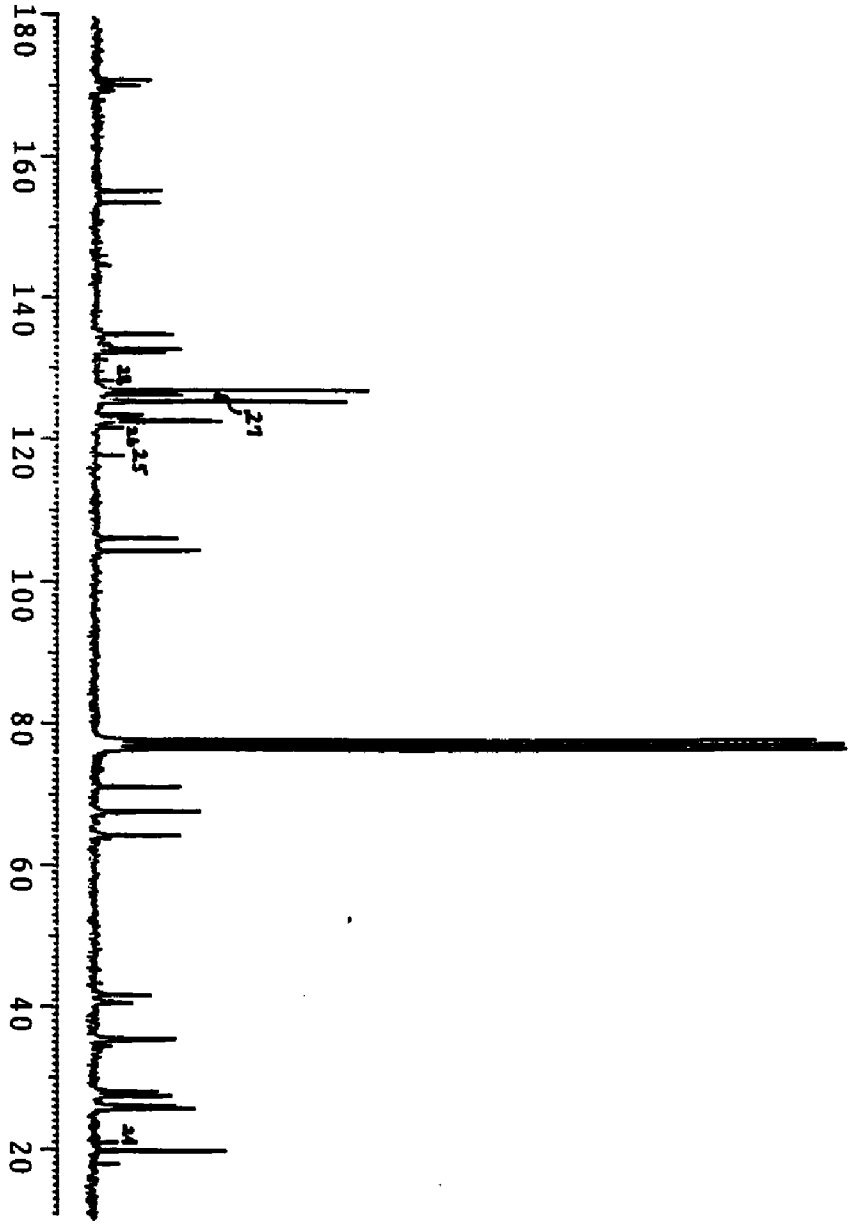
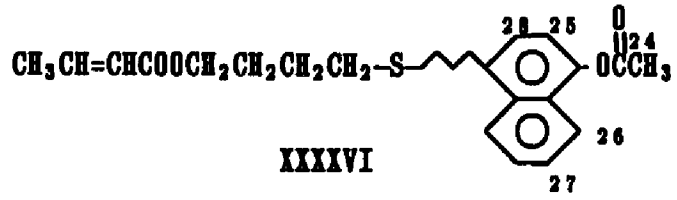


FIGURE 47
^{13}C SPECTRUM OF ACETYLATED NZ/β-BL COPOLYMER-
$CDCL_3$ SOLVENT



XXXVI

5.1.9 *Effect of Temperature on Polymerization*

Table 16 in Section 5.1.3 shows the number average molecular weights of the copolymer as determined by GPC analysis by the use of polystyrene as the standard. A typical GPC chromatogram is shown in Figure 48. The tail end of the chromatogram is hidden under a peak which is due to the presence of LiBr in the solvent (DMF). The molecular weight of the copolymer was found to be low, not exceeding more than 4000 in any of the investigated samples.

