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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW
CONJUGATED POLYMERS

City University of New York

PH.D. 1986

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**SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF
NEW CONJUGATED POLYMERS**

by

Yen Wei

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

1986

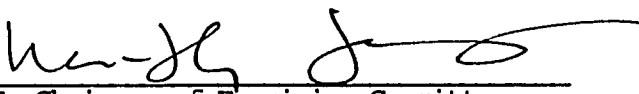
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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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ABSTRACT

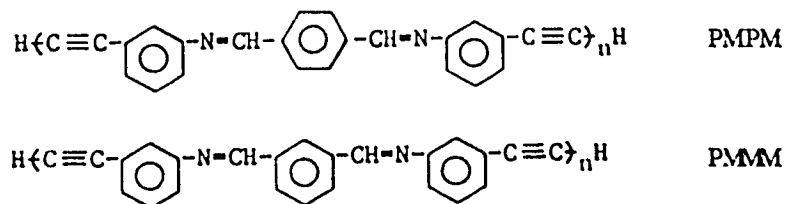
SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NEW CONJUGATED POLYMERS

by

Yen Wei

Advisers: Professors George Odian and Nan-Loh Yang

Two new polymers, PMPM and PMMM, have been synthesized via an oxidative coupling polymerization of the ethynyl-terminated monomers, MPM and MMM, and characterized by means of elementary analysis, and IR, ^1H and ^{13}C NMR both in solid state and in solutions, and UV spectroscopy.



The polymers are insoluble in most neutral organic solvents but they dissolve in and react with strong protonic acids besides protonation of the imine groups. Different reactions of the polymers with a variety of acids such as trifluoroacetic acid (99%), MeSO_3H (98%) and concentrated H_2SO_4 (98%). The number average molecular weights of PMPM and PMMM were determined to be 1500 and 16000, respectively, by end group analysis.

Various 4- and 4'-substituted trans-N-benzylideneanilines were synthesized and the effects of substituents on the chemical shifts of appropriate protons were analyzed by the Hammett single parameter and Taft dual substituent parameter (DSP) techniques. It is concluded that the trans-N-benzylideneanilines in the neutral solvents have a twisted conformation but upon protonation, they have a coplanar conformation. This conclusion was further confirmed and extended to the polymers by studies of their UV spectra. Both PMPM and PMMM exhibit superior thermal stabilities under N₂ atmosphere. The thermal reactions in both N₂ and air at different temperatures were studied by means of TGA, DSC and IR spectroscopy. A weight gain around 295°C was observed for the polymer samples in the TGA measurements and is attributed to reactions between the chemically active species generated from the diethynylene triple bonds and the atmospheric H₂O and/or O₂ to yield carbonyl and other oxygen-containing groups. PMPM and MPM show narrow ESR absorptions originated from the unpaired electrons delocalizing over a fairly large conjugated system. Protonation causes a dramatic increase of the signal intensities owing to the conformation change. PMPM doped with I₂ shows further increase of the signal intensity. No ESR signal was found for PMMM or MMM. Pure PMPM is an insulator, but upon protonation or doping, its conductivity increases to 10⁻⁶ or 10⁻⁴ Ohm⁻¹cm⁻¹, respectively.

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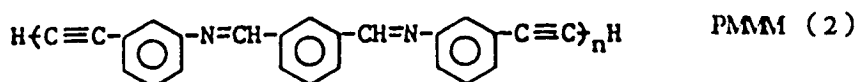
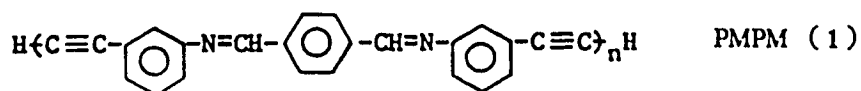
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1.0 INTRODUCTION

It is well known that polymers with extended π -electron systems exhibit interesting electronic and thermal behaviors[1]. In spite of increasing activity in this field, most conjugated polymers have not been thoroughly characterized and there is a lack of systematic knowledge about the relationship between molecular structure and polymer properties. The difficulties encountered by their characterization are due to their insolubility in most organic solvents. For further progress in this field, it is important to investigate a broad spectrum of diversified polymeric systems and to develop a better understanding of the structure of conjugated polymers. Bearing this in mind, we have synthesized and conducted thorough investigation on two new polymers, (1) and (2):



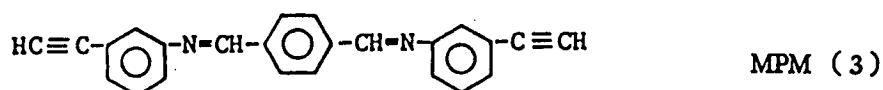
Both polymers contain aromatic imine and diethynylene groups. Polymers with imine or diethynylene linkage have been studied. This thesis represents the first investigation on polymers carrying both units on the same chain.

Aromatic polyazomethines are of active interest[2-9] because of their high thermal stability[2-6] and good semiconducting properties [7,8]. However, most of them have not been characterized thoroughly and have only elementary analysis, IR and thermal analysis results to support the structures due to their poor solubilities. Little is known about the behavior and conformation of the polymers in solution. The conformation of small molecules of aromatic azomethines, trans-N-benzylideneaniline (5) and its derivatives has been a subject of considerable discussion. Extensive evidences[10] indicate that the molecules have a nonplanar conformation. The conformation of protonated trans-N-benzylideneanilines has received relatively little attention. No report on the conformation of the aromatic polyazomethines, neither unprotonated nor protonated, was found in the literature. It is extremely important to develop an understanding of the conformation of the aromatic polyazomethines. Conformation of the polymers controls the extent of conjugation, hence it directly affects the thermal and electronic properties of the polymers.

Many polymers with conjugated triple bonds show interesting electronic properties in the undoped [11] or doped form[12]. The triple bonds can also provide sites for

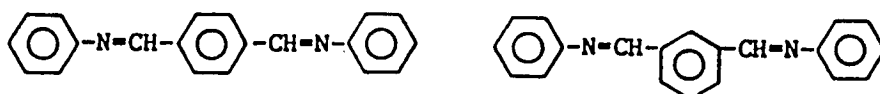
crosslinking without an interruption of the conjugation backbone, thus potentially leading to a highly extended conjugated system. . Again, the conjugated polymers with diethynylene group have not been well characterized owing to their poor solubility. Only a few soluble ones such as poly(1,3-diethynylene benzene) have been studied by ^{13}C NMR spectroscopy[13].

The polymers, (1) and (2), were synthesized via a copper-amine-catalysed oxidative coupling polymerization[49] of the monomers, $\text{N,N}'$ -(1,4-phenylenedimethylidyne)-bis-(3-ethynylaniline) (3) and $\text{N,N}'$ -(1,3-phenylenedimethylidyne)-bis-(3-ethynylaniline) (4), respectively.



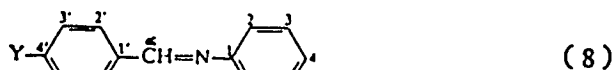
Synthesis of the monomer, MPM (3), was reported by Walton[8] without details of characterization. In order to study the structures and the conformation of PMPM (1) and PMMM (2) in both solid state and in solution, model compounds, trans- N -benzylideneaniline(5), trans- $\text{N,N}'$ -(1,4-phenylenedimethylidyne)-bis-aniline(6), trans- $\text{N,N}'$ -(1,3-

phenylenedimethyldiylne)-bis- aniline(7), and two series of substituted trans-N- benzylideneanilines (8 and 9) were prepared. Only limited spectroscopic data for the compounds (6-7) are available in the literature.

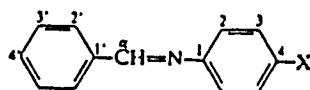


(6)

(7)



Y = N(CH₃)₂, OH, OCH₃, CH₃, H, F, Cl,
COOCH₃, COOH, CN, NO₂



X = OH, OCH₃, CH₂CH₃, CH₃, H, F, Cl, I,
COOCH₃, CN, NO₂

(9)

In this thesis, considerable attention is directed toward the characterization of the new polymers(1 and 2) and their monomers (3 and 4) by means of elementary analysis, IR, UV, ¹H and ¹³C NMR spectroscopy in solid state, in neutral and in various acidic media such as MeSO₃H, concentrated H₂SO₄, and trifluoroacetic acid (TFA). The reactions of the compounds (1-

4) in various acids, such as addition of water to the triple bonds, and protonation and hydrolysis of the imine groups were studied extensively. The conformation of the trans-N-benzylideneanilines were established by a ^1H NMR spectral study of the effects of substituents in the 4'- or 4- positions (compounds 8 and 9, respectively) on the chemical shifts of the 2'- and α -protons in sulfuric and trifluoroacetic acids, and a comparison of the results with those in the neutral solvent DMSO. The proton chemical shifts were correlated with Hammett and Taft substituents with a view towards evaluating the resonance and inductive contributions of the substituents. To gain further insight into the conformation of the polymers, UV absorption spectra of the polymers(1 and 2), the monomers(3 and 4) and the model compounds(5-7) were studied in both neutral solvent CH_2Cl_2 (except the polymers since they were insoluble) and acidic media. All absorption bands were systematically assigned and were discussed in relation to the conformation. The rigidity of the polymer chains was studied by viscometry with methanesulfonic acid and TFA solutions. The thermal properties and the thermal reactions at various temperature levels of heat treatments of the polymers and the monomers were examined by means of DSC, TGA and IR spectroscopy in both nitrogen and air. Paramagnetism and electrical conductivities of the polymers were studied and the results were related directly to the structure and conformation of the polymers in the neutral and protonated forms as well as upon

doping with iodine.

2.0 BACKGROUND

Since the new polymers, PMPM(1) and PMMM(2), have both imine double bonds and triple bonds in their conjugated systems, it is necessary to review separately in the following sections two types of conjugated polymers, the aromatic polyazomethines and the conjugated polymers containing triple bonds in the main chains.

2.1 AROMATIC POLYAZOMETHINES

The aromatic polyazomethines are polymers containing the -C=N- unit as linkages between other divalent aromatic groups in the linear backbone of the polymer chain. In 1923, Adams and coworkers[14] prepared the first polyazomethine by condensing terephthalaldehyde with benzidine and o-dianisidine, respectively. During the period 1950-1968, a number of aromatic polyazomethines[2] were synthesized, mainly by D'Alelio and coworkers, because of their high thermal stability. These polymers were the products of the condensation of arylene dicarbonyl compounds with arylene diamines in a variety of solvents, such as benzene, DMF, acetic acid, etc. The polymers were isolated as precipitated yellow-to-orange infusible, non-melting brickdust condensation products of relative low

molecular weights (500-1000) and had limited utility. The successful synthesis of a large variety of high molecular weight polyazomethines were first reported in 1967 [15] by the use of (a) the melt-polymerization technique, instead of the conventional solution method, and (b) some novel polymerizations.

The aromatic polyazomethines in general exhibit relatively high thermal stabilities. The temperature range for a significant decomposition (ca. 5% weight loss in TGA) is about 350-550°C. Under nitrogen atmosphere, some polymers were found to have only ca.20% weight loss at 900°C.

Since the recent surge of interest in conducting or semi-conducting polymers, aromatic polyazomethines become a subject of active interest because of their semiconducting and paramagnetic properties[8,16].

The low molecular weight aromatic polyazomethines fail to show ESR absorption unless they are treated at high temperatures, but the high molecular weight ones demonstrate narrow signals without a hyperfine structure, indicating the existence of unpaired electrons in the polymers[18]. Most of the pure aromatic polyazomethines are insulators at room temperature with D.C. conductivities in the range of 10^{-9} - 10^{-16} Ohm⁻¹cm⁻¹ [7b]. However, those polymers have a correlation between the conductivity and temperature defined by the following equation,

$$\sigma = \sigma_0 e^{-(E/2kT)} \quad (1)$$

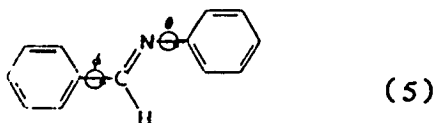
where σ and σ_0 are the conductivities at temperature T K and 273 K, respectively, and E is the energy of activation of the conductivities[7b]. The values of σ_0 for those polymers are 10^{-4} to $10^0 \text{ Ohm}^{-1} \text{ cm}^{-1}$. The conductivities of some aromatic polyazomethines and polyphenylene, a well known conducting polymer upon doping are compared in Table 1[7b, 18,19]. Without dopant, they are all insulators and have similar conductivity. After doping with iodine , polyphenylene becomes a very good semiconducting polymer with a conductivity $10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at room temperature[18]. The conductivities of aromatic polyazomethines doped with iodine were reported upto $5.8 \times 10^{-7} \text{ Ohm}^{-1} \text{ cm}^{-1}$ [19].

It is noted that almost all of the aromatic polyazomethines are not well characterized because of their insolubility. For most of the polymers, only IR and elementary analysis data were used to suggest chemical structures. Some polymers were found to dissolve in strong protonic acids. The polymer properties in solution, e.g. intrinsic viscosity, were studied [5,20].

Table 1 CONDUCTIVITIES ($\text{Ohm}^{-1} \text{cm}^{-1}$) OF SOME CONJUGATED POLYMERS				
Polymer	σ_{298K}	σ_0	E (eV)	
$\langle \text{C}_6\text{H}_4 \rangle_n$	10^{-12}	-	3.5	
$\langle \text{C}_6\text{H}_4 \rangle_n - \text{I}_2$	10^{-5}	-	0.87	
$\langle \text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{N}=\text{CH}-\text{C}_6\text{H}_4 \rangle_n$	2.0×10^{-17}	2×10^{-3}	1.7	
$\langle \text{CH}=\text{N}(\text{CN})-\text{C}_6\text{H}_2(\text{CN})-\text{N}=\text{CH}-\text{C}_6\text{H}_4 \rangle_n$	1.4×10^{-10}	4.0×10^{-4}	0.77	
$\langle \text{C}_6\text{H}_4-\text{CH}=\text{CH} \rangle_n$	2.0×10^{-14}	1.5×10^{-1}	1.54	
$\langle \text{C}_6\text{H}_4-\text{CH}=\text{CH} \rangle_n - \text{AsF}_5$	6.2×10^{-2}	-	-	

2.2 CONFORMATION OF AROMATIC POLYAZOMETHINES AND RELATED COMPOUNDS

The orbitals of the π -electrons in the aromatic polyazomethines have been considered as overlapping and the resultant mixing of wave functions results in delocalized molecular orbitals encompassing all nuclei of the coplanar polymer backbone [5].



However, a considerable discussion of the conformation of the aromatic azomethines, trans-N-benzylideneaniline(5) and its derivatives, indicates that the benzaldehyde ring is essentially coplanar with the imine double bond (i.e. the torsion angle ϕ is close to 0) but the aniline ring is twisted out of the PhCH=N plane (i.e. the torsion angle θ is considerably larger than 0). This twist conformation is supported by x-ray crystallography[21], IR and photoelectron spectroscopy[22-24], gas-phase electron diffraction[25] and some theoretical studies [26,27]. Estimates of the torsion angle θ range from 30 to 55 degrees, depending on the experimental techniques used and the physical state of the sample.

Conjugation between the benzaldehyde ring and CH=N π -

electrons should result from coplanarity of the two systems. On the other hand, one expects that conjugation between the aniline ring and CH=N π -electrons is precluded owing to the non-planarity resulting from the twisting of the torsion angle θ . Conjugation between the aniline ring and the nitrogen lone pair of electrons may be responsible for the non-planarity of the aniline ring and CH=N.

^1H , ^{13}C and ^{15}N NMR spectra of various substituted trans-N-benzylideneanilines have been examined in order to elucidate these points. A number of ^1H NMR studies have been carried out on trans-N-benzylideneanilines substituted separately on the benzaldehyde and aniline rings[23,28-31]. The chemical shifts, $\delta_{\text{H-}\alpha}$, of the α -proton (the proton of the CH=N group) measured in cyclohexane, chloroform, carbon tetrachloride and DMSO correlates with the Hammett constants for para substituents on the benzaldehyde ring. Electron-donating and -withdrawing groups cause upfield and downfield shifts, respectively.

There was no correlation for para substituents on aniline ring as the chemical shift was unaffected by both electron donation and electron withdrawal. These results support the twist conformation for the trans-N-benzylideneaniline system in which the imine double bond is conjugated with the benzaldehyde ring but not with the aniline ring. The lack of a Hammett correlation for substituents on the aniline ring also indicates the absence of any type of inductive effect of a ring

substituent on the H- α chemical shift, including inductive transmission by direct field effect, sigma-bond polarization and a combination of pi-bond delocalization and either sigma-bond polarization or direct field effect. These conclusions are generally supported by ^{15}N and ^{13}C NMR studies of substituted trans-N-benzylideneanilines in chloroform, DMSO and methanol[32-36].

The conformation of protonated trans-N-benzylideneanilines has received relatively little attention. Pavlik and van Putten [37] studied the ^1H NMR of trans-N-benzylideneaniline(5), its six monomethylated and two sym-tri-methylated derivatives in 96% H_2SO_4 , and concluded that the aniline ring is twisted out of the plane of the iminium double bond. No information is available on whether the extent of twisting (i.e. the value of θ) is the same or different for protonated (5) compared with unprotonated (5). Gil and Saraiva[38] found that protonation results in a significant downfield shift in $\delta_{\text{H}-\alpha}$ for 4-methyl-4'-nitro- trans-N-benzylideneaniline relative to the unsubstituted compound, whereas there is a negligible difference in $\delta_{\text{H}-\alpha}$ for the two compounds in chloroform.

The UV absorption spectral pattern of trans-N-benzylideneaniline(5) in a neutral solvent is remarkably different from those of pi-iso-electronic trans-stilbene and trans-azobenzene[39-49]. Stilbene has an intense absorption band at ca.295 nm (ϵ =24000) and a less intense band at 229 nm (ϵ =14200) [40] while the spectrum of trans-N

-benzylideneaniline(5) (the spectra are given in Section 4.3.2) exhibit a shoulder at 310 nm ($\log \epsilon = 3.49$) and a maximum at 263.5 nm ($\log \epsilon = 4.27$). The intensity of the first band is considerably reduced compared to that of trans-stilbene. Such differences have been reasonably explained in terms that trans-N-benzylideneaniline takes a non-planar conformation. Ismaclskii[41] and Ebara[42] analyzed UV spectra of various substituted trans-N-benzylideneanilines and postulated that the aniline ring is perpendicular to the PhCH=N plane and its π -electrons conjugate with the lone pair of electrons on the nitrogen atom of the imine group. This model was examined and accepted later by El-Bayoumi and coworkers[40] also in their extensive study of UV spectra of various substituted trans-N-benzylideneanilines. On the other hand, Brocklehurst[43] and Smith[44] proposed a model in which the aniline ring is rather twisted around the C-N bond and not necessarily perpendicular to the rest of the molecule. They suggested [43,44] that the 310 nm band of trans-N-benzylideneaniline corresponds to the intense 295 nm band of trans-stilbene and the appearance of the 310 nm band can be explained in terms of a solution equilibrium between planar and nonplanar forms. Recent studies[39] agree more with Brocklehurst's model based on the fact that the torsion angle is not necessarily 90 degrees.

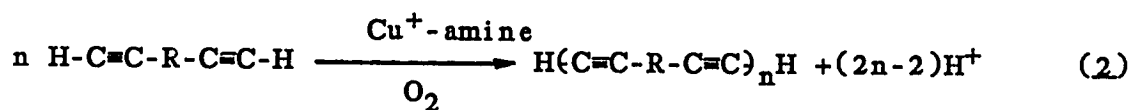
What is the cause of this nonplanarity? There were two possible explanations. One was that the molecule itself is not

coplanar due to steric effects between the alpha- and ortho-hydrogen atoms[46]. Another explanation is that the non-planarity is due to the interferences from the lone pair of electrons of the imine group[39,43,47]; the loss of π -electron energy in the twisted trans-N-benzylideneaniline can be compensated by delocalization of the nitrogen lone pair into the π -orbitals of the aniline ring[47]. If the nitrogen lone pair of electrons is localized by protonation or by nitron formation, a planar structure for the molecules is favored. Although studies on the protonation of trans-N-benzylideneanilines in concentrated H_2SO_4 [40,43,48] all lead to a conclusion that the protonated molecules must be more planar , the interpretation of the UV spectra were quite different and the assignment of the spectra was not clear. Brocklehurst[43] compared the first band and El-Bayoumi[40] compared the second band of the spectra of trans-N-benzylideneaniline, with and without protonation.

It seems that most people working on aromatic polyazomethines still believe in the existence of a conjugated system extended through the whole coplanar chain, although the discussion on the conformation of trans-N-benzylideneanilines indicates that might not be true.

2.3 POLYMERS WITH DIETHYNYLENE AND/OR ETHYNYLENE GROUPS IN THE CONJUGATED SYSTEM

Synthesis of the polymers with diethynylene groups in their conjugated backbones via oxidative coupling polymerization were reported first by A.S.Hay[49], and by other workers[50] .



(10)

(11)

R= A variety of divalent conjugated groups

Ethynyl-terminated monomers(10) were polymerized with cuprous-amine complex as catalyst and oxygen as oxidant at ambient temperature in a variety of solvents to generate the diethynylene polymers(11) of which most are not soluble in water and organic solvents. This polymerization method was developed from the oxidative coupling reactions known as Glaser[51a] and Eglinton[51b] couplings for the organic preparation of diethynylene compounds. Among a number of diethynylene polymers, poly(p-diethynylenebenzene)(12) and poly(m-ethynylenebenzene) (13), i.e. R= p-Ph- and m-Ph- in (11), respectively, are of most interest.

The properties of poly(p-ethynylenebenzene) were studied by Kotlyarevskii and coworkers[50]. The structure of the

polymer was only supported by its IR spectrum and elementary analysis due to its insolubility. The polymer has high temperature stability. The electrical conductivity at room temperature was less than 10^{-14} to 5×10^{-11} $\text{Ohm}^{-1} \text{ cm}^{-1}$ at 120°C . Interesting photo-conductivities were observed. The polymer showed ESR signals due to unpaired electrons in the conjugated chain.

Poly(m-diethynylenebenzene)[49a] was reported as a pale yellow polymer and soluble in some solvent such as chlorobenzene and nitrobenzene at temperatures above 100°C . The good solubility made characterization possible. Thus the polymer was studied by means of IR, ^1H and ^{13}C NMR spectroscopy[13]. The results supported the structure very well and indicated the absence of undesired side product during the oxidative coupling polymerization. Thermal properties of this polymer were studied extensively by Newkirk and coworkers[52]. The polymer decomposes at ca. 200°C upon heating in nitrogen. When the polymer was preheated overnight at 160°C , no major decomposition was observed up to 835°C (ca. 7.1% weight loss). A weight gain was observed when the polymer was heated to the temperature just before the decomposition and was exposed to air. Chemical changes of the polymer upon heating were studied by IR absorption spectrum in a thin film after each of seven heat treatments at progressively higher temperatures up to 600°C in nitrogen. An increase in the amount of polynuclear aromatics and a decrease in the amount of the m-disubstituted aromatic

rings and the diethynylene groups indicate the thermal crosslinking of the triple bonds and the aromatic rings at elevated temperatures. Infrared absorptions of some carbonyl, OH, and C-O-C groups were observed at ca. 170°C. The intensities of these groups reaches a maxima at 300°C followed by a gradual decrease. The presence of the oxygen-containing groups was attributed to reaction of the specimen with atmospheric O₂, H₂O or both during transfer from oven to spectrometer.

Yang, Odian and Pemawansa[12] reported that polymers(14 and 15) containing triple bonds can be synthesized via a nuclear coupling polymerization, with AlCl₃ as the Lewis acid catalyst and O₂ or CuCl₂ as the oxidant, from diphenyl acetylene and diphenyl butadiyne, respectively.



(14)



(15)

The polymers with M_n of 3.9x10³ and 1.8x10³, respectively, have considerable solubilities in CS₂ and chloroform, and were characterized by elementary analysis, IR, and ¹H and ¹³C NMR spectroscopy. High thermal stabilities were reported. The polymers(14 and 15) demonstrate narrow ESR signals and have D.C. conductivities of 1.6x10⁻⁶ and 2x10⁻⁵ Ohm⁻¹ cm⁻¹, respectively, after doping with AsF₅.

A number of ethynyl-terminated prepolymers[8,53,54] were

prepared and undergo a thermal crosslinking through the acetylenic groups to yield polymer networks. Most of the networks so formed show high thermal stabilities and good overall mechanical properties; some of them demonstrate excellent conductivities. For example, Walton[8] synthesized MPM(3) (employed as monomer in this thesis) and found that with an intensified heat treatment at high temperature, MPM forms an extended conjugated polymer network which has a conductivity as high as $1.1 \times 10^{-2} \text{ Ohm}^{-1} \text{ cm}^{-1}$.

3.0 EXPERIMENTAL

3.1 SYNTHESIS OF MONOMERS AND MODEL COMPOUNDS

N,N'-(1,4-phenylenedimethyldiyl)-bis-(3-ethynylaniline)(3)

Method 1) A solution of terephthalaldehyde (4.02g., 0.030 mol) in toluene (100 ml) was added dropwise over a 1 hour period to a stirred refluxing solution of 3-ethynylaniline (7.37 g. 0.063 mol) in 100 ml of toluene under nitrogen atmosphere. A slight excess of the 3-ethynylaniline was used to insure reaction of both aldehyde groups. The water generated from the condensation was trapped with a Berrett distilling receiver. After 3 hours, about 1 ml of water (theoretical yield is 1.08 ml.) was collected from the reaction. Further refluxing was carried out for another 24 hours until no more water was produced. The mixture was filtered hot, and the filtrate volume reduced to 50 ml. The greasy red residue was discarded. Upon cooling the filtrate in a ice-water bath, 9.26 g (93% yield) of crude MPM(3) was obtained. Recrystallization from absolute ethanol gave a pure product with 95% recovery. The product was dried in vacuum overnight at 50°C.

Method 2) A solution of terephthalaldehyde (2.00 g, 0.015 mol) in absolute ethanol (80 ml) was added to a stirred refluxing solution of 3-ethynylaniline (3.80 g, .0032 mol) in absolute

ethanol (100 ml) over 20 minute period. Stirring and refluxing were continued for 24 hours. The volume of the solution was then reduced to 30 ml. Upon cooling with ice bath, the crude product was crystallized with 96% yield. Recrystallization of the crude product from absolute ethanol gave a 95% recovery.

N,N'-(1,3-phenylenedimethyldiyl)-bis-(3-ethynylaniline)(MMM.4)

Similar to the procedure for the preparation of MPM, MMM was synthesized by condensation of 1,3-phthaldehyde and 1,3-ethynylaniline and purified by recrystallization from absolute ethanol. However, the recrystallization was achieved better in diethyl ether (92% recovery) than that in ethanol(88% recovery). The yield using the method (a) was 85%. The purified product is a pale yellow fine crystalline material. This compound has not been reported in the literature.

Model Compounds(5-7) were synthesized by condensation of the benzaldehyde, 1,4- and 1,3-phthaldehyde with aniline[8,55]. Stoichiometrical amounts of the two reactants were refluxed in toluene or ethanol for about 5 hours, and about three-quarters of the solvent distilled off, the reaction mixture cooled to precipitate the product. The products were purified by recrystallization from absolute ethanol. The structure of the compounds was confirmed by IR, NMR spectroscopies.

Various 4'- and 4-substituted trans-N-benzylideneanilines (8 and 9) were synthesized by condensation of the appropriately substituted benzaldehyde and aniline[55]. The experimental procedure was the same as the preparation of (5-7). The products were purified either by vacuum distillation or recrystallization from absolute ethanol. The melting points (boiling point for the 4-methyl derivative) of the purified compounds agreed well with literature values[29]. The 4-ethyl derivative had a boiling point of 167-168°C at 6 Torr; no literature value was found for this compound. Integrations of ¹H NMR absorption spectra for each of the compounds established their structures.

3.2 Polymerization

PMPM (1)

To a 250-ml Erlenmeyer flask was added 0.020 g (0.0020 mol) CuCl and 30 ml of pyridine. The mixture was stirred for 30 min. and then filtered. The filtrate consisted of the cuprous- pyridine complex which served as both catalyst and solvent for the oxidative coupling polymerization. Oxygen was bubbled through the vigorously stirred solution at 40°C throughout the entire period of the reaction; then there was added 6.60 g (0.020 mol) of N,N'-(1,4-phenylenedimethylidyne)-bis-(3-ethynylaniline)(MPM) in 80 ml of pyridine. A vigorous reaction ensued and the temperature of

the solution slightly increased. In 15 minutes, a precipitate began to settle from the solution. The reaction was continued for another 30 minutes. Then the mixture was poured into 300 ml of methanol and filtered. The crude product thus obtained was washed with methanol three times, then exhaustively extracted in a Soxhlet extractor under vacuum by pyridine (ca. 40°C/40 mmHg) for 24 hours to remove the copper catalyst from the polymer. The polymer was washed with methanol in the Soxhlet extractor for 10 hours and dried in vacuo (ca. 6 Torr) at 40°C overnight. 6.3 g of polymer powder was obtained. The yield was 95%.

PMM

To 20 ml of pyridine 0.010 g of CuCl (0.0010 mol) was added. The mixture was stirred for 30 minutes and filtered into a 250-ml Erlenmeyer flask where the solution was vigorously stirred and oxygen was bubbled through. Then, 3.32 g of N,N'-(1,3-phenylenedimethyldiyn)-bis-(3-ethynylaniline)(MM) (0.010 mol) was added into the solution. The reaction mixture was maintained for 1 hour at 40°C. No precipitate formed during this period. The solution then was poured into methanol and the precipitate formed. The precipitate was filtered and washed with methanol in a Soxhlet extractor for 6 hours. Then the crude product was dissolved in 100 ml of pyridine giving a blue solution due to the copper-pyridine complex. This solution was poured into methanol and

the precipitate generated and filtered. This operation was repeated until the polymer solution in pyridine showed no more blue color. A 1:3 (v/v) mixed solvent of tetramethylethylenediamine/pyridine increased the efficiency of this process remarkably. The product was washed with methanol in the Soxhlet extractor for 10 hours and dried in vacuo overnight at 40°C.

PMM with low molecular weight used in DSC measurement was synthesized and purified using the same method as for the higher molecular weight one. Except 30 minute polymerization time was allowed instead of 1 hour. Low overall yield (30%) was obtained.

To ascertain that the imine group in the monomers is not affected during the oxidative coupling polymerization, a model compound, trans-N-benzylideneaniline(5) was used to undergo the same conditions of the polymerization. Thus, 2.0 grams of (5) was added to a vigorously stirred CuCl-pyridine complex solution (40 ml) with oxygen bubbling through the system at 40°C. The solution was maintained under such conditions for 1 hour followed by a vacuum distillation to remove pyridine. Then 30 ml of absolute ethanol were added to the residue. The mixture was filtered and trans-N-benzylideneaniline was crystallized from the filtrate upon cooling in an ice bath. After recrystallization from absolute ethanol, the recovery was 80%. upon

comparing proton NMR and IR spectra of the compound(5) after undergoing the oxidative coupling conditions with that before undergoing such conditions, no significant difference was found.

3.3 Measurements

Infrared Spectra of the polymers, monomers and model compounds(1-7) were recorded with a Beckman 6260 Infrared Spectrophotometer. The scanning range was generally from 4000 to 600 cm^{-1} with a 300 $\text{cm}^{-1}/\text{min.}$ scan speed. The absorption band position were calibrated with standard polystyrene film. KBr pellets of the samples were made with ca. 20 mg of sample and ca. 600 mg of KBr. All measurements were made at room temperature. The IR spectra of the polymers after heat treatments were taken in the same manner. Polymers were heated in a programmed rate 20 $^{\circ}\text{C}/\text{min.}$ in the thermogravimetric analyzer under nitrogen or air atmosphere. After reaching the desired temperature, the polymer samples with the sample pan were transferred quickly to a dessicator with nitrogen passing through, where the samples were allowed to cool to room temperature. Then KBr pellets of the polymer samples were made up followed by a quick measurement.

Nuclear Magnetic Resonance (NMR) spectra were recorded on

IBM NR- 80 and Bruker WP200 spectrometers in the pulsed Fourier-transform mode and equipped with a variable temperature 5-mm probe. For ^1H NMR measurements, the spectrometers operate at 80 and 200 MHz, respectively. The general acquisition parameters were 16-100 scans, 30 degree pulse angle, 1300 and 3012 Hz sweep widths, 8K and 16K data points, 3.1 and 2.7 second acquisition time for NR80 and WP200, respectively. Usually no additional delay time between pulses other than the acquisition time was used. For ^{13}C NMR spectra, the spectrometers operated at 20.13 and 50.33 MHz, respectively, in the pulsed Fourier-transform mode and equipped with a variable temperature 5 mm probe. Generally the acquisition of the spectra was with 1000-10000 scans, 30 degree pulse angle, 1.360 and 0.623 second acquisition times, 16K and 32K data points, and about 1-5 second additional delay between pulses besides the acquisition time. Sample solutions were made up in deuterated chloroform(99%D), or DMSO-d(99.5%D) or TFA(99%D) with tetramethylsilane(TMS) added as internal standard. Undeuterated TFA(99%), concentrated H_2SO_4 (98%) and methanesulfonic acid(98%) were also employed as solvents with D_2O in a external capillary tube to lock the spectrometer. The concentration range of the samples was about 5-15%(w/v). The spectra were generally recorded within the same day of sample preparation at 30°C .

For the ^1H NMR measurement of 4'- and 4-substituted trans-N- benzylideneanilines, the chemical shifts were reproducible

to better than ± 0.005 ppm. The chemical shifts in TFA-d and D_2SO_4 were obtained by extrapolation to infinite dilution of the values from sample concentrations in the range 0.5-12% (w/v). The chemical shifts for the various trans-N-benzylideneanilines varied linearly with the concentration in this range. The maximum variation of the chemical shift with concentration was 0.005 ppm/% for all compounds except the 4'- and 4-nitro derivatives, for which the variation was about three times larger. The NMR spectra in TFA-d and D_2SO_4 were generally recorded within 1 day of sample preparation. Separate experiments indicated no significant change in the spectrum whether it was measured immediately after sample preparation or after storage for periods as long as several weeks. The reported chemical shifts in $DMSO-d_6$ are not values obtained by extrapolation to infinite dilution. Spectra in $DMSO-d_6$ were recorded for each compound at a single concentration in the range 8-12% (w/v). It was not necessary to obtain extrapolated values, since spectra of most of the 4'- and 4-substituted trans-N-benzylideneanilines in $DMSO-d_6$ have been reported previously.

Solid state ^{13}C NMR spectrum of PMM was taken with cross polarization and magic angle spinning techniques by Drs. R. Stark and J. Dickenson at the University of Massachusetts. The spectrometer operated at 50.33 MHz at ambient temperature. The acquisition parameters were 100 scans, 0.051 second acquisition

time without additional delay between pulses and 20,000 Hz sweepwidth.

Ultraviolet-visible Absorption spectra were taken with a Cary 118C spectrophotometer in methylene chloride, absolute ethanol, TFA(99%), concentrated sulfuric acid(98%), and methanesulfonic acid(98%) in a concentration range 10^{-7} - 10^{-4} mol/l. A pair of calibrated quartz cells with 1 cm pathlength was used and the baseline was corrected using pure solvents. The spectra were recorded generally within one day of sample preparation at room temperature. The molar extinction coefficients of the monomers and the polymers in acidic solutions were obtained by the following method. The sample solutions with the different concentrations were made up at different time so that the time interval between the sample preparation and the measurement was the same, 30 minutes, for each concentration. The extinction coefficients of these compounds(1-4) were all measured at 30 minutes after the sample preparation.

Viscosities of the polymers were measured with an Ubbelohde viscometer at 30.0°C in MeSO_3H (98%) in a concentration range 1-6 g/dl. The measurement for each concentration was also made at ca. 30 min. after the sample preparation.

Electron Spin Resonance (ESR) spectra were recorded on a

JEOL Model JES-Me-3X, X-band, ESR spectrometer with a TE₁₀₅ cylindrical dual cavity at room temperature with the magnetic field centered at 3305.0 gauss and a response time of 0.03 second in general. The modulation width was selected to minimize the linewidth of the signals; a 2-gauss width was usually used. The linewidth was measured as the distance between two peaks of the first derivative signal. The spin density of the samples was obtained by comparison of the area under the absorption curve with the area of the ESR signal of a DPPH standard taken under identical spectrometric conditions. The quantity of DPPH was determined experimentally by measurement of its optical density in benzene at a wavelength 519 nm and $\log \epsilon = 4.89$; the result obtained was comparable to that from weight measurement.

Doping of the Polymers with iodine were carried out at 75°C under vacuum. The molar ratio of iodine to the polymer repeat unit was 1:4. Thus, to a polymerization tube wrapped with a light-proof black paper, 0.257 g (7.7×10^{-4} mole) of PMPM and 0.786 g (3.1×10^{-3} mole) of iodine were added and mixed well. The polymerization tube was then sealed under vacuum and submerged completely into an oil bath at 75°C for 48 hours. The tube was kept sealed until the conductivity measurement.

Direct Current Conductivity measurements were carried out

using two methods.

Method 1) Direct measurement: the polymer sample was compressed in between two 440-C stainless steel pellets using a polypropylene guide ring. The D.C. electrical resistance of the samples was measured at room temperature using a Keithley Model 160 digital multimeter. The contact time of the doped polymer with the electrode was less than 15 minutes. By measuring the thickness and the contact area, the electrical conductivities of the samples were calculated.

Method 2) Ohm's law method: The circuit for measurement of resistance by Ohm's law is given in Fig.1, where

a) is the sample chamber in which the polymer sample pellet is made by applying pressure(ca. 100 kg/cm^2) between two stainless steel dies. (the pressure was released before the measurement);

b) is a variable resistor and the resistance, R_0 , was set at the similar value of the sample resistance, R_s ;

c) is a voltage regulator which supplies electrical current with different voltages, V_0 , to the circuit; and

d) is a voltmeter from which the potential drop on the variable resistor(b) is recorded, V_s .

An equation correlating V_0 with V_s can be derived simply from Ohm's law,

$$V_o = \left(\frac{R_s + R_o}{R_o} \right) V_s \quad (3)$$

By changing the output voltage, V_o , a series of V_s can be obtained. From the slope of the plot of V_o against V_s , the resistance, R_s , and the conductivity, σ_s , of the polymer sample can be calculated.

$$\sigma_s = L/R_s A = L/[(\text{slope})R_o - R_o]A \quad (4)$$

where L and A are the thickness and the area of the sample pellet, respectively. The output voltages, V_o , were always in the range leading to a constant slope in the plot.

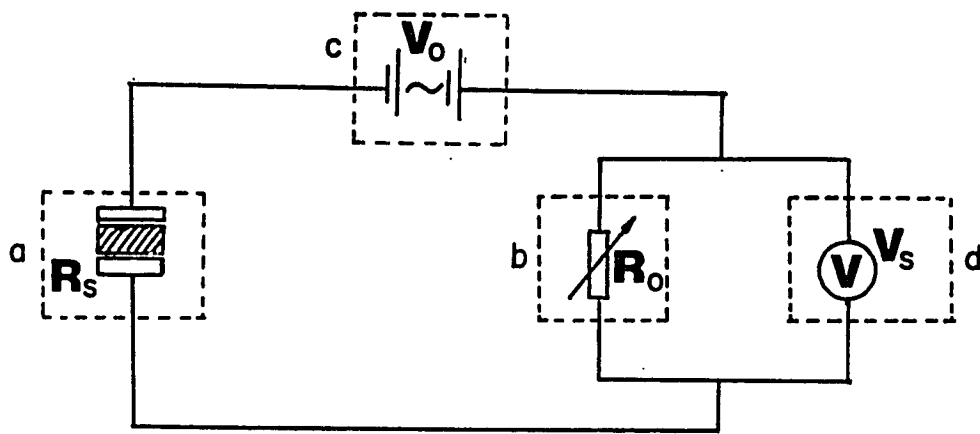
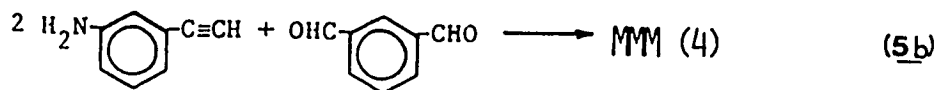
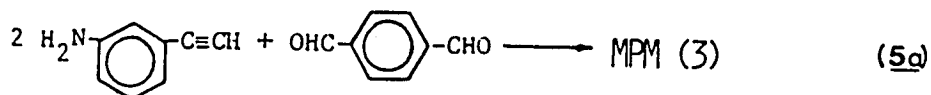


Fig.1. Circuit diagram for measurement of resistance by Ohm's law

4.0 RESULTS AND DISCUSSION

4.1 SYNTHESIS OF MONOMERS AND POLYMERIZATION

N,N' -(1,4-phenylenedimethyldiyl)-bis-(3-ethynylaniline) (MPM, 3) and N,N' -(1,3-phenylenedimethyldiyl)-bis-(3-ethynylaniline) (MMM, 4) were synthesized by condensation of 3-ethynylaniline (16) with 1,4- and 1,3-phthalaldehyde, respectively, in toluene or absolute ethanol and purified by recrystallization from absolute ethanol or anhydrous diethyl ether [8,55].