No correlation was observed between the copolymer structure and the reaction temperature as indicated by the results shown in Table 16. In all instances, the copolymer was rich in NZ units. The ratio of NZ/β-BL units contained in the copolymer was determined by comparison of the integral value for the methylene proton adjacent to an aryl ether and an ester linkage (protons 6 and 7 in structure XXIXb) at 4.00 ppm to that of the methine protons (protons 8 and 9 in structure XXIXb) at 4.97 and 5.23 ppm, respectively. The relative amounts of homopolymer linkages and copolymer linkages involving the β-BL moiety was also determined for the copolymer by comparison of the integral values of the two methine signals at 4.97 and 5.23 ppm for the copolymer and homopolymer linkages, respectively. In each instance the copolymer contained a higher percentage of copolymer linkages than homopolymer linkages as demonstrated by the results

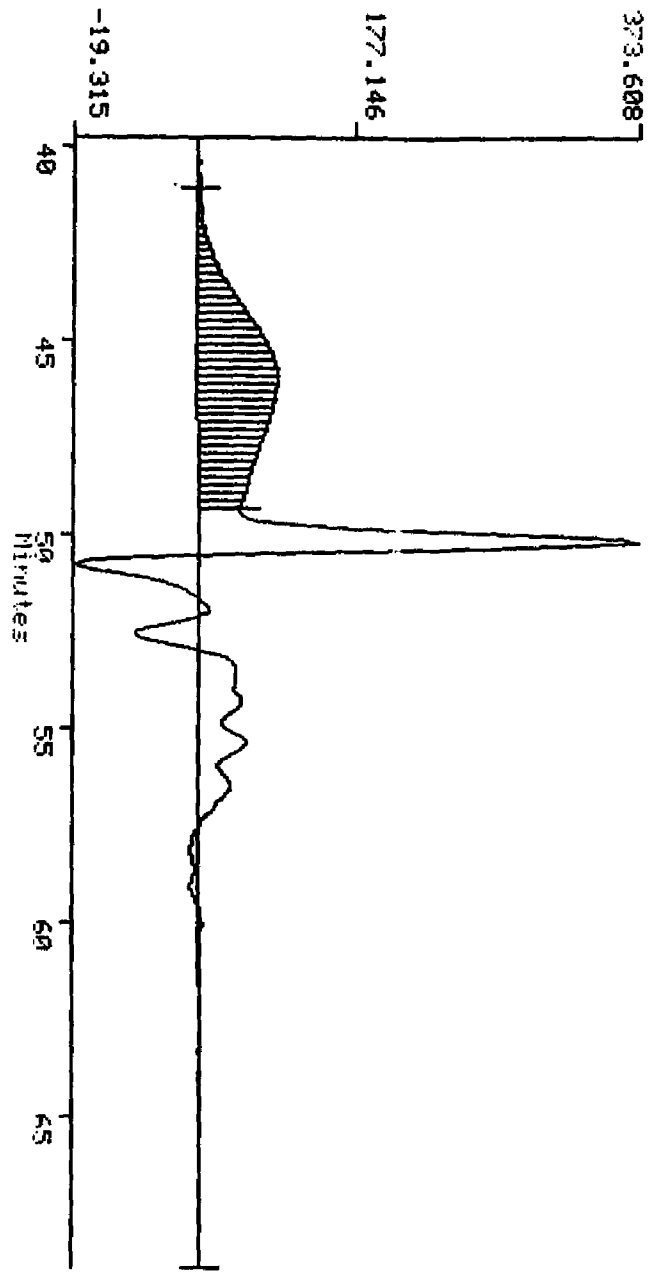


FIGURE 48
GPC CHROMATOGRAM OF THE NZ/ø -BL COPOLYMER

shown in Table 16. No attempt was made to determine the relative percentages of copolymer linkages to homopolymer linkages for the NZ moiety due to the lack of two discernible baseline resolved signals.