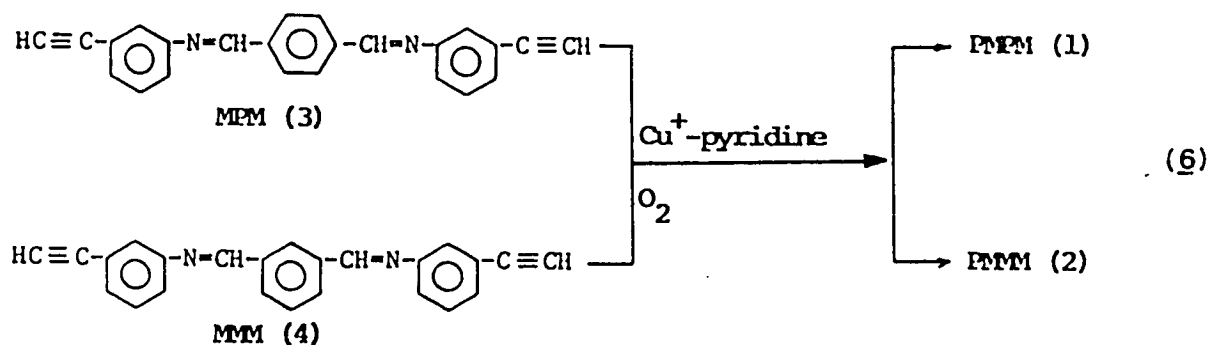


Scheme 1. Synthesis of the monomers.

The monomer MPM(3) is recovered as brick-yellow cube-like fine crystals with a melting point 139.5-140.0°C in good agreement with the literature value (138.5-139.5°C). The monomer MMM(4) is recovered as slightly yellowish cube-like

crystalline material with a melting point 92.5-93.0°C. Since this is the first synthesis of the monomer MM(4), no literature value of the melting point is available.

Polymerization of the ethynyl-terminated monomers was carried out by oxidative coupling reaction using oxygen as the oxidant in the presence of a cuprous-pyridine complex as catalyst in pyridine at 40°C [49].



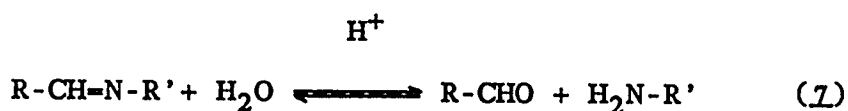
Scheme 2. Oxidative coupling polymerization

In order to avoid any undesired side reactions on the triple bonds the polymerization was carried out in a constant temperature bath with vigorous stirring. During the entire synthesis and purification, the temperature was controlled below 60°C.

A model compound, trans-N-benzylideneaniline(5) was sub-

jected to the same conditions of the oxidative coupling polymerization. Infrared and ^1H NMR spectra of the recovered compound(5) were compared with those of the original compound(5) and no significant difference was found. This experiment shows the imine groups in the monomers are most likely unaffected by the oxidative coupling polymerization.

The oxidative coupling polymerization was studied extensively by Hay and coworkers[49]. In a general procedure of oxidative coupling polymerization, the Cu^+ catalyst is removed after the polymerization by precipitating the polymer in methanol containing some hydrochloric acid. The acid decomposes the Cu- pyridine or Cu-polymer complex and removes the copper catalyst from the system. However, this general procedure could not be used in the polymerization of PMPM and PMMM because they contain imine groups which are very sensitive towards hydrolysis by small amounts of water with hydrochloric acid acting as catalyst.



Therefore, a new procedure for removing the copper catalyst was designed based on the formation of Cu-pyridine or Cu- tetramethylethylenediamine complex. The polymer PMPM is not soluble in pyridine. The crude product of the polymer was extracted with pyridine using a Soxhlet extractor under vacuum

for 24 hours. The characteristic blue color of Cu-pyridine disappeared after about 4 hour extraction. Then the polymer was washed with methanol over a 10-hours period in the Soxhlet extractor. A different method of purification was necessary for PMMM since it is soluble in pyridine before drying. The purification was carried out by repeating the process of dissolving the polymer in pyridine followed by precipitating the polymer in methanol until the blue color of the polymer solution in pyridine disappeared. The polymer was then washed with methanol in the Soxhlet extractor overnight. Both polymers were dried at 40°C under vacuum overnight.

4.2 CHARACTERIZATION OF POLYMERS AND MONOMERS

4.2.1 SOLUBILITY AND ELEMENTARY ANALYSIS

The polymer PMPM(1) was isolated as a yellow infusible, nonmelting powder. It is insoluble in any common organic solvent such as DMSO, DMF, THF, hexafluoroethanol, m-cresol, nitrobenzene, and methylene chloride, etc. at room temperature or near the boiling point of the solvents employed. Some swelling was observed but less than 0.5% weight loss of the sample were found in these cases. The crude product of PMMM is soluble in pyridine. However, after purification and drying, the solubility was remarkably reduced owing to the slight crosslinking of the imine group in the polymer[56]. No noticeable solubility of purified PMMM was found in other organic solvents although the polymer swelled in some solvents. The only good solvents for PMPM and PMMM are strong protonic acids such as 98% sulfuric acid, 98% methanesulfonic acid and 99% TFA, etc. When the acidic solutions of the polymers were poured into excess cold water, the raw materials could not be recovered since quick hydrolysis of the iminium bond occurred[2,4]. By evaporating TFA from the solution, both PMPM and PMMM can be recovered.

Elementary analysis data are in good agreement with the calculated values as presented in Table 2. One comment should

be made here, that is, during the polymerization and purification, the solvents and reagents must be completely dry and moisture-free because the imine group in the polymers is very sensitive towards hydrolysis leading to unsatisfactory elementary analysis results. For instance, the pyridine employed was treated with aluminum hydride for 10 hours followed by a vacuum distillation and was stored in a container with the molecular sieves. However, both purified PMPM and PMMM are stable at room temperature over a long storage time, and are not sensitive towards hydrolysis[4]. PMPM powder was refluxed with 20% HCl aqueous solution for 12 hours, with no significant hydrolysis being observed.

Table 2 Elementary Analysis Data

Compound	No.	Calculated Values			Analytical Results		
		C%	H%	N%	C%	H%	N%
MPM	3	86.71	4.86	8.43	86.18	4.56	8.15
MTM	4	86.71	4.86	8.43	86.40	4.54	8.27
PMPM	1	87.18	4.28	8.48	86.75	4.50	8.51
PMTM	2	87.18	4.28	8.48	86.62	4.61	8.72

4.2.2 IR AND ^{13}C NMR SPECTRA IN SOLID STATE AND IN NEUTRAL SOLVENTS

Infrared spectra of the polymers, monomers and the model compounds are summarized in Table 3 and the IR spectra of PMPM and MPM are given in Fig.2. All IR results are indicative of the formation of a polymer backbone through the coupling of the acetylenic group rather than through an addition polymerization of the triple bonds. The band assignment for the polymers and monomers was made based on literature values[24,57,58] and comparison with the model compounds.

A most characteristic band for detection of the acetylenic group is the stretching vibration of the hydrogen atom attached to the triple-bonded carbon atom which appears at about 3300 cm^{-1} . The monomers, MPM and MMM, had strong, sharp absorptions at 3280 and 3275 cm^{-1} , respectively. Their polymers, PMPM and PMMM, showed weak absorption at 3290 and $\text{ca.}3300\text{ cm}^{-1}$, respectively. By comparing the relative intensities of this band, PMMM showed the least amount of acetylenic group among the monomers and the polymers (Fig.3). The polymer PMPM had an acetylenic group content lower than that for the monomers but higher than that for PMMM indicating PMPM had a lower molecular weight than PMMM. The triple bond stretching usually occurs near 2100 cm^{-1} and its intensity is extremely variable, often very weak[57]. The monomers, MPM and MMM, showed weak absorp-

tions due to the triple-bond stretching at 2105 and 2100 cm^{-1} , respectively. The polymers, e.g. PMPM, showed two new weak bands at 2145 and 2200 cm^{-1} besides a very weak 2105 cm^{-1} band. These two bands are assigned to the stretching vibrations of triple bonds in the diethynylene group. However, these bands were too weak to be informative. Another band of the acetylenic group is a bending vibration of the hydrogen atom attached to the triple-bonded carbon atom, which usually falls in the range 610-700 cm^{-1} [57,58]. The monomers, MPM and MMM, showed broad bands at 637 and 635 cm^{-1} , respectively, but the polymers had very weak corresponding bands.

By far the greatest volume of data to be found in the literature [24,58] related to the C=N stretching frequency. In most cases it is a strong and fairly sharp band located at ca. 1600 cm^{-1} . The frequency is usually lower when the imine group is conjugated with other groups as vinyl and phenyl. The monomers, MPM and MMM, showed strong bands at 1615 and 1620 cm^{-1}

, respectively. The polymers had the C=N stretching at slightly higher frequencies, 1618 cm^{-1} for PMPM and 1625 cm^{-1} for PMMM. Apparently, MPM and PMPM have stronger conjugation than MMM and PMMM do. This tendency can be found in the N=C vibration frequencies of the model compounds (5-7) as well. Compound (7) had the N=C absorption at 1625 cm^{-1} which is of lower frequency than that for N-benzylideneaniline (5) since the former (7) has carried a meta-substitution of -CH=N-Ph group, thus extending the conjugation system. The N=C stretch-

ing frequency of (6) is even lower than that of (7) because a para- substitution of the $-\text{CH}=\text{N}-\text{Ph}$ group further extends the conjugation.

The substitution pattern of the phenyl groups was identified by its C-H out-of-plane rocking vibrations in the range $900-750\text{ cm}^{-1}$ as shown in Table 3.

^{13}C NMR spectral data for the monomers and the model compounds in chloroform- d and $\text{DMSO}-d_6$, and for PMPM in the solid state are listed in Table 4. Spectral assignments were made based on comparison of the chemical shifts of these spectra and the peak intensities, along with the information gained from the off-resonance decoupling and the crossover decoupling techniques[57]. Since MPM and MMM each have one carbon signal missing in chloroform- d and $\text{DMSO}-d_6$, respectively, data in both solvents are reported for the ^{13}C NMR.

Fig.4 shows the ^{13}C NMR spectra of MPM in $\text{DMSO}-d_6$ (Fig.4a) and of PMPM in solid state (Fig.4b) obtained using both cross polarization and magic angle spinning. The chemical shifts of PMPM are quite similar to those of MPM and are in good agreement with the values calculated from the model compounds(Table 5). The signal farthest downfield is assigned to the trans-imine carbon atom. Besides the complete resolution of the 8 types of aromatic carbon atoms, there is a small extra peak at 123 ppm in the PMPM spectrum. By comparing the chemical shifts of PMPM with those of MPM, this extra peak is

assigned to the C-3 at the polymer chain-end. Two weak signals at 84 and 78 ppm in the spectrum of PMPM are attributed to the acetylenic end group since the acetylenic carbon atoms give similar chemical shifts in MPM. The observation of the end group signal indicates a low molecular weight for PMPM. Two diethynylene carbon atoms in the polymer chain show signals at 81 and 76 ppm, respectively. Although studies on small imines led to the conclusion that they exist completely (>99%) in the trans-form both in the solid state and in the solution[59], one would still expect that the polymer might have some cis-units in the solid state trapped due to the poor chain mobility. However, the solid state ^{13}C NMR spectrum of PMPM showed no cis-units in the polymer.

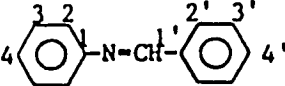
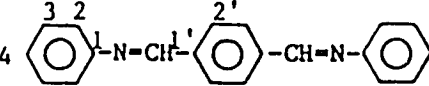
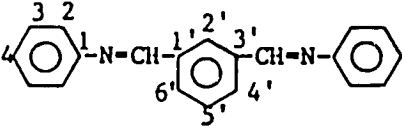
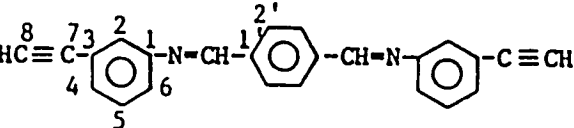
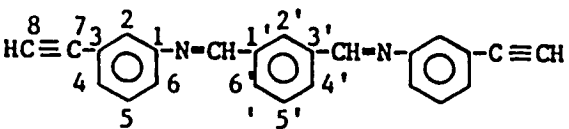
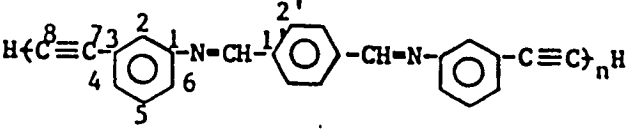
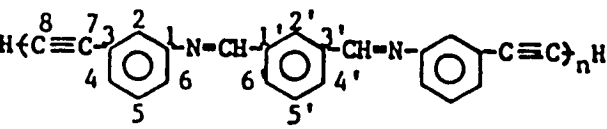
Table 3 . ASSIGNMENT OF I.R. SPECTRA OF THE POLYMERS, MONOMERS AND
MODEL COMPOUNDS IN SOLID STATE (KBr)

Compound	No.	$\equiv$ C-H Stret.	Imine $\equiv$ C-H Stret.	Aromatic C-H Stret.	C $\equiv$ C Stret.	C $\equiv$ CC $\equiv$ C Stret.	Imine N=C Stret.	$\equiv$ C-H Bending Mono-	Aromatic out-of-plane Bending	
									Para-	Meta-
1	3290	2860	3050	2105	2145	1618	637	-	827	780
2	3300	2860	3050	(2105)	2138	1625	610	-	-	790
3	3280	2860	3025	2105	2210	1618	637	-	833	690
4	3275	2865	3048	2100	-	1620	635	-	-	795
5	-	2855	3030	-	-	1627	-	759	-	683
6	-	2873	3055	-	-	1613	-	690	830	780
7	-	2862	3055	-	-	1625	-	690	-	690
								760	-	798
								690		695

Table 4 Assignment of ^{13}C NMR Spectra in Neutral Solvents and Solid State

Cpd.No.	Solvent	1	2	3	4	5	6	7	8	1'	2'	3'	4'	5'	6'	Remark
5	DCCl_3	159.9	152.1	120.8	128.6	125.7				136.4	128.7	129.0	131.1			
6	DCCl_3		152.1	120.8	128.6	125.7				139.0	129.2					Calc.
		159.3	151.8	120.9	129.1	126.3				138.7	129.2					
	DMSO-d_6	158.9	150.9	120.3	128.3	125.5				138.1	128.5					
7	DCCl_3		152.1	120.8	128.6	125.7				136.8	128.9					Calc.
		159.5	151.8	120.9	129.2	126.2				136.9	129.4					129.5 131.3 129.2 131.2
	DMSO-d_6	159.8	151.2	120.9	129.2	126.0				136.4	129.2					128.3 131.3
3	DCCl_3		151.4	124.5	122.9	129.9	128.7	120.6		139.0	129.2					Calc.
		160.0	151.7	124.1	123.1	129.8	129.2	121.9	83.3	78.6	138.6	129.2				
	DMSO-d_6	160.9	151.3	123.8	122.7	129.6	129.4	122.2	83.3	80.4	138.8	129.1				
4	DCCl_3		151.4	124.5	123.0	129.8	128.9	120.6		136.9	129.4					129.2 131.2 129.5 131.5
		159.9	151.7	124.2	123.0	129.8	129.2	121.8	83.3	79.6	136.6	129.3				
	DMSO-d_6	159.8	151.3	123.7	122.6	129.5	129.2	122.1	83.1	80.8	136.3	128.4				129.5 131.8
1	Solid State		152.0	124.9	122.9	130.3	129.4	121.9		138.7	129.2					Calc.
		159	151	125	122	133	130	120	81	76	138	129				
	$\text{PhC}\equiv\text{CH}$		122.3	132.1	128.1	128.2			83.3	77.7						
	$\text{PhC}\equiv\text{CC}\equiv\text{CPh}$		122.3	132.5	128.7	129.5			81.7	74.0						

Table 5 **Numbering System of Compounds (1-7)**
for their Carbon-13 NMR Spectral Assignments

Cpd. No.	Compound
5	
6	
7	
3	
4	
1	
2	

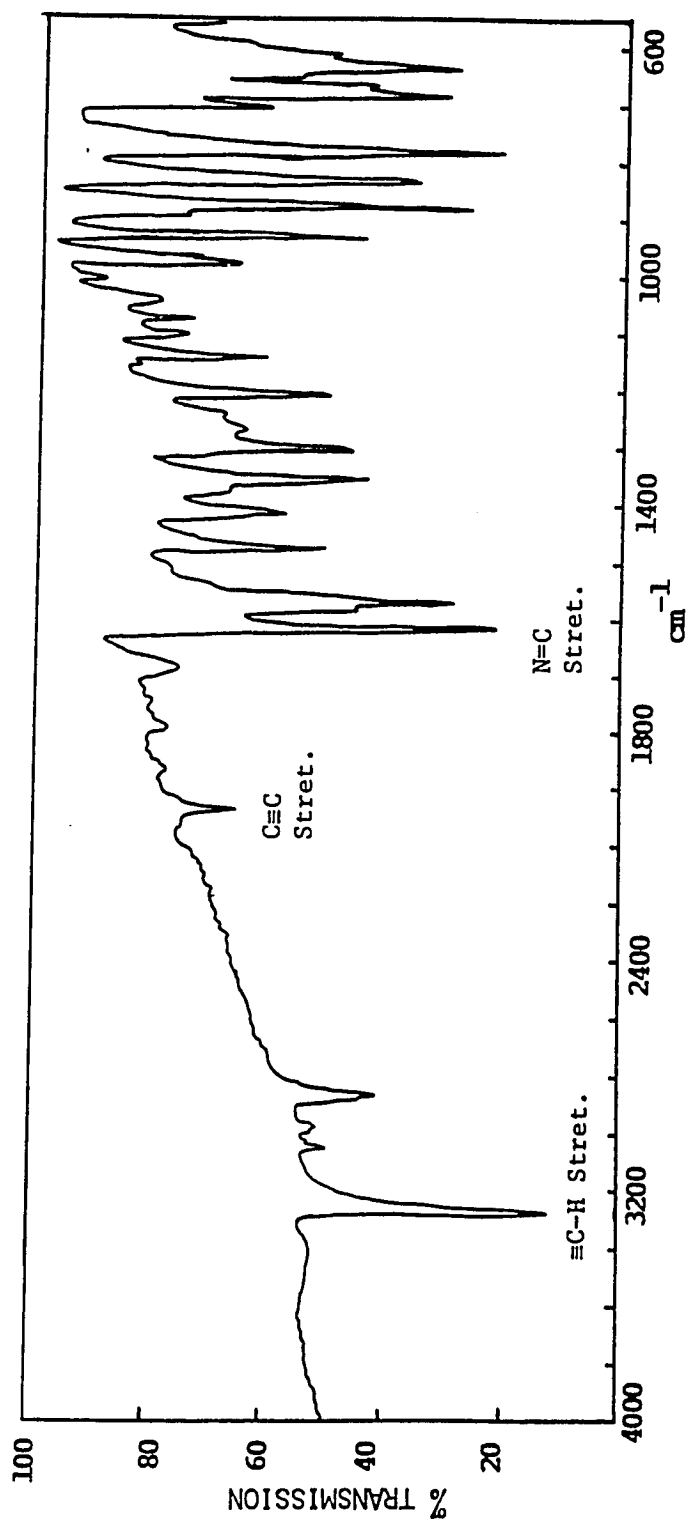


Fig.2a. IR spectrum of MEM(3) (KBr)

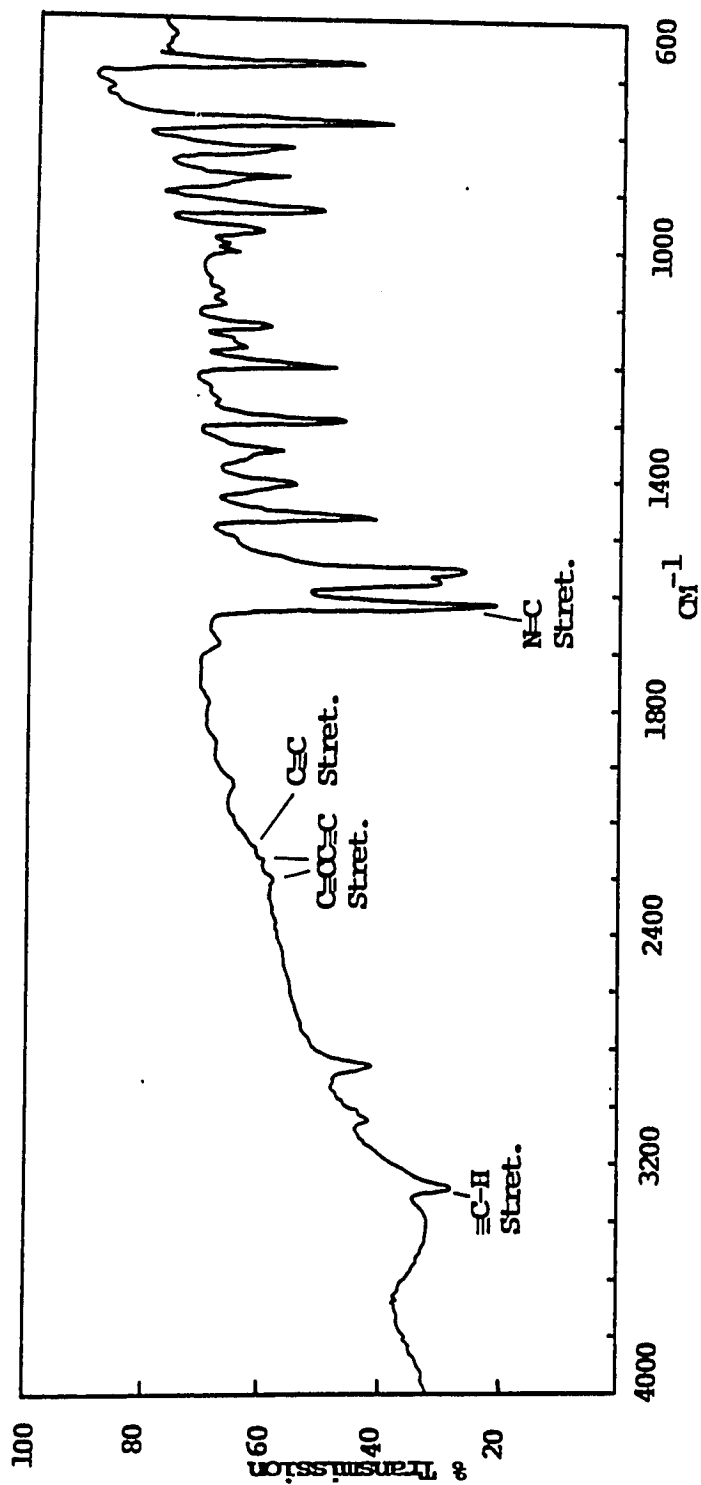


Fig.2b. IR spectrum of PMEM(1) (KBr)

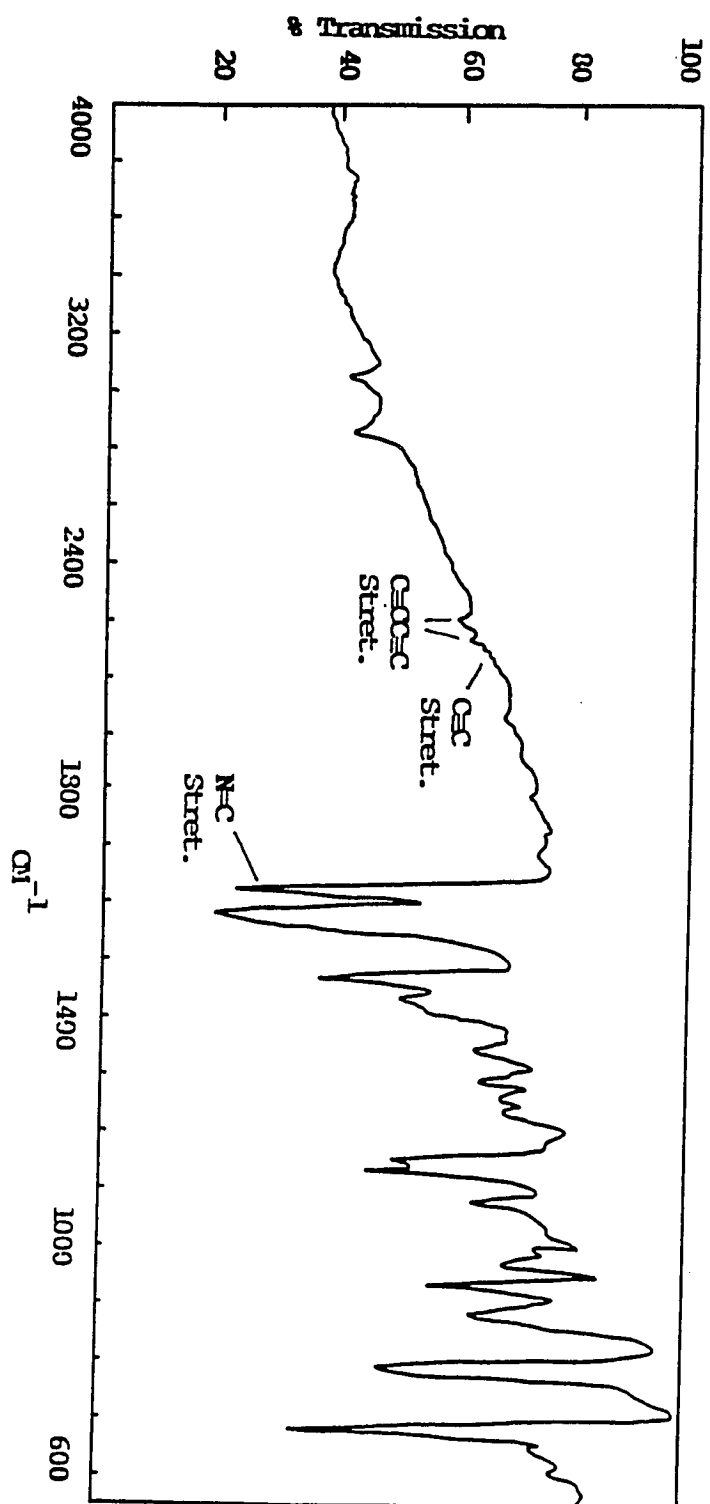


Fig.3. IR spectrum of PMAM(2) (KBr)

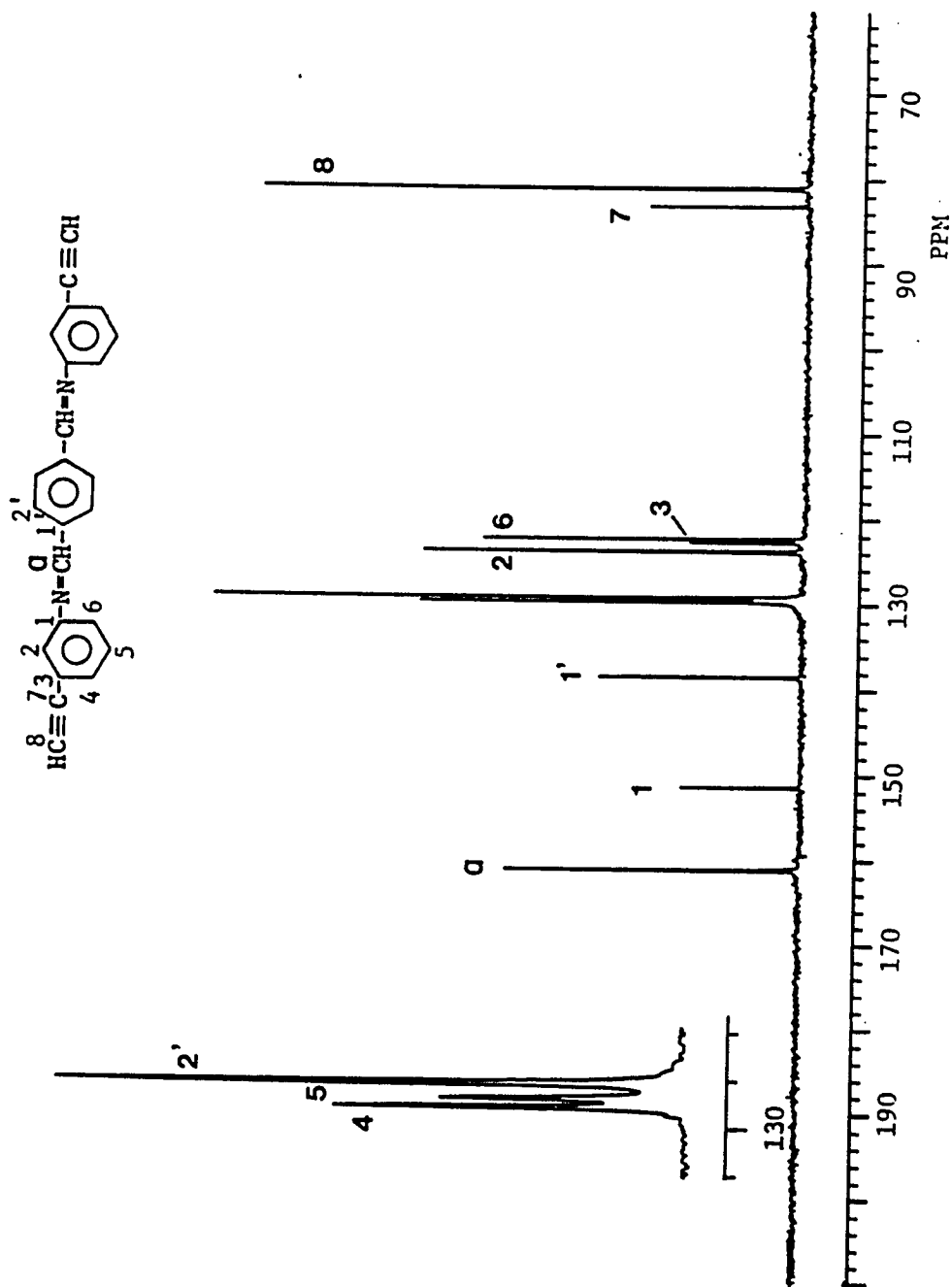


Fig.4a. ^{13}C NMR spectrum of MPM in DMSO-d_6

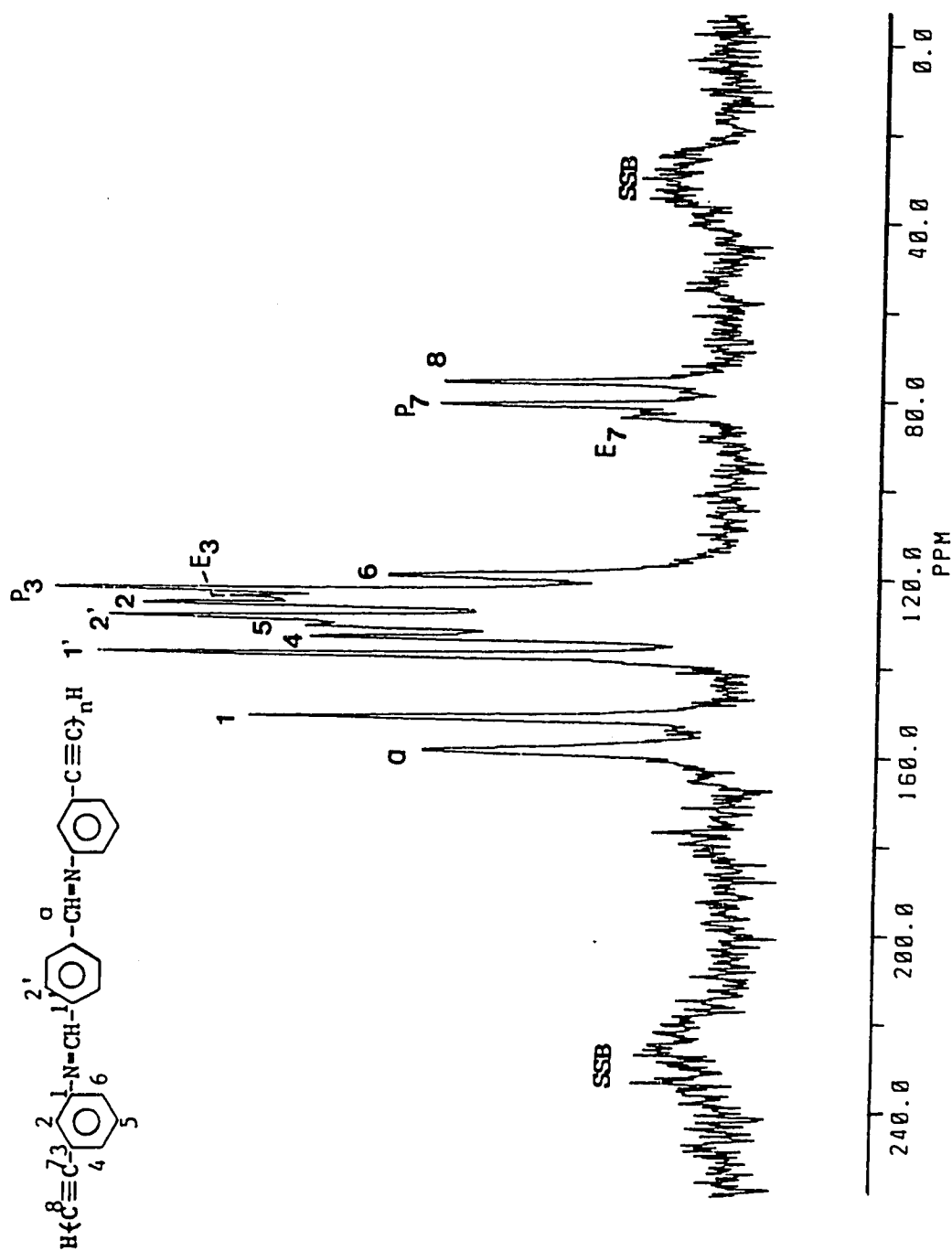


Fig.4b. ^{13}C NMR spectrum of PMEM in solid state (E refers to the carbon atoms in the polymer chain end; P and the numbers, to those in the polymer chain center.)

4.2.3 ^1H AND ^{13}C NMR SPECTRA AND REACTIONS IN ACIDIC MEDIA

Although PMM is slightly soluble in pyridine, the best solvents are acids. When PMPM and PMM dissolve and are protonated in acid, the color changes from yellow to orange for PMM and to red for PMPM. The results presented in this section, like those of Olah and Kreienbohl[60], show that these protonated imines exist exclusively as iminium ion(22), with negligible contribution by the aminocarocation(23).



(22)



(23)

The polymer solutions in sulfuric acid and methanesulfonic acid seemed to be quite stable because the color of the solutions stands for at least 20 hours, whereas the color of the solutions of the polymers in TFA fades within about 2 or 3 hours. The polymer behavior and structure in each of three acids mentioned above will be discussed below.

In methanesulfonic acid, the polymers, the monomers and the model compounds all dissolve readily at ambient temperature to generate stable iminium ions which yield well resolved ^1H NMR spectra. The chemical shifts and coupling constants, along with those in chloroform-d solvent for reference, are summarized in

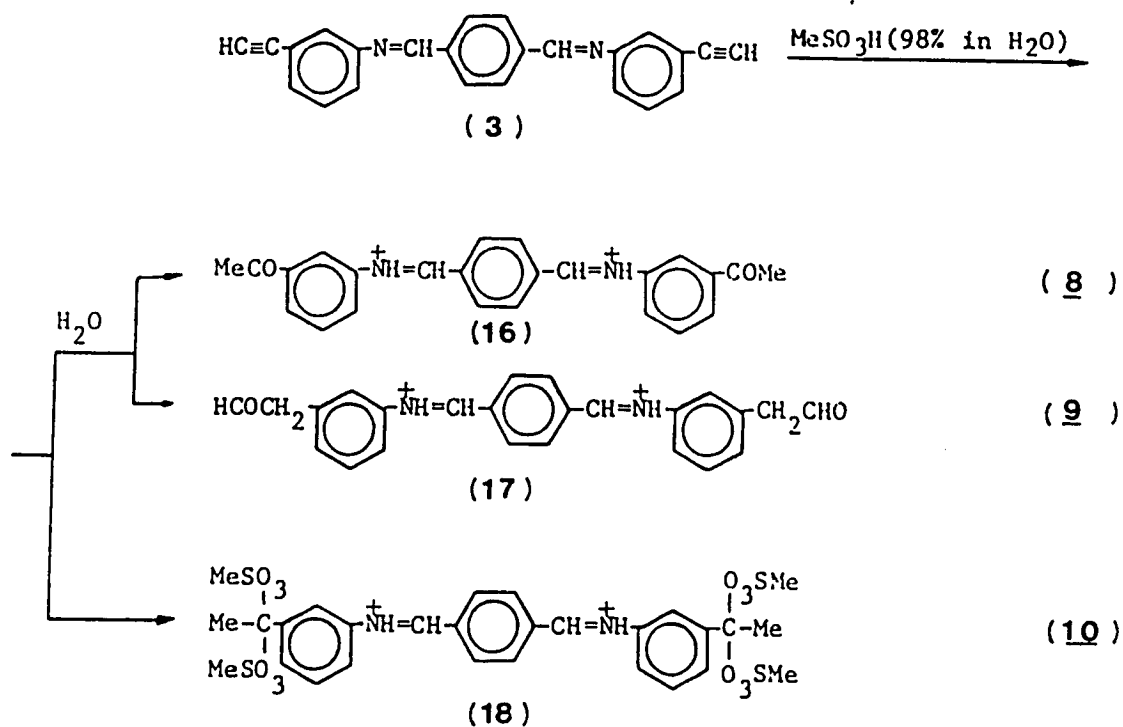
Table 6.

The protonation of the imine group was complete in methanesulfonic acid because no unprotonated imine proton, i.e., $-N=CH-$ proton, was observed in the spectra. The iminium, i.e. $-NH=CH-$, proton appears as a doublet in the region 9.25-9.64 ppm with a coupling constant of about 17 Hz, as expected for the trans- protons on a double bond [37,57,60]. This observation suggests that the imine group in both the small molecules and the polymers exists exclusively in trans-form. The N-H signal was observed in the region 12.12-12.78 ppm. All assignments in the ^1H NMR spectra presented in Table 6 were achieved by comparison with data in the literature[37,57,60], consideration of substituent effect, proton decoupling experiment, and signal intensities.

The spectra of the model compounds(5-7) and PMMM(2) remain stable over a long time period. The spectra recorded 10 minutes after sample preparation were found to be identical to those recorded 10 hours later. However, the spectra of the monomers(3 and 4) and PMPM(1) showed time dependence within the first hour and they remained stable thereafter. Fig.5 gives a comparison of the ^1H NMR spectra of MPM(10% w/v in methanesulfonic acid) taken 10 min. after the sample preparation (Fig.5a) and 1 hour later with the same sample (Fig.5b). The doublet signals at 12.65 ppm and 9.53 ppm in which one peak of the doublet is overlapped with the doublet signal at 9.65 ppm, and the signals at ca. 7-8 ppm in Fig.5a disappear

in Fig.5b.

Such time dependence of the spectra obviously are not caused by the protonation since the disappearing signals at 12.65 and 9.53 ppm were doublets with the same coupling constant ca.17 Hz, which must be the two protons in the protonated imine group, i.e., N-H and =CH- protons, respectively. A downfield shift of these two protons suggests a change of the substituent to a stronger electron-withdrawing group. It was documented [61a] that acetylenic compounds undergo an addition of one water molecule in aqueous acid solution with Hg^{++} catalyst (or in concentrated sulfuric acid) to generate a ketone as the main product. Therefore, an addition of water to the acetylenic group of MPM could rationalize the above observations as showed in Scheme 3.