The formation of a random copolymer instead of an alternating copolymer may be explained by two facts. First, the generated nucleophilic end of the zwitterion (either a phenoxide or a carboxylic anion) may react with one of the two electrophilic specie present in excess in the reaction mixture (thiophenium ring or β-BL monomer). Second, the β-BL monomer is known to undergo hydrolysis when heated in the presence of water to form β, β'-oxydibutyric acid.[31] This compound was never isolated in this reaction system since only the methanol insoluble fraction of the reaction mixture was investigated. By the β-BL monomer reacting with the water, the system would no longer contain a stoichiometric molar equivalent of the two monomers. The NZ monomer would be present in excess in the reaction system, hence possibly explaining why the copolymer is rich in NZ units. The presence of water in this system is unavoidable since the NZ monomer is isolated as a dihydrate and attempts to remove the water of hydration has resulted in polymerization of the NZ zwitterion.[14]

6.0 CONCLUSION II

The copolymerization of tetrahydro-1-(4-hydroxy-1-naphthyl)-thiophenium hydroxide inner salt (NZ zwitterion) with β-butyrolactone (β-BL) resulted in the formation of a random copolymer rich in the NZ moiety. The copolymerization was conducted in solution (N, N-dimethyl-formamide) over a temperature range varying from 35 to 100°C. The copolymer structure was characterized by the use of ^{1}H and ^{13}C NMR, a Spectral Editing Technique (DEPT), IR spectroscopy, and the preparation and characterization of the monomers and the respective homopolymers. The copolymer ratio was found to vary between 1.4-1.6:1.0 as shown in Table 16. The relative percentages of β-BL homopolymer and copolymer linkages was found to vary between 41:59 to 46:54. In all cases there existed a higher percentage of copolymer linkages to homopolymer linkages. The molecular weight of the copolymer, as determined by GPC, was low, never exceeding 4000.

Polymerization occurred by a ring opening mechanism whereby the phenoxide end of the NZ zwitterion attacks either the α carbon on the thiophenium ring to form a NZ-NZ homopolymer linkage or the β carbon of the β-BL monomer to form a NZ/β-BL copolymer linkage. Polymerization proceeds in this manner with the generated nucleophilic end always having a choice of two electrophiles (thiophenium ring or β-BL monomer) to react with to form a random copolymer. Termination occurs predominately by a chain transfer mechanism whereby the phenoxide end of the macrozwitterion abstracts a H^{+} from the β carbon of the β-BL monomer to form olefinic and naphtholic end groups. The

polymer end group was verified by the preparation of a model end group compound, 1-(tetramethylenethio)-4-naphthol β-methyl acrylate (vinyl naphthol compound), acylation of the naphthol group and by the addition of bromine across the double bond. The chemical shift of the olefinic protons of the vinyl naphthol compound was in good agreement with the assigned copolymer signals. Acylation of the copolymer was deemed successful by the appearance of a signal at 21.0 ppm in the ^{13}C spectrum which was assigned to the methyl carbon of the acyl group. Acylation of the vinyl naphthol compound also resulted in a signal at 20.8 ppm in the ^{13}C spectrum.

The formation of a random copolymer for this system was not entirely surprising since the β-BL monomer can also react with the water present from the water of hydration of the zwitterion to form β, β'-oxydibutyric acid; thus destroying the stoichiometric equivalent molar ratio of the two monomers. The decrease in concentration of the β-BL monomer could possibly explain why the copolymer structure is random and rich in the NZ moiety. Since two electrophiles (thiophenium ring and β-BL) are present in excess in solution, competition exists between the electrophiles and the nucleophilic end of the zwitterion.

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