Scheme 3. Reactions of ethynyl end group in MeSO₃H.

Product (16) is from an addition followed Markovnikov's rule, and (17) is an anti-Markovnikov addition product. The water came from the solvent (remember, 98% methanesulfonic acid was employed.). After all water molecules in the solvent have been consumed, the methanesulfonic acid molecule may attack the triple bond to form an addition product (18). The main product would be expected reasonably to be the one following the Markovnikov's rule, i.e. the product (16). The methyl proton signal of compound(16) were not observed in the spectrum (Fig.5b) since it would be hidden by the intensive

methyl peak (3.12 ppm) of the solvent, undeuterated methanesulfonic acid. A ^1H NMR spectrum of pure acetophenone taken in methanesulfonic acid also showed the overlap of the methyl signals. The existence of the acetyl group was ascertained by ^{13}C NMR spectroscopy which will be discussed later. Thus, the gradual change of the substituent from a weak electron-withdrawing acetylenic group to a stronger electron-withdrawing acetyl group caused the corresponding changes in the ^1H NMR spectra. The small signals around the main signals in Fig.5b might be due to an incomplete addition or to some side reaction products, (17) or (18).

Similarly, the time dependence of the MMM spectrum can be explained. The spectrum of PMPM showed a time dependence but less than those of MPM and MMM because only the acetylenic end group reacts. The polymer PMMM exhibited no noticeable time dependence in its spectrum owing to its high molecular weight. The presence of the acetylenic end group was at a level too low to generate noticeable signals of acetyl group. The end group in PMPM can be readily identified by comparing its spectrum in methanesulfonic acid (Fig.6) with that of MPM (Fig.5b).

Addition of water to the end group of PMPM gives a polymer (19) with the acetyl group at both chain ends.

Table 6 Assignments of ^1H NMR Spectra of the Polymers, Monomers and Model Compounds

Cpd.	No.	Solvent	$-\dot{\text{N}}\text{H}=$	$-\text{N}=\text{CH}-$	a	b	c	d	e	f
5		MeSO_3H	12.12(d 17.2)	9.25(d 17.2)	8.27(d 7.5)	7.97(t 7.2)				
		DCCl_3		8.40(s)	7.87(m)	/	7.34(m)	/		
6		MeSO_3H	12.65(d 17.2)	9.49(d 17.2)	8.60(s)	7.93(s)	7.74(s)			
		DCCl_3		8.47(s)	7.98(s)	7.39(m)	7.23(m)			
7		MeSO_3H	12.56(d 16.9)	9.47(d 17.2)	9.01(s)	8.74(d 7.6)	8.19(t 7.6)	7.89(s)	7.74(s)	
		DCCl_3		8.45(s)	8.40(s)	8.03(d 7.7)	7.56(t 7.7)	/	7.34(m)	/
3		MeSO_3H	12.80(d 17.1)	9.65(d 17.1)	8.65(s)	8.61(s)	8.46(d 7.9)	8.29(d 7.9)	7.98(t 7.9)	
		DCCl_3		8.47(s)	7.98(s)	/	7.33(m)	/		
4		MeSO_3H	12.78(d 17.2)	9.64(d 17.2)	9.11(s)	8.83(d 7.5)	8.28(m)	8.60(s)	8.44(d 7.6)	7.98(t 7.6)
		DCCl_3		8.44(s)	8.34(s)	8.00(d 7.7)	7.53(t 7.7)	/	7.32(m)	/
1		MeSO_3H	12.70(d 17.1)	9.55(d 17.1)	8.62(s)	8.12(s)	8.00(d 7.5)	7.91(d 7.5)	7.79(t 7.5)	
		TFA	-	9.67(d 12.0)	8.66(s)	/	7.89(m)	/		
2		MeSO_3H	12.61(d 17.1)	9.52(d 17.1)	9.01(s)	8.77(d 7.4)	8.23(m)	7.78(m)		
		TFA	-	9.56(d 11.5)	9.01(s)	8.60(d 7.0)	8.36(t 7.0)	7.80(m)		

Table 7 **Numbering System of the Compounds (1-7)**
for their Proton NMR Spectral Assignments

Cpd. No.	Compound
5	
6	
7	
3	
4	
1	
2	

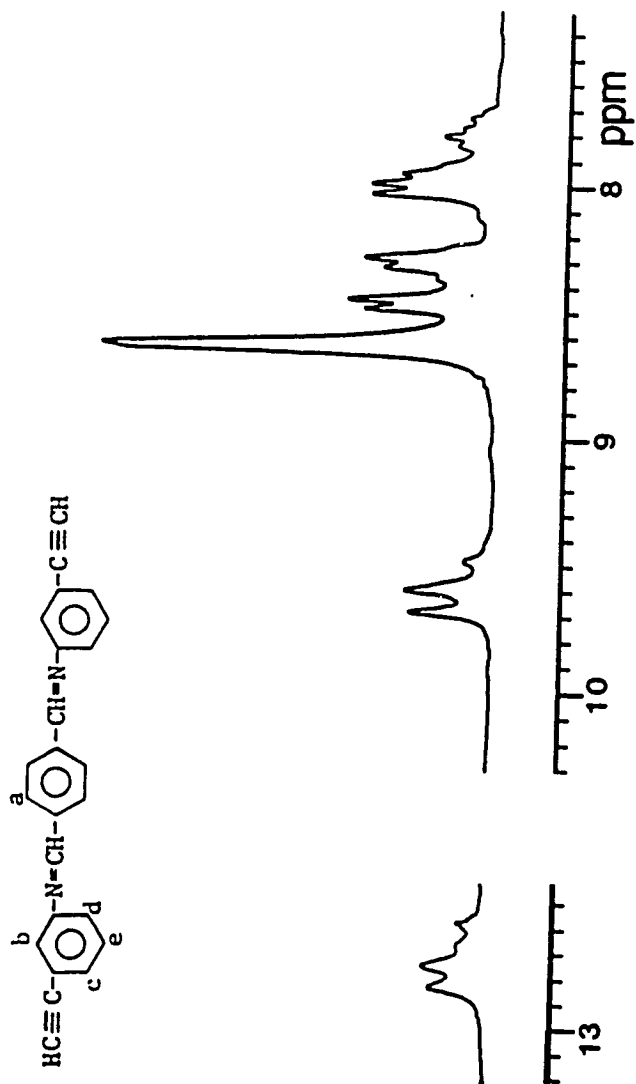


Fig.5a. ^1H NMR spectrum of MEM in MeSO_3H at 10 min after sample preparation

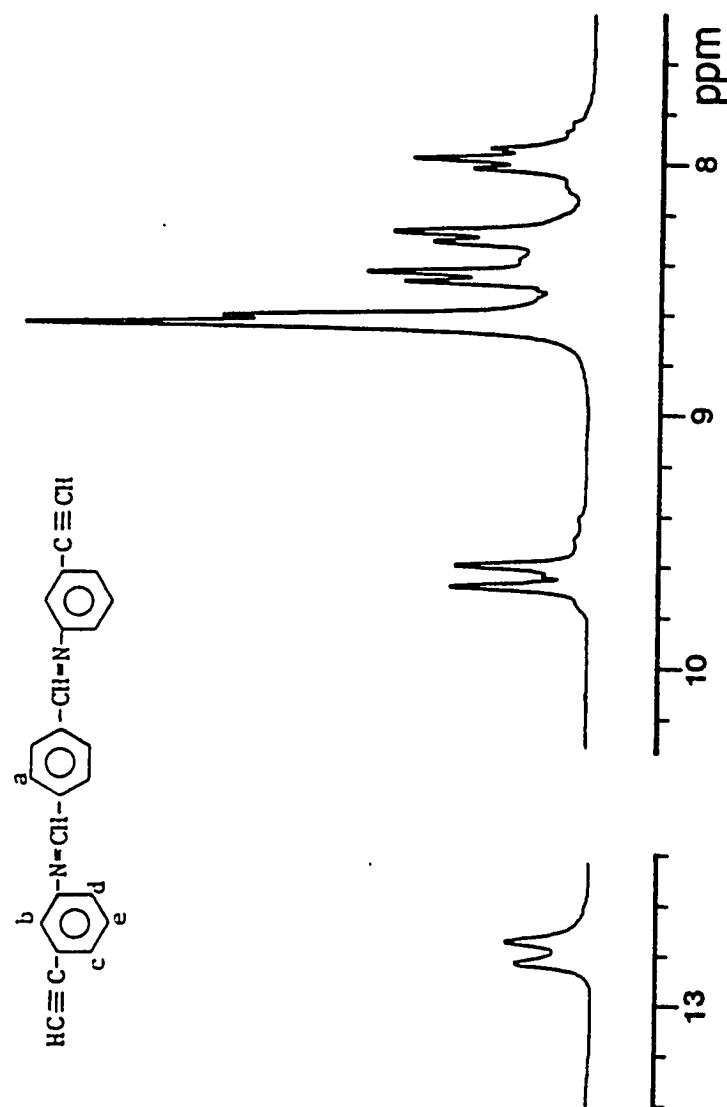


Fig.5b. ^1H NMR spectrum of MPM in MeSO_3H at 60 min. after sample preparation

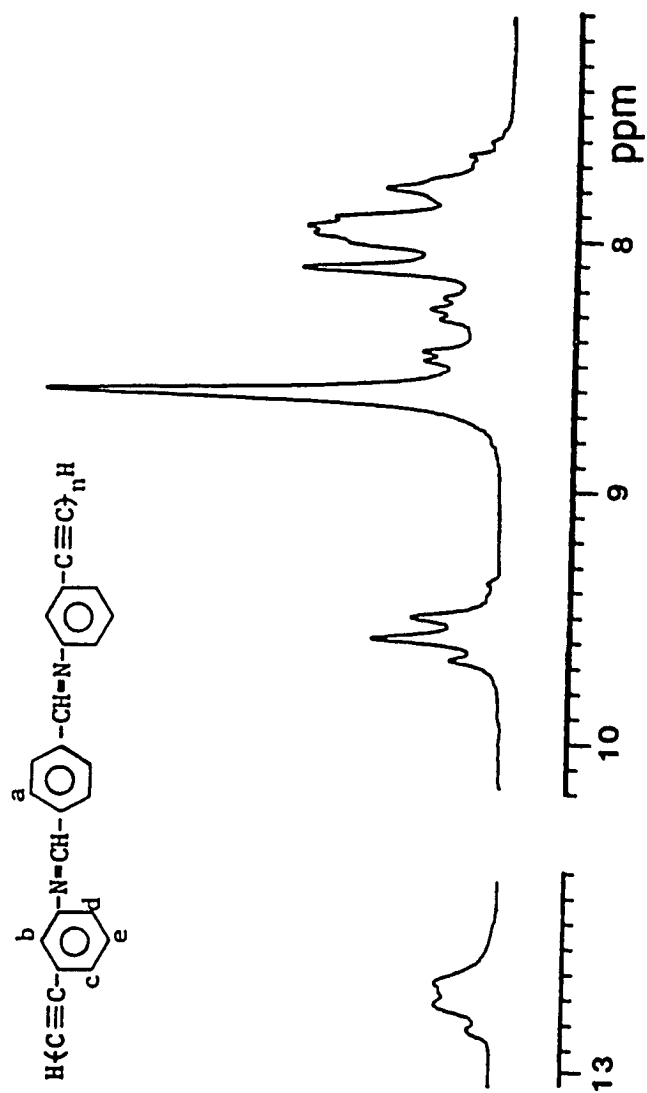
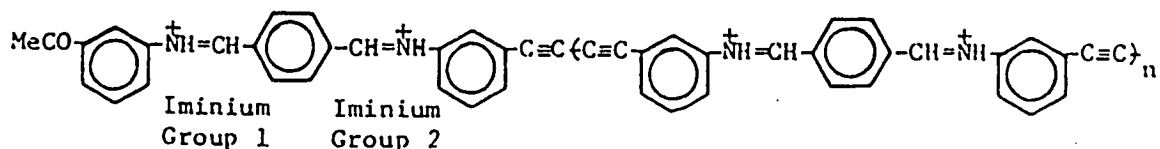


Fig. 6. ^1H NMR spectrum of PMPM in MeSO_3H at 60 min. after sample preparation



(19)

It is expected that in (19) the electron-withdrawing effect from the acetyl group could be transmitted through the phenyl ring to the first iminium group and through another phenyl ring to the second iminium group with much reduced strength, and up to the third and the fourth iminium groups, the effect should be negligible. We found this was true in the spectrum of PMPM. The spectrum of PMPM(Fig.6) showed two doublet signals at 12.80 and 12.70 ppm, with the latter having higher intensity than the former. Comparing to the spectrum of MPM (Fig.5b) , the doublet at 12.80 ppm is assigned to the N-H proton in the first iminium group of the PMPM chain-end, and the doublet at 12.70 ppm to the N-H proton of the iminium group in the center of the polymer chain. Similarly, two doublets at 9.64 and 9.55 ppm which appeared as a triplet signal owing to an overlap of one peak from each doublet are assigned to the $-\text{CH}-$ protons of the iminium groups at the end and the center of the polymer chain, respectively. These as-

signments were verified by proton decoupling experiments in which decoupling of the 12.80 ppm signal had no effect on the 9.55 ppm signal but changed the 9.64 ppm signal to a singlet; whereas decoupling of the 12.70 ppm signal only changed the 9.55 ppm signal to a singlet. The signals of the N-H and -CH- protons in the spectrum of MPM (Fig.5b) are quite sharp, but those in the spectrum of PMPM (Fig.6) are broadened. This broadening of the signals could be attributed to the long range effect of the end group, i.e. the electron-withdrawing effect from acetyl group transmits not only to the first iminium group in (19) but also to the second and/or the third iminium groups with, however, much reduced strength. Obviously, from the intensities of these two doublets, the molecular weight of PMPM could be estimated. The doublet signals at 8.46(J=7.7 Hz) and 8.29 (J=7.8 Hz) are assigned to the aromatic protons at c and d positions of the end group. These two proton signals were found in the spectrum of MPM at the same chemical shifts. The other aromatic proton peaks of the end group all would be hidden by those of the chain center.

The effect of the end-group is much clearer in the ^{13}C NMR spectra of the polymers in methanesulfonic acid solution. The chemical shifts of the model compounds (5-7), the monomers (3 and 4) and the polymers (1 and 2) are listed in Table 8. All assignments are based on the comparison of these spectra, the calculation of the chemical shifts from the model compounds, the intensity of the signals and the information obtained from

the off-resonance decoupling experiments for each compound. The model compounds and PMMM have ^{13}C NMR spectra which possess the correct number of types of the carbon atoms as expected. However, the spectra of the monomers and PMPM are very complicated in that there are many signals with low intensity besides those main signals assigned in Table 8.

From the ^{13}C NMR spectrum of MPM(3) shown in Fig.7, the first feature attracting attention is the lack of signals of two acetylenic carbon atoms which would appear in the range 76-84 ppm. A signal at 208.7 ppm which remains singlet in the off-resonance decoupling experiment suggests the existence of a carbonyl group. A peak at 26.5 ppm which becomes a quartet upon off-resonance decoupling shows a methyl group. The ^{13}C NMR spectrum of protonated acetophenone in methanesulfonic acid supports these assignments with the similar signals at 217.6 and 25.2 ppm for the carbonyl and methyl group, respectively. These observations further prove the conclusion that an addition of water to the acetylenic group takes place to destroy the latter by generating the acetyl group in methanesulfonic acid. There are some small signals in the aromatic carbon area. For instance, the peak at 130.5 ppm, and the shoulders around 132.2 ppm peak. These might be from the products of the minor side reactions or residue of unreacted MPM molecule. A noted side reaction could be an addition of methanesulfonic acid to the acetylenic triple bond to produce an acetal type of adduct(18) which are observed in some

spectra with high sample concentration. The signal at 130.5 ppm in Fig.7 consists of only one data point and is ruled out from the consideration.

Similar observations were made for the ^{13}C NMR spectrum of MMM(4) in methanesulfonic acid solution. The addition products, acetyl group, was also identified by the signals at 208.2 and 26.5 ppm. Again, no acetylenic carbon signal was observed.

The ^{13}C NMR spectra of the polymers, PMPM and PMMM, are given in Figs. 8 and 9, respectively. Two diethynylene carbon atoms show two signals at 81.0 and 75.7 ppm for both polymers. In comparison of the spectra of PMPM (Fig.8) and MPM (Fig.7), the peak at 26.5 ppm in both spectra is apparently attributed to the end-group in which the acetylenic group has changed to an acetyl group by addition of water in methanesulfonic acid. And the signal at 167.4 ppm in the polymer spectrum is assigned to the iminium carbon atom at the end unit of the polymer chain whereas the iminium carbon atoms in the center of the polymer chain appears slightly upfield at 166.7 ppm. In the aromatic carbon signal area, all signals from the end unit of the polymer chain are resolved with low intensities. Their chemical shifts are very similar to those of the monomer, MPM. The noticeable end-group effect shows that PMPM has a relative low molecular weight. The carbonyl carbon atom in the end-group of PMPM was not observed in the PMPM spectrum owing probably to its longer relaxation time. There is no significant end-group effect in the ^{13}C NMR spectrum (Fig.9) im-

plying higher molecular weight. The chemical shifts of all signals are in good agreement with the calculated values.

From the above discussion on ^{13}C NMR spectra, one can conclude that in methanesulfonic acid, a) the protonation of the imine group is complete for both polymers (1 and 2) and all the small molecules (3-7); and b) the water molecule is readily added to the acetylenic triple bond to give an acetyl group as a main product, but has no noted reaction with the diethynylene triple bonds. Lower reactivity of the diethynylene triple bonds than that of the acetylenic triple bond has been observed and reported before [61b]. Since all of the observed peaks in the NMR spectra of the polymers can be assigned to the corresponding polymer structures, there is no evidence for noticeable irregular linkages or moieties in the polymers. This is also the case for the ^1H NMR spectra where vinyl protons, for example, would be discernible if any. Thus, the polymers do not appear to be highly branched or to have undergone reactions other than the normal oxidative coupling during the polymerization. Additional reactions as the Strauss coupling reaction[62]



are copper catalyzed and can occur at elevated temperatures, but usually require acidic conditions. This reaction could

lead to disubstituted vinyl groups in the polymer backbones, but would not result in branching. Not only is there no evidence for these groups in the ^1H and ^{13}C NMR spectra, but also there are no characteristic olefinic absorption in the infrared spectra of either polymers.

In TFA, proton NMR spectra of the polymers (1 and 2) also show some time dependence. The spectrum of PMPM(1) in TFA(10% w/v) recorded at 30 min. after the sample preparation was similar to that of its monomer, MPM(3), in chloroform except the chemical shift changes due to the protonation. However, for the polymer weak signals at 10.20 ppm and in the aromatic carbon area as well as around the signal of the acetylenic proton in the end-group were observed. After 15 hours. from the sample preparation, a spectrum was taken with the same sample. The intensities of these weak signals increased, indicating an involvement of some chemical reaction. A proton NMR spectrum of terephthalaldehyde in TFA exhibited signals of the aldehyde proton at 10.18 ppm and of the aromatic protons at 8.30 ppm, both were found in the spectrum of PMPM. This suggests that the polymer (1) undergoes a hydrolysis in TFA. By comparing the integration of all aromatic proton signals with that of 10.20 ppm signal in the spectra of PMPM, a percentage of hydrolysis of the imine group was estimated to be 18% at 30 min. and 23% at 15 hours. Therefore, the hydrolysis is quite rapid within 30 min. after the dissolution of the polymer.

However, the hydrolysis slows down then and only 5% more imine is hydrolyzed during the next 15 hours. This can be explained by assuming that a limited amount of water is present in TFA(<1%) and this shifts the equilibrium between hydrolysis and condensation. Further support for this explanation is that addition of water to the system sharply increases the intensity of the 10.20 ppm signal. In TFA, there is no sign of any addition of water to the acetylenic triple bond in contrast to that in methanesulfonic acid. A ratio of the signal integration for all aromatic protons to that for the acetylenic proton remains essentially the same in the spectra of PMPM(1) taken at either 30 min. or 15 hours. Similar observations have been made for PMMM.

Both polymers (1 and 2) in TFA generate quite complicated ^{13}C NMR spectra. A carbonyl carbon peak at 197.7 ppm in the PMPM spectrum further proves the existence of hydrolysis in comparison with a carbonyl carbon chemical shift of 199.0 ppm for terephthaldehyde in TFA. Around the signals of the iminium carbon (167.6 ppm) and the alpha-carbon of diethynylene (i.e. C-7, 81.5 ppm), several small peaks were observed owing to the effect of different stages of hydrolysis, i.e. short or long chain residues of the hydrolyzed polymer in the system. The signal for the beta-carbon(i.e. C-8) of the diethynylene group at 77.68 ppm appears alone without small additional peaks since it is further away from the hydrolyzing site and therefore experiences a much smaller effect than the alpha-carbon

does. The absence of a methyl carbon signal in the spectrum indicates that addition does not occur at the acetylenic triple bond. In the ^{13}C NMR spectrum of PMMM(2), the carbonyl carbon signal from the hydrolysis appears at 197.0 ppm, and two diethynylene carbon signals at ca. 81.0 and 77.5 ppm, respectively.

In concentrated sulfuric acid, the solution of PMPM(1) has a more intense color than that in TFA and methanesulfonic acid. Proton NMR spectrum of PMPM in conc. sulfuric acid is similar to that in methanesulfonic acid. No hydrolysis was observed. However, its ^{13}C NMR spectrum is very complex with a poor signal to noise ratio and shows neither acetylenic nor diethynylene carbon signal. Y.Vo-Quang and coworkers reported[63] that diphenyl butadiyne reacts with concentrated sulfuric acid to yield many products among which 64% of 2,5-diphenyl furan (20c) and 13% of $\text{PhCH}_2\text{COCH}_2\text{COPh}$ (20a and b) were found as shown in Scheme 4. It is reasonably to propose that similar reactions occur in PMPM(1) in concentrated sulfuric acid.

Table 8 Assignments of ^{13}C NMR Spectra of the Polymers, Monomers and Model Compounds in Methanesulfonic Acid

Cpd. No.	N=CH	1	2	3	4	5	6	7	8	1'	2'	3'	4'	5'	6'	Remark
5	166.7	136.2	121.5	133.3	130.9					126.9	132.0	130.7	139.5			
6		136.2	121.5	133.3	130.9					129.1	135.6			133.3	143.1	Calc.
	165.2	136.1	121.9	133.1	131.2					128.7	136.2			132.5	140.8	
7		136.2	121.5	133.3	130.9					137.9	134.4					Calc.
	165.1	136.9	122.2	133.4	123.7					133.6	134.4					
3		138.1	127.3	136.5	128.9	135.4	135.3			128.7	136.2					Calc.
	167.4	137.0	125.4	136.8	129.1	134.3	123.3			133.8	134.1					
4		138.1	127.1	136.2	136.4	135.1	135.2			128.7	136.2			132.5	140.8	Calc.
	167.3	136.9	125.2	136.8	131.8	134.1	123.1			128.6	137.0			132.2	141.6	
1		136.3	126.2	127.2	127.7	133.6	123.2			133.6	134.4					Calc.
	166.7	136.4	125.6	123.8	131.7	132.2	123.3	80.98	75.7	133.8	133.9					
2		136.3	125.9	126.9	135.2	133.3	122.9			128.7	136.2			132.5	140.8	Calc.
	165.8	136.5	125.5	123.8	132.8	131.7	123.6	80.93	75.7	128.7	136.7			131.9	141.5	

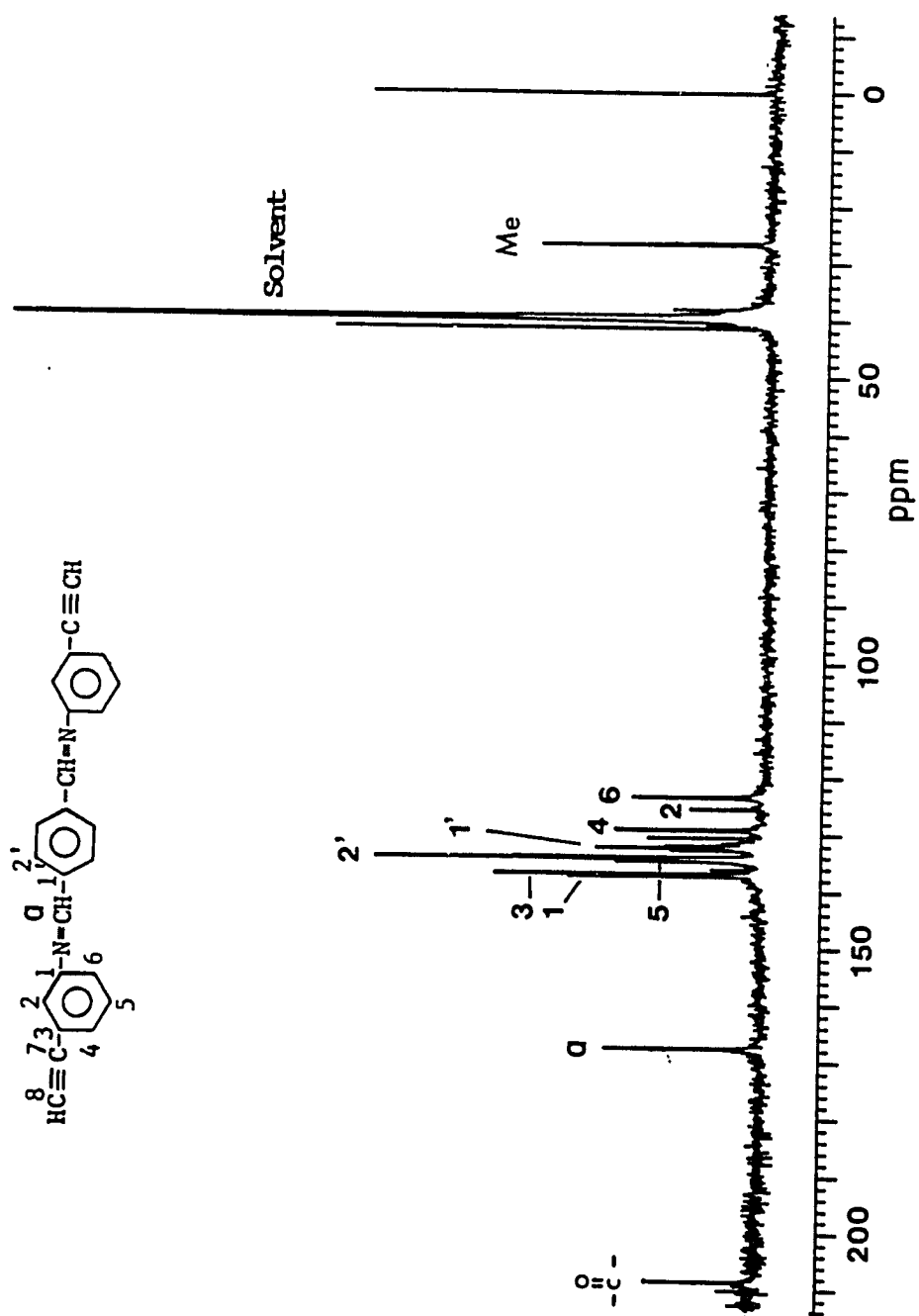


Fig.7. ^{13}C NMR spectrum of MEM in MeSO_3H

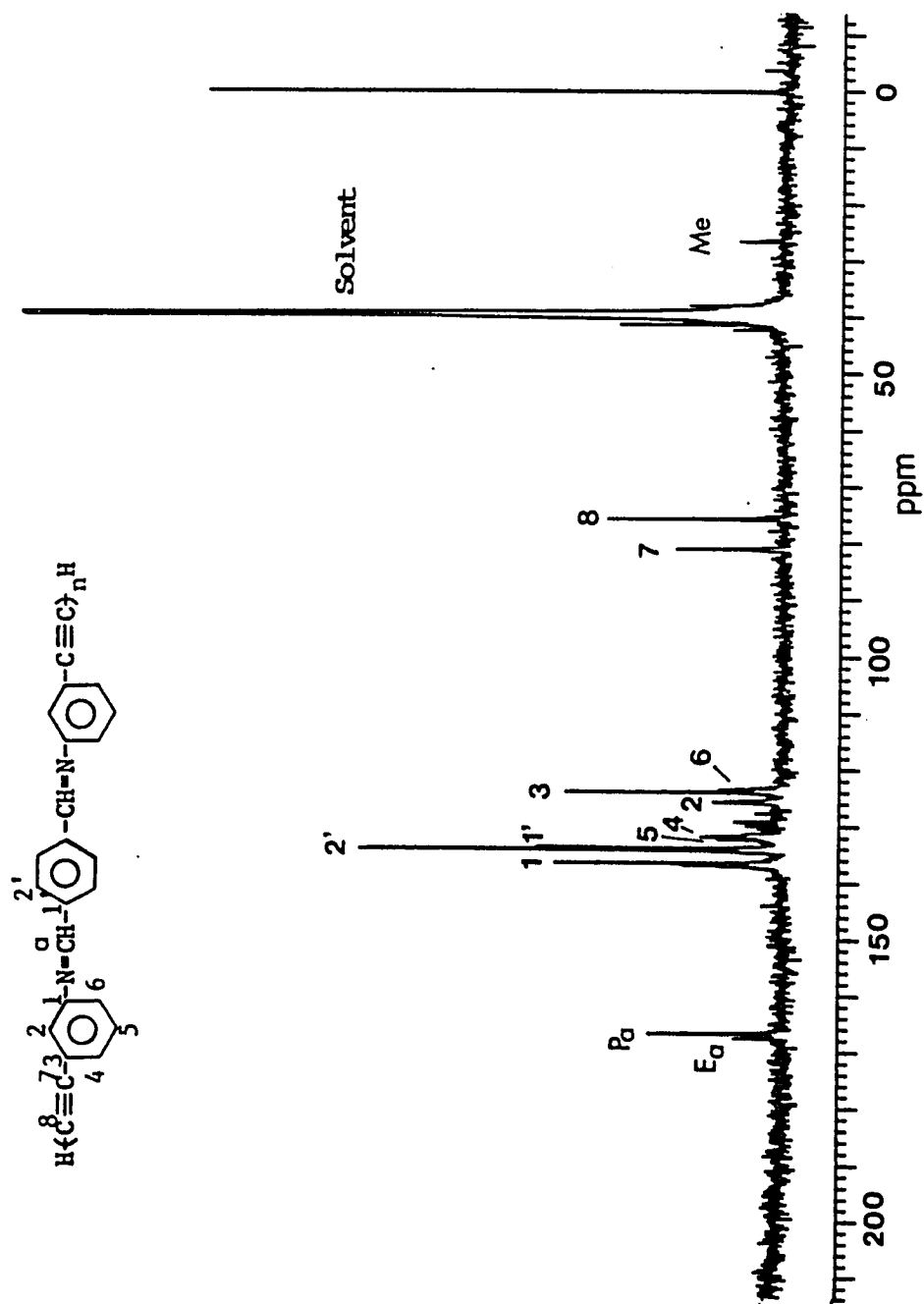


Fig.8. ^{13}C NMR spectrum of PMPM in MeSO_3H

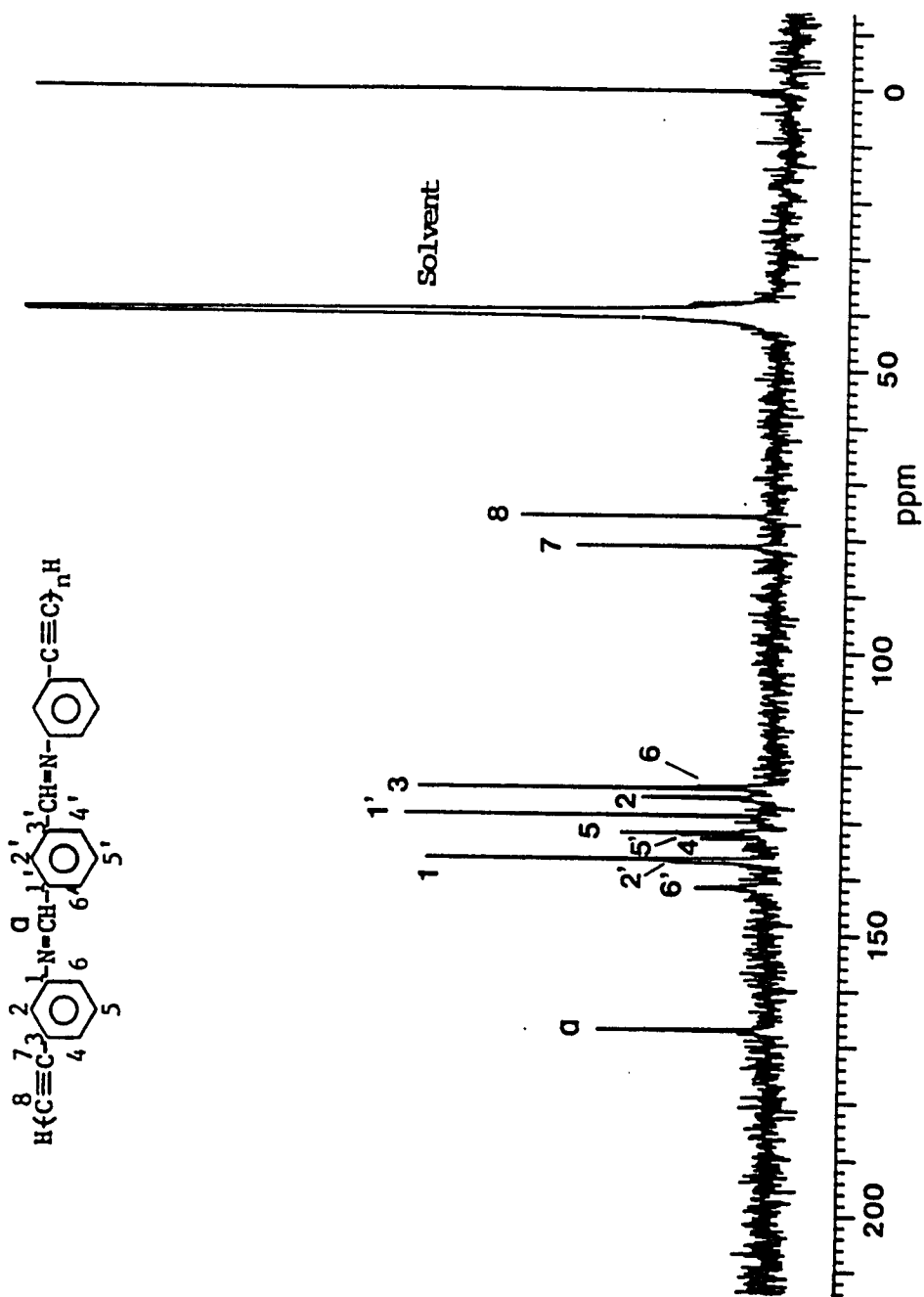
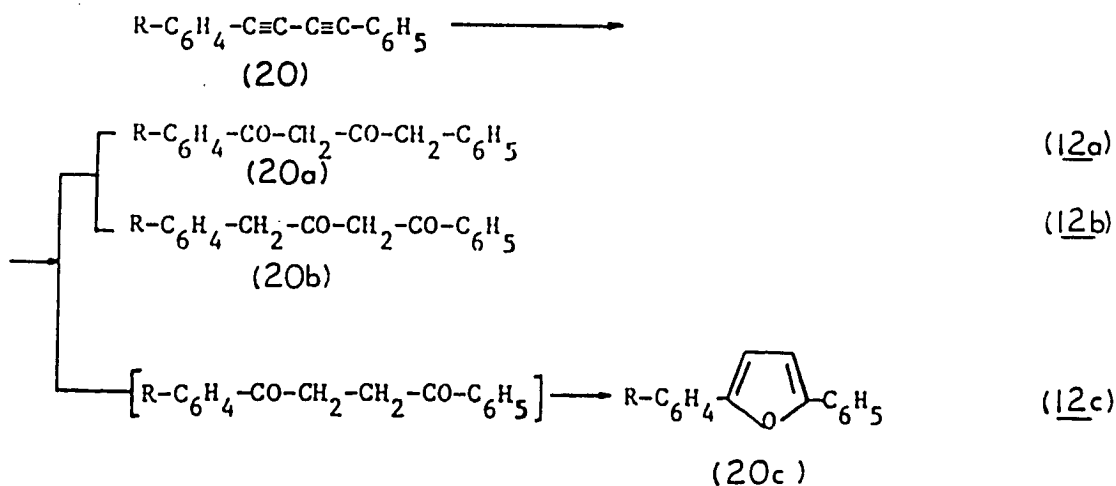


Fig.9. ^{13}C NMR spectrum of ENAM in MeSO_3H



Scheme 4. Reactions of diethynylene group in concentrated H_2SO_4 .

The polymer chain containing a furan ring would be a main product. The more intense color and the poor S/N ratio might be attributed to better conjugation between the furan and phenyl rings, possibly better than that between diethynylene and phenyl groups. The furan proton was not observed in the proton NMR spectrum of PMPM because its signal might overlap with the signals of the aromatic protons. Addition of water to the acetylenic end-group also produces an acetyl group as the main product which was confirmed by observing a methyl and a carbonyl carbon signals at 26.5 and 220.8 ppm, respectively, in the ^{13}C NMR spectrum of PMPM(1) in concentrated H_2SO_4 . In the same solvent, a ^{13}C NMR spectrum of acetophenone shows the

methyl and the carbonyl carbon signals at 25.3 and 219.9 ppm, respectively.

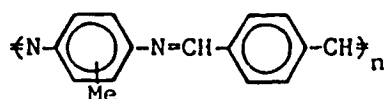
4.2.4 MOLECULAR WEIGHT OF POLYMERS

The molecular weight of the polymers(1 and 2) was measured by means of NMR spectroscopy from a) the ratio of the signal integration of all aromatic protons to that of the acetylenic protons at the chain-end in the proton NMR spectra of the polymers in TFA; b) the ratio of the signal integration of the iminium protons or carbons in the center of the polymer chains to those at the chain-ends in the ^1H or ^{13}C NMR spectra of the polymers in methanesulfonic acid. As an example for the method a), a spectrum of PMPM in TFA-d is given in Fig.15. The ratio of the integration of two aromatic peaks at 8.66 and 7.89 ppm to that of the acetylenic proton at 3.35 ppm is ca. 26.7, corresponding to a molecular weight of 1470. All methods gave very similar results. Thus, the number average molecular weight is ca. 1500 ($n=4-5$) for PMPM(1) and ca. 16000 ($n=50-55$) for PMMM. The lower molecular weight for PMPM is expected because the propagation of the polymer chain is limited by its poor solubility in the polymerization system. The difference of the molecular weights between two polymers is also reflected in their intrinsic viscosities which were measured in methanesulfonic acid at 25°C giving $[\eta] = 20.8 \text{ ml/g}$ for PMPM and $[\eta] = 48.0 \text{ ml/g}$ for PMMM. B.Millaud and C.Strazielle[20] reported a

Mark-Houwink relation,

$$[\eta] = 1.9 \times 10^{-3} M^{1.20} \quad (13)$$

for a polyazomethine (21) in concentrated sulfuric acid.



(21)

Because the similarity between (21) and the polymers (1 and 2), the molecular weights of PMPM and PMAM were calculated by using this relation to be 2300 and 4700, respectively. The result for PMPM is comparable to that from NMR, but for PMAM it is too low. B. Millaud et al. concluded [20] that the polymer (21) has a semi-rigid conformation since the exponent α of the viscosity law ($\alpha = 1.20$) is between a flexible chain ($\alpha = 0.8$ in a good solvent) and the rigid rod ($\alpha = 1.6$). Therefore, PMPM could possess a semi-rigid conformation as (21) and PMAM could be more flexible.

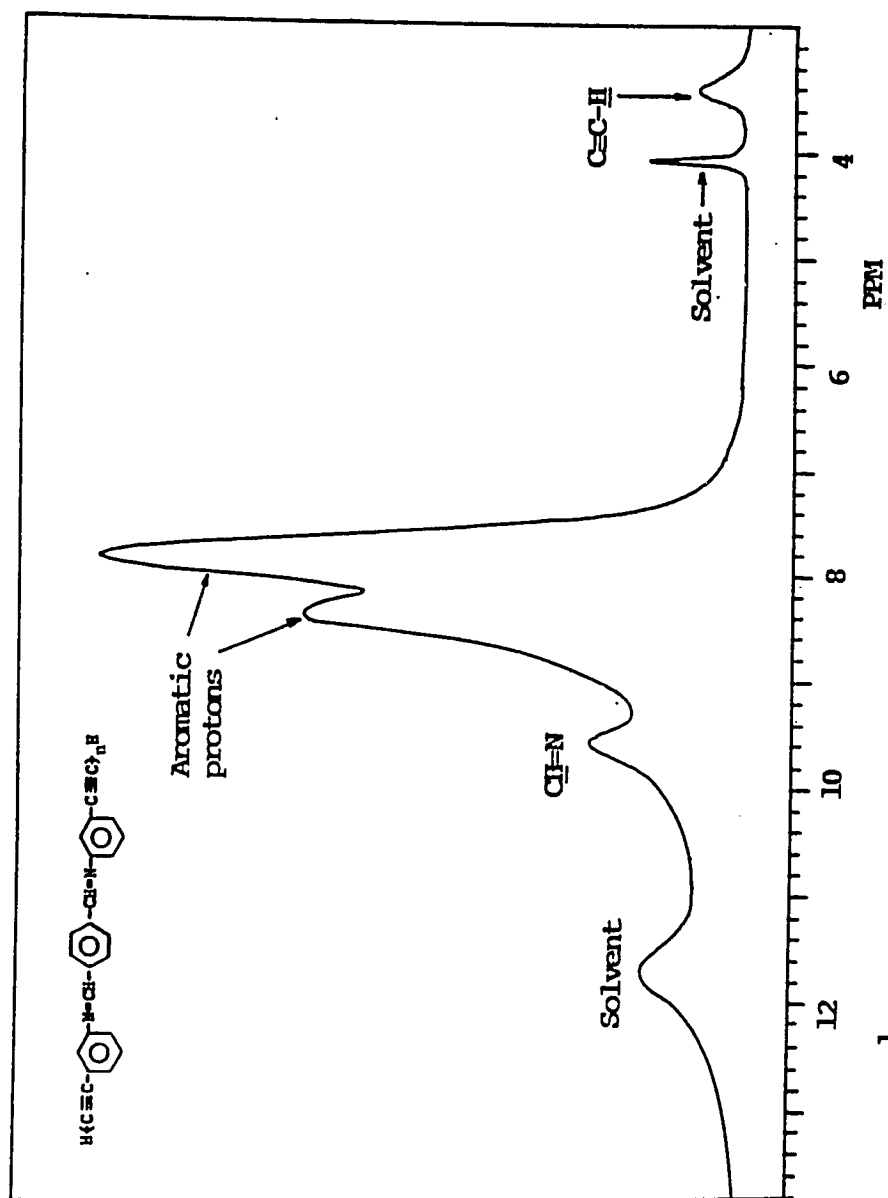


Fig. 15. ^1H NMR Spectrum of PEM in TFA-d .

4.3 CONFORMATION OF AROMATIC AZOMETHINES AND POLYMERS

Conformation of the polymers, PMPM and PMMM, as well as the compounds (3-9) has been studied by means of ^1H NMR and UV spectroscopies in various media.

4.3.1 ^1H NMR SPECTRA OF 4'- AND 4-SUBSTITUTED TRANS-N-BENZYLIDENEANILINES IN ACIDIC SOLUTION

4.3.1.1 SPECTRAL ASSIGNMENTS

The various 4-substituted trans-N-benzylidene anilines dissolve in TFA-d and D_2SO_4 at ambient temperatures to generate stable iminium ions which yield well resolved ^1H NMR spectra. The iminium proton ($\text{H}-\alpha$) appears as a singlet since the nitrogen holds a D instead of ^1H . The structure of the protonated imine group as the trans-iminium ion was ascertained by using undeuteriated TFA or H_2SO_4 (with D_2O in an external capillary tube to lock the spectrometer). No significant change in chemical shifts were found. The signal for $\text{H}-\alpha$ was a doublet, with a coupling constant in the range 14-17 Hz, as expected for trans-protons on a double bond [37,57,60]. The cis H-H coupling constants are considerably lower. No N-H single was observed, probably owing to the quadrupole interaction with the ^{14}N [37,60]. (Similar results were observed in a mixture of deuteriated and undeuteriated acids.) The ^1H NMR spectra in the various acid media showed protonation(with ^1H or D) to be complete, i.e. the protonated trans-N-benzylideneanilines consist exclusively of the iminium ion

(22). The assignment of signals in the ^1H NMR spectra of the various trans-N-benzylideneanilines in TFA- d will now be considered. The assignment of the most downfield signal(in the region 8.9-9.5 ppm) to H- α is well established [37,60]. Assignment of H-2' and other aromatic proton signals is more difficult. The aromatic protons of both compounds (9) and (8) can be divided into three groups. Figure 10a and 10c show the spectra of 4-methoxy- and 4'methoxy-trans-N-benzylideneanilines (15% w/v) as typical examples. For the 4-methoxy compound (Fig.10a), one observes doublets at 8.21 ppm ($J=7.04\text{Hz}$), each for two protons, and a multiplet at 7.71-7.92 ppm for five protons. (The fine structure of the multiplet is more clearly seen at lower concentrations). The coupling constants for the 8.21 and 7.16 ppm signals indicate that these protons are not in the same benzene ring. This was verified by a proton decoupling experiment in which decoupling of the 8.21 ppm signal had no effect on the 7.16 ppm signal. When the 4-substituent is changed from CH_3O to the more electron-withdrawing NO_2 group, the 7.16 ppm signal shifts considerably downfield to 8.58 ppm, showing this signal to be due to the protons ortho to the substituent, i.e. H-3. The 8.21 ppm signal is far less affected when the substituent is changed, and this most downfield of the aromatic signals is assigned to the H-2' protons, since H-2' is nearest the iminium group. The signals in the 7.71-7.92 ppm region are due to the H-3', H-4' and H-2 protons, but individual signal assignments were not

possible. 4'-Methoxy-trans-N-benzylideneaniline has a ^1H NMR spectrum (Fig.10c) similar to that of the 4-methoxy compound, with two doublets at 7.28 and 8.24 ppm, each for two protons, and a singlet at 7.63 ppm for five protons. The two doublets represent protons in the same benzene ring, as indicated by their having the same coupling constant ($J=8.99\text{Hz}$). A decoupling experiment verifies this conclusion; decoupling at 8.24 ppm changes the signal at 7.28 ppm from a doublet to a singlet. When the 4'-methoxy is replaced by a 4'-nitro group, there is a drastic shift of the 7.28 ppm doublet downfield to 8.58 ppm. The 7.28 and 8.24 ppm signals are assigned to the H-3' and H-2', respectively. The five proton signal at 7.63 ppm is due to the H-2, H-3 and H-4, protons, but individual signal assignments were not made. The ^1H NMR spectra of the various trans-N-benzylideneanilines in D_2SO_4 are the same as those in TFA-d in terms of the relative positions and splitting patterns of signals, but all signals are shifted upfield by about 0.6 ppm in D_2SO_4 relative to TFA-d. Signal assignments in DMSO-d_6 follow in a similar manner from those described above for TFA-d. Figures 10b and 10d show the ^1H NMR spectra of the 4-methoxy and 4'-methoxy compounds (12% w/v), respectively, in DMSO-d_6 . For 4-methoxy-trans-N-benzylideneaniline (Figure 10b), one observes doublets at 6.97 and 7.31 ppm, each for two protons, a multiplet at 7.46-7.54 ppm for three protons and a multiplet at 7.87-7.99 ppm for two protons. The two doublets have the same coupling constant ($J=8.87\text{Hz}$) indicating that

these protons are next to each other on the same benzene ring. When the 4-substituent is changed from methoxy to nitro, the 6.97 ppm signal shifts drastically downfield to 8.26 ppm while the 7.31 ppm signal is far less affected. The 7.31 and 6.97 ppm signals were assigned to the H-3 and H-2 protons, respectively. The multiplet at 7.87-7.99 ppm (the most downfield signal other than the imine proton signal at 8.63 ppm) is assigned to H-2' since the H-2' protons are closer to the electron-withdrawing imine groups than the H-3' and H-4' protons. The 7.46-7.54 ppm multiplet is assigned to the H-3' and H-4' protons. The ^1H NMR spectrum of 4'-methoxy-trans-N-benzylideneaniline (Fig.10d) consists of coupled doublets ($J=8.78$ Hz) at 7.06 and 7.91 ppm, each for two protons, and a multiplet at 7.15-7.53 ppm for five protons. (The doublets in this spectrum as well as those in the other spectra are not simple doublets. They are each actually part of an AB quartet or, to be even more precise, part of an AA'BB' system). The doublet at 7.06 ppm moves drastically downfield to 8.17 ppm when the 4'-substituent is changed from methoxy to nitro. The 7.06 and 7.91 ppm doublets are assigned to the H-3' and H-2' protons, respectively. The five proton multiplet is assigned to the H-2, H-3, and H-4 protons.

The H-2' protons are isochronous, having the same chemical shift. Similar observations were made for the H-3' and H-3 protons in those compounds where the assignments of these

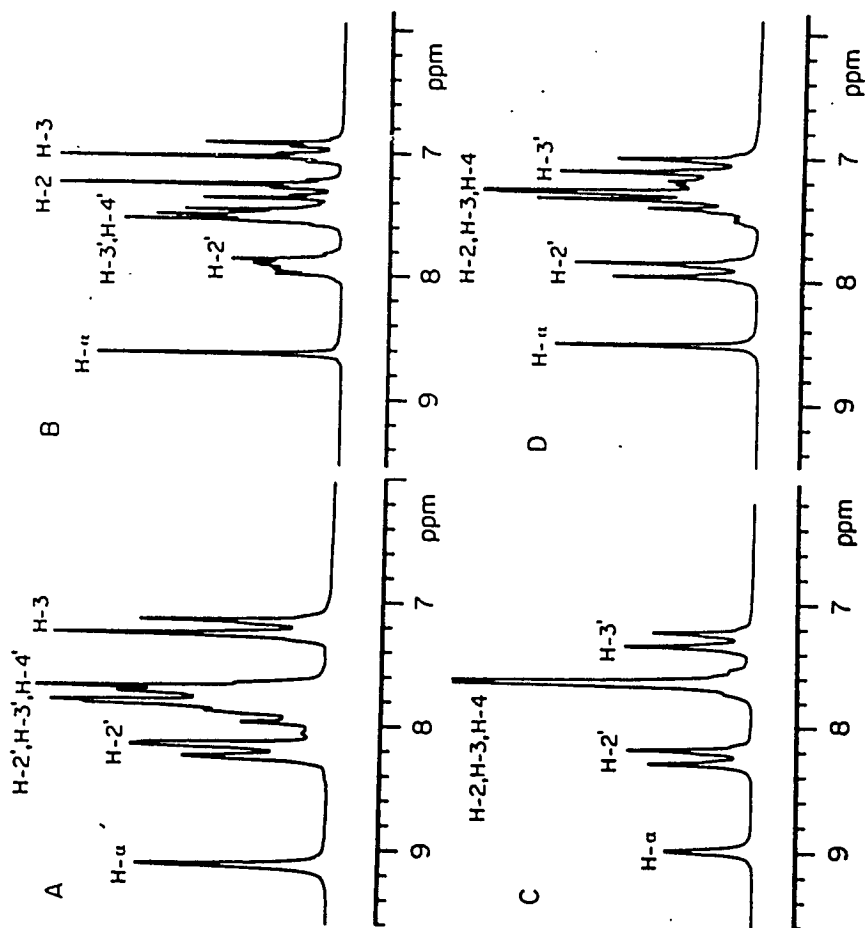


Fig.10. ^1H NMR spectra of 4- and 4'-methoxy-trans-N-benzylideneanilines. A) $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{OCH}_3$ in TFA-d. B) $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{OCH}_3$ in DMSO- d_6 . C) $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$ in TFA-d. D) $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$ in DMSO- d_6 .

protons were unambiguous. One concludes that the conformations of the trans-N-benzylideneaniline system are averaged at this temperature by rapid rotation about the dihedral angles θ and ϕ , as previously reported by Gil and Saraiva[38].

4.3.1.2 SUBSTITUENT EFFECTS ON CHEMICAL SHIFTS

Since previous work established the coplanarity of the benzaldehyde ring and the imine group, the emphasis in the present study was on the relationship of the aniline ring with the imine group and benzaldehyde ring. Thus, the effect of 4-substituents on the chemical shifts of H- α and the protons on the benzaldehyde ring were of most interest. Of the various protons on the benzaldehyde ring, the 2'-proton was found to be essentially the only one whose assignment was unequivocal for all compounds (see below) and our study was limited to this aromatic proton, in addition to H- α .

The chemical shifts, $\delta_{\text{H-}\alpha}$ and $\delta_{\text{H-2'}}$, of the α - and 2'-protons in the 4- and 4'-substituted trans-N-benzylideneanilines in various solvents are shown in Tables 10 and 9, respectively. The effect of substituents on δ was analysed by the Hammett-type relationship:

$$\delta = \delta_0 + \rho\sigma \quad (14)$$

where δ_0 is the chemical shift of the unsubstituted compound

(i.e. substituent-H), σ is the Hammett substituent constant and ρ indicates the sensitivity of δ towards changes in electron donation or electron withdrawal. Positive and negative ρ values correspond to downfield shifts by electron-withdrawing and electron-donating substituents, respectively. Calculated values are shown in Tables 10 and 9. (para σ values were used for all correlations except those of the 4'-substituents on H-2'; meta values were used for the latter, since the 4'-substituent and H-2' have a meta relationship).

$\delta_{H-\alpha}$ for the 4'-substituted trans-N-benzylideneanilines in DMSO shows a good correlation with σ . The ρ value is 0.259 ± 0.015 , which agrees well with the values obtained by other workers. Khoo[29] found $\rho = -0.24$ in DMSO while Inamoto and co-workers, Sandhu and Mago [30] and Tabei and Saitou [23] found ρ to be in the range 0.14-0.18 in cyclohexane, chloroform and carbon tetrachloride. $\delta_{H-\alpha}$ for the 4-substituted trans-N-benzylideneanilines was found to be essentially independent of σ , as $\rho = -0.00617 \pm 0.00926$. This result also agrees well with those of previous workers[23,28-30]. The ρ values for $\delta_{H-2'}$ for the 4'- and 4-substituted trans-N-benzylideneaniline were found to parallel those for $\delta_{H-\alpha}$, with values of 0.451 ± 0.062 and 0.038 ± 0.018 , respectively. The results for both $\delta_{H-\alpha}$ and $\delta_{H-2'}$ support the twist conformation (5) for trans-N-benzaldehyde ring. The lack of coplanarity precludes the transmission of the electronic effect of a substituent on the aniline ring, not

only by resonance but apparently also by induction.

The results in acidic media are in marked contrast to those in neutral DMSO, especially with respect to the effect of substituents in the aniline ring on $\delta_{H-\alpha}$ and $\delta_{H-2'}$. Electron-withdrawing and electron-donating substituents cause significant downfield and upfield shifts, respectively, in both $\delta_{H-\alpha}$ and $\delta_{H-2'}$ for the 4-substituted trans-N-benzylideneaniline in TFA-d and D_2SO_4 (Table 10). The ρ values for $\delta_{H-\alpha}$ are 0.306 and 0.305, respectively, in TFA-d and D_2SO_4 ; the ρ values for $\delta_{H-2'}$ are 0.141 and 0.170, respectively; cf. the corresponding values in neutral DMSO of 0.00617 and 0.0380, respectively. The Hammett plots for some of these correlations are shown in the lower plots in Figs. 11-13. Thus, protonation of the imine group results in a very significant transmission of electronic effects from a para substituent on the aniline ring to and through the iminium group to the ortho position (i.e. H-2') on the benzaldehyde ring. There is negligible transmission of electronic effects when the imine is not protonated.

Some comment is necessary on the results in TFA-d versus D_2SO_4 . The trends in ρ are exactly the same in the two acids. In fact, the ρ values are independent of the acid within the error limits for ρ . However, the chemical shifts in D_2SO_4 are upfield from those in TFA-d, perhaps owing to differences in solvation in the two solvents and/or the tightness with which

the negative counter-ion (HSO_4^- versus CF_3COO^-) is bound to the positive iminium nitrogen. The chemical shifts for the hydroxy- and methoxy-trans-N-benzylideneaniline were excluded from the calculation of ρ in D_2SO_4 . The methoxy and hydroxy groups are (at least partially) protonated in D_2SO_4 , as evidenced by the fact that each ^1H NMR spectrum consists of a combination of signals for the protonated and unprotonated compound. Further, the chemical shifts for H- α and H-2' in D_2SO_4 deviate considerably (in a downfield direction) from the δ versus σ plots. No corresponding evidence was observed for protonation of the methoxy and hydroxy groups in TFA-d. The chemical shift for 4'-dimethylamino-trans-N-benzylideneaniline was excluded from the calculation in acidic media, since the dimethylamino group is protonated in both TFA-d and D_2SO_4 .

The effect of substituents on $\delta_{\text{H}-\alpha}$ and $\delta_{\text{H}-2'}$ for the 4'-substituted trans-N-benzylideneanilines in TFA-d is shown in Table 9. Hammett plots yielded $\rho = -0.541$ for $\delta_{\text{H}-\alpha}$ (lower plot in Fig.13) and $\rho = -0.547$ for $\delta_{\text{H}-2'}$. Comparison with the corresponding ρ values in DMSO indicates that electronic effects are more strongly transmitted through the benzaldehyde ring in the protonated trans-N-benzylideneaniline system than in the unprotonated system. This is reasonable, since the protonated system places a higher electronic demand on the substituent. The most interesting aspect, however, is that the increase in ρ for the 4'-substituted trans-N-

-benzylideneaniline is less than that for the 4-substituted series. Protonation results in a very significant change in electronic transmission from and through the aniline ring, through the iminium group, over to H-2' on the benzaldehyde ring.

The Taft dual substituent parameter (DSP) method[64-66] was applied to the chemical shift data in order to gain insight into the mode of electronic transmission in protonated trans-N-benzylideneanilines. The DSP technique relates the substituent chemical shift (SCS) to a linear combination of polar and resonance factors according to

$$\text{SCS} = \rho_I \sigma_I + \rho_R \sigma_R \quad (15)$$

where SCS is the difference in chemical shift between the unsubstituted and substituted trans-N-benzylideneanilines defined as $\delta - \delta_0$ (i.e. a downfield shift by a substituent yields a positive SCS), σ_I and σ_R are substituent constants defining the polar and resonance electronic transmission effects, respectively, of substituents and σ_I and σ_R measure the susceptibility of SCS to the polar and resonance effects of substituents. While one set of σ_I values has wide utility in all reactions, four different σ_R scales have been defined, σ_R^{BA} , σ_R^+ , σ_R^0 and σ_R^- , depending on whether the detection (reaction) site is a weak or strong electron donor or electron

acceptor.

SCS values are fitted to Eqn (15) using literature values of σ_I and σ_R by a multiple linear regression computer program to yield the values of ρ_I and ρ_R . The "goodness" of the fit is measured by the parameter $f = SD/RMS$, where SD is the standard deviation of the fit and RMS is the root-mean-square of the data. Good correlations are those with $f < 0.1$, acceptable correlations have f values of 0.1-0.2 and poor correlations have $f > 0.2$. The results of a DSP correlations can be graphically represented by reformulating Eqn (15) in the form

$$SCS = \bar{\rho} \bar{\sigma} \quad (16)$$

where $\bar{\rho}$ and $\bar{\sigma}$ are apparent single substituent parameters defined by

$$\bar{\sigma} = (\sigma_I + \lambda \sigma_R) / (1 + |\lambda|) \quad (17)$$

$$\rho_I = \bar{\rho} (1 + |\lambda|) \quad (18)$$

$$\rho_R = \bar{\rho} / (1 + |\lambda|) \quad (19)$$

$$\lambda = \rho_R / \rho_I \quad (20)$$

$\bar{\sigma}$ is obtained from the computed ρ_I and ρ_R values by the application of Eqns(17)-(20), and this allows a plot of SCS versus $\bar{\sigma}$.

The DSP fit of the chemical shift data was superior to the single-parameter Hammett fit. This is apparent in the graphical representations of the DSP results shown as the upper plots in Figs. 11-13. Table 11 shows the results of the DSP analysis on the σ_R^0 scale. σ_R^0 gave the best correlation for both $\delta_{H-\alpha}$ and $\delta_{H-2'}$ in the 4-substituted trans-N-benzylideneanilines in both TFA-d and D₂SO₄, although most of the other σ_R scales also yielded acceptable ($f < 0.2$) correlations. σ_R^0 gave acceptable correlations for $\delta_{H-\alpha}$ in the 4'-substituted compounds in all solvents, although the correlations with σ_R^{BA} and σ_R^+ were better in DMSO-d₆ and TFA-d, respectively. The DSP results for $\delta_{H-2'}$ in the 4'-substituted trans-N-benzylideneanilines gave unacceptable correlations ($f > 0.2-0.3$) (the Hammett correlations were also poor for $\delta_{H-2'}$ in the protonated compounds; see Table 9). $\delta_{H-2'}$ in the 4'-substituted series is also the only system studied in which the substituent and detection site are meta to each other. Similar results have been observed in other meta-substituted benzene systems [67,68]. The chemical shifts of meta-protons often yield poor correlations with both the Hammett and DSP equations.

We also attempted a DSP analysis of our chemical shift data for H- α and H-2' of the 4-substituted trans-N-benzylideneanilines in DMSO-d₆, to ascertain whether the lack of a substituent effect on chemical shifts is due to can-

cellation of comparable inductive and resonance effects of opposite directions. No satisfactory DSP correlation was found. If opposing inductive and resonance effects are present, the DSP analysis shows the effects to be very small. The upper limits of ρ_R and ρ_I are 0.05 at most, based on an evaluation of the precision and accuracy of our chemical shift data and DSP analysis.

Consider the ρ_I and ρ_R values for $\delta_{H-\alpha}$. Protonation of the trans-N-benzylideneaniline system increases the sensitivity of $\delta_{H-\alpha}$ toward substituents on the aniline ring to a level comparable to the sensitivity of the unprotonated system toward substituents on the benzaldehyde ring. It is interesting that the values of ρ_I and ρ_R are very similar to those for the chemical shift of the cis- β -proton in para-substituted styrenes ($\rho_I=0.155$, $\rho_R=0.467$)[69,70]. Further, the resonance factor is more important than the polar factor in all systems, with λ being about 2 in the trans-N-benzylideneaniline systems and about 3 in the styrene system. A similar value of λ is found for $\delta_{H-2'}$ for the protonated 4-substituted trans-N-benzylideneanilines (as well as $\delta_{H-\alpha}$ for both the unprotonated and protonated 4'-substituted systems)

The λ values indicate that the resonance effect is more important (but not overwhelmingly) than the polar effect for

electronic transmission from and through the aniline ring, through the iminium group and over to H-2' on the benzaldehyde ring. What is the nature of the resonance and polar effects? There are two basic mechanisms for resonance interaction between a substituent and reaction site-mesomeric polar and through-resonance [66]. In the through-resonance model the effect of a substituent is direct, with π -delocalization from the substituent to and through the ring and then to the reaction site. If through-resonance is important in the protonated 4-substituted trans-N-benzylideneanilines, resonance structures 24d and 24e (Scheme 5) for electron-donating and electron-withdrawing substituents, respectively, are the dominant reason for electronic transmission by resonance. Electron-donating substituents cause upfield shifts for H- α and H-2' by increasing the electron densities at H- α and H-2'. Electron-withdrawing substituents cause downfield shifts by decreasing the electron densities at H- α and H-2'. The through-resonance mechanism is consistent with σ_R^0 yielding the best or, at least, acceptable fits in our DSP analysis, since the probe sites H- α and H-2' are neither strong electron-acceptor nor strong electron-donor sites.

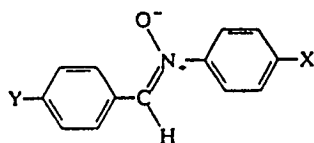
In the mesomeric polar mechanism the effect of a substituent X on the aniline ring is transmitted to the various ring positions (4,3,2,1) by π -delocalization, and from those sites to H- α by field effect and/or σ -bond polarization. The transmission from H- α to H-2' would involve field effect

and/or σ -bond polarization and/or π -delocalization. As with the through-resonance model, the upfield and downfield effects of electron-donating and electron-withdrawing substituents can be rationalized. The lack of substituent effects in unprotonated 4-substituted trans-N-benzylideneanilines argues for the through-resonance mechanism being dominant relative to the mesomeric polar mechanism in the protonated system. We are unable to rationalize any structural difference between the protonated and unprotonated system which would make the mesomeric polar mechanism operative in the former and inoperative in the latter. On the other hand, it is reasonable to propose that the presence or lack of coplanarity between the imine π -bond and aniline ring π -electron system is responsible for the operation or non-operation of the through-resonance mechanism. Considerable evidence (described in the Introduction) indicates that the lack of coplanarity in the unprotonated trans-N-benzylideneanilines is due to delocalization of the nitrogen lone pair of electrons over the aniline ring. It is proposed that protonation prevents delocalization of the nitrogen lone pair, with subsequent coplanarity and π -conjugation between the imine group and aniline ring. This is consistent with the bathochromic shift observed in the UV absorption spectrum of trans-N-benzylideneaniline on protonation [40,43,48]. Coplanarity would not be a requirement for the mesomeric polar mechanism to be operative.

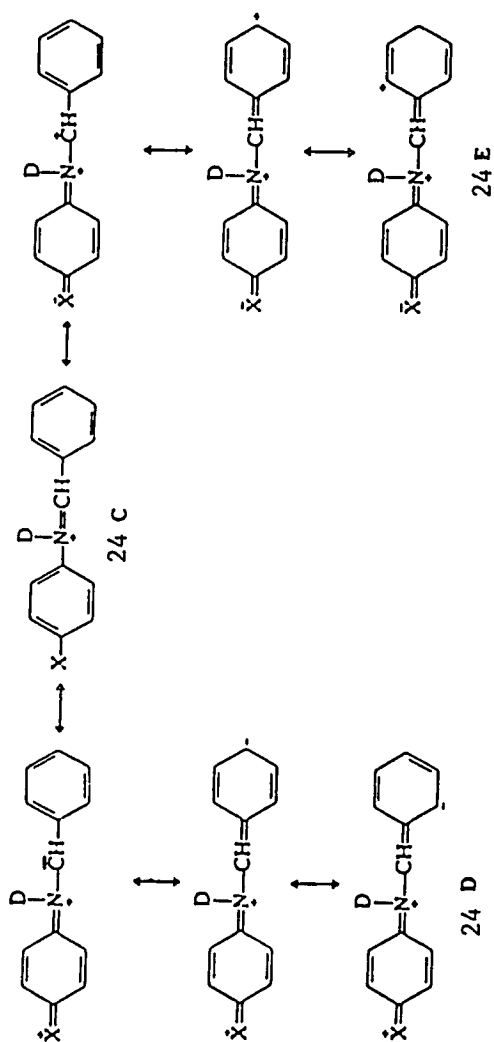
There are two mechanisms for polar electronic transmission- classical inductive and π -inductive [66]. The classical inductive mechanism for the 4-substituted trans-N-benzylideneanilines would involve electronic transmission by field effect and/or σ -bond polarization. The π -inductive (also referred to as π -polarization) mechanism would involve electronic transmission from the substituent to the ipso-carbon (i.e. C-4) by σ -bond polarization and/or field effect, from the ipso-carbon to other ring sites by π -delocalization, from the ring sites to N by field effect and/or σ -bond polarization and from N to H- α and H-2' by π -delocalization and/or field effect and/or σ -polarization. We conclude that the π -inductive mechanism is predominantly responsible for polar electronic transmission in protonated 4-substituted trans-N-benzylideneanilines. The lack of polar electronic transmission in the unprotonated system precludes the presence of the classical inductive mechanism, which should be more or less independent of coplanarity. The presence or absence of coplanarity should affect the extent of electronic transmission by π -polarization.

Recently, Arumugam et al.[71] reported on the effect of substituents on H- α in 4- and 4'-substituted (Z)-N-benzylidenenaphenyl-amine N-oxides (25) in CDCl_3 solution. Hammett correlation yielded ρ values of 0.12 and 0.20, respectively, for substituents in the aniline (Y=H, X=substituent) and benzaldehyde (X=H, Y=substituent) rings.

These results support those of the present study in indicating that a positive charge on the imine nitrogen leads to coplanarity and π -conjugation between the imine group and aniline ring. However, the systems are smaller than in the protonated trans-N-benzylideneanilines, attributable to the smaller positive charge on nitrogen in the former.



(25)



Scheme 5

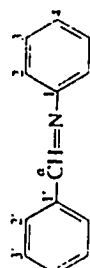


Table 9. Chemical shifts of α -H and H_2 , protons of

Y	δ in DMSO-d ₆ (PPM) ^a		δ in TFA-d ₄ (PPM) ^b		δ in D ₂ SO ₄ (PPM) ^b	
	α -H	H_2	α -H	H_2	α -H	H_2
(CH ₃) ₂ N	8.39	7.74				
OH	8.45	7.77				
OCH ₃	8.52	7.91	8.94	8.18		
CH ₃	8.57	7.87	8.94	8.21		
H	8.62	7.97	9.10	8.12	8.43	7.52
F	8.62	8.01	9.22	8.24	8.54	7.64
Cl	8.63	7.98	9.24	8.38	8.51	7.75
COOCH ₃	8.73	8.09	9.20	8.21	8.52	7.59
COOH	8.72	8.07	9.41	8.48	8.77	7.93
CN	8.75	8.12	9.43	8.53	8.78	8.02
NO ₂	8.79	8.17	9.47	8.47	8.77	7.93
P	0.259±0.015	0.451±0.062	9.52	8.57	8.80	8.12
r ^e	0.985	0.920	0.514±0.046	0.547±0.116	0.427±0.069	0.628±0.201
			0.969	0.854	0.930	0.810

^aDetermined at 8-12% (w/v).

^bExtrapolated value at infinite dilution.

^cCorrelated with σ_p .

^dCorrelated with σ_m .

^eCorrelation coefficient.

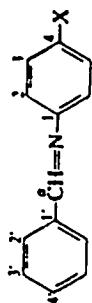


Table 10 Chemical shifts of α -H and H_2 , protons of

X	δ in DMSO- d_6 (PPM) ^a		δ in TFA-d (PPM) ^b		δ in D_2SO_4 (PPM) ^b	
	α -H	H_2	α -H	H_2	α -H	H_2
OH	8.61	7.90	9.11	8.19		
OCH ₃	8.63	7.94	9.09	8.18		
CH ₃	8.62	7.94	9.15	8.20	8.47	7.61
CH ₃ CH ₂	8.62	7.95	9.16	8.21	8.48	7.61
H	8.62	7.97	9.22	8.24	8.54	7.64
F	8.63	7.94	9.19	8.23	8.48	7.63
Cl	8.62	7.96	9.21	8.23	8.52	7.65
I	8.60	7.94	9.23	9.23	8.55	7.65
COOCH ₃	8.64	7.98	9.38	8.31	8.71	7.73
CN	8.63	7.93	9.42	8.33	8.73	7.75
NO ₂	8.62	7.99	9.43	8.34	8.73	7.76
ρ	0.00617 $\pm$ 0.00926	0.0380 $\pm$ 0.018	0.306 $\pm$ 0.029	0.141 $\pm$ 0.016	0.305 $\pm$ 0.046	0.170 $\pm$ 0.018
r^c	0.217	0.575	0.961	0.948	0.929	0.963

^a Determined at 8-12% (w/v).

^b Extrapolated value at infinite dilution.

^c Correlation coefficient.

Table 11 DSP analysis of chemical shift data

Compounds	Proton	Solvent	ρ_I	ρ_R	SD	f	λ
X- ϕ N=CH ϕ	α -H	TFA-d	0.239	0.439	0.0150	0.123	1.83
		D ₂ SO ₄	0.215	0.507	0.0158	0.132	2.36
	H ₂	TFA-d	0.107	0.205	0.0102	0.181	1.92
		D ₂ SO ₄	0.139	0.244	0.0061	0.090	1.75
Y- ϕ CH=N ϕ	α -H	DMSO-d ₆	0.185	0.396	0.0258	0.202	2.14
		TFA-d	0.327	0.725	0.0426	0.201	2.22
		D ₂ SO ₄	0.312	0.644	0.0372	0.199	2.06

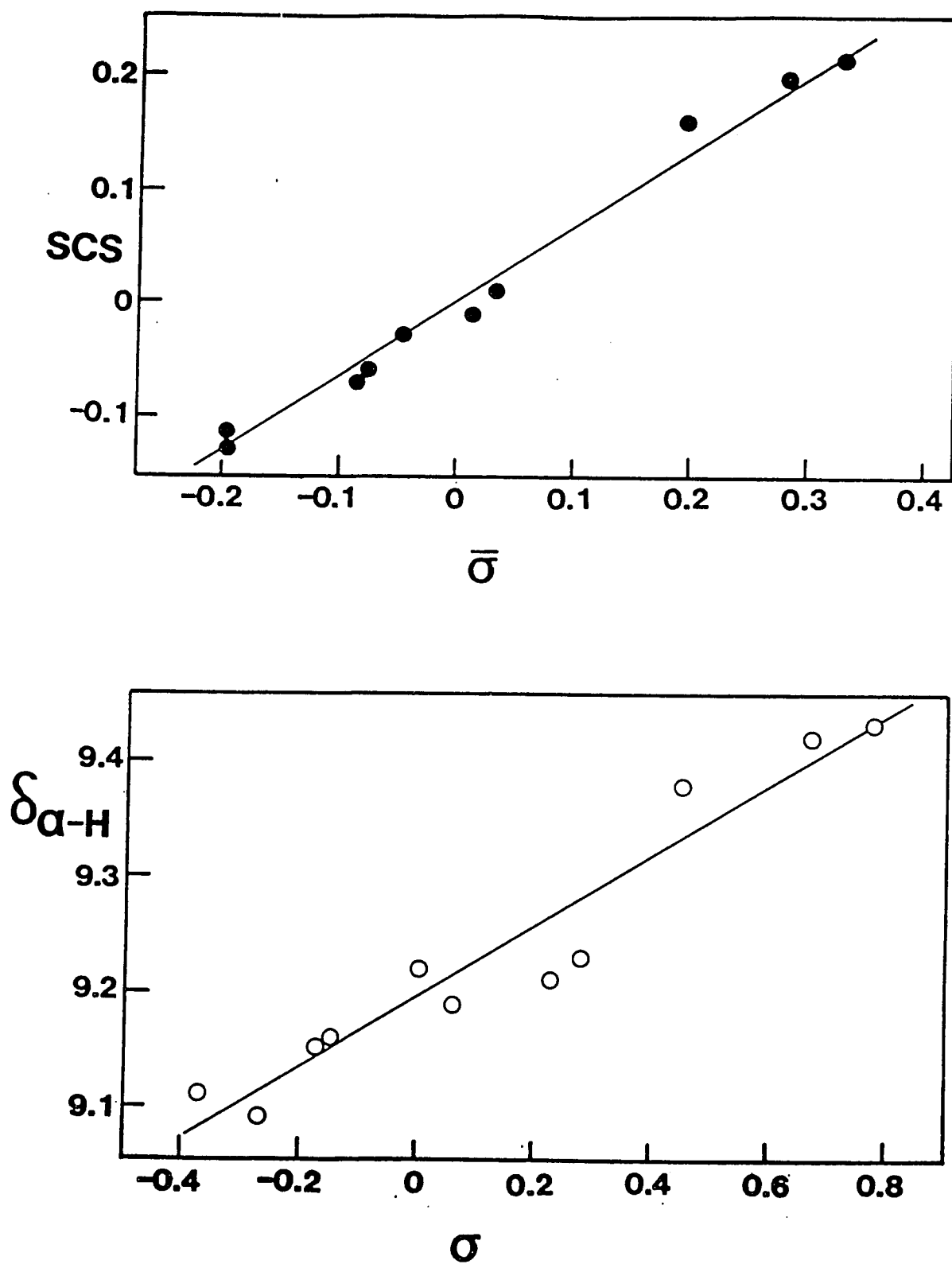


Fig.11. Hammett (o) and DSP plots (●) for $\delta_{\alpha-H}$ for $\text{XC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$ in TFA-d.

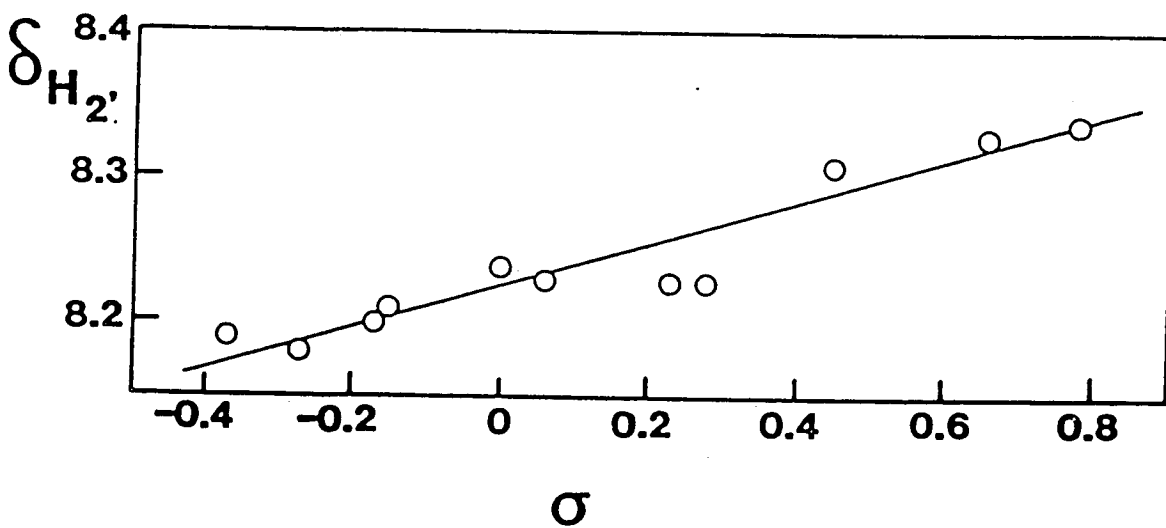
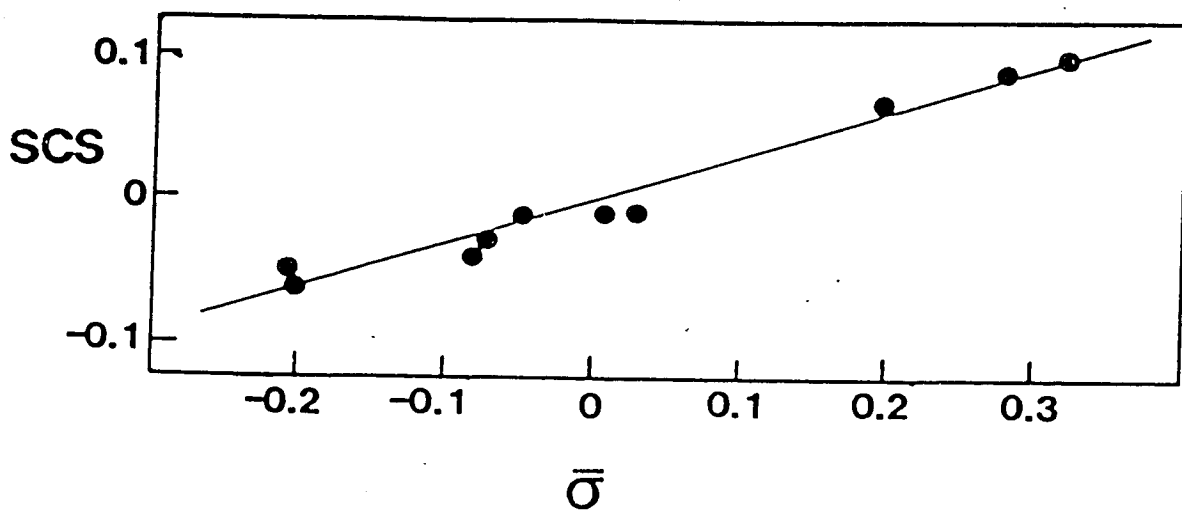


Fig.12. Hammett (o) and DSP (●) plots for $\delta_{H_2'}$, for $XC_6H_4N=CHC_6H_5$ in TFA-d.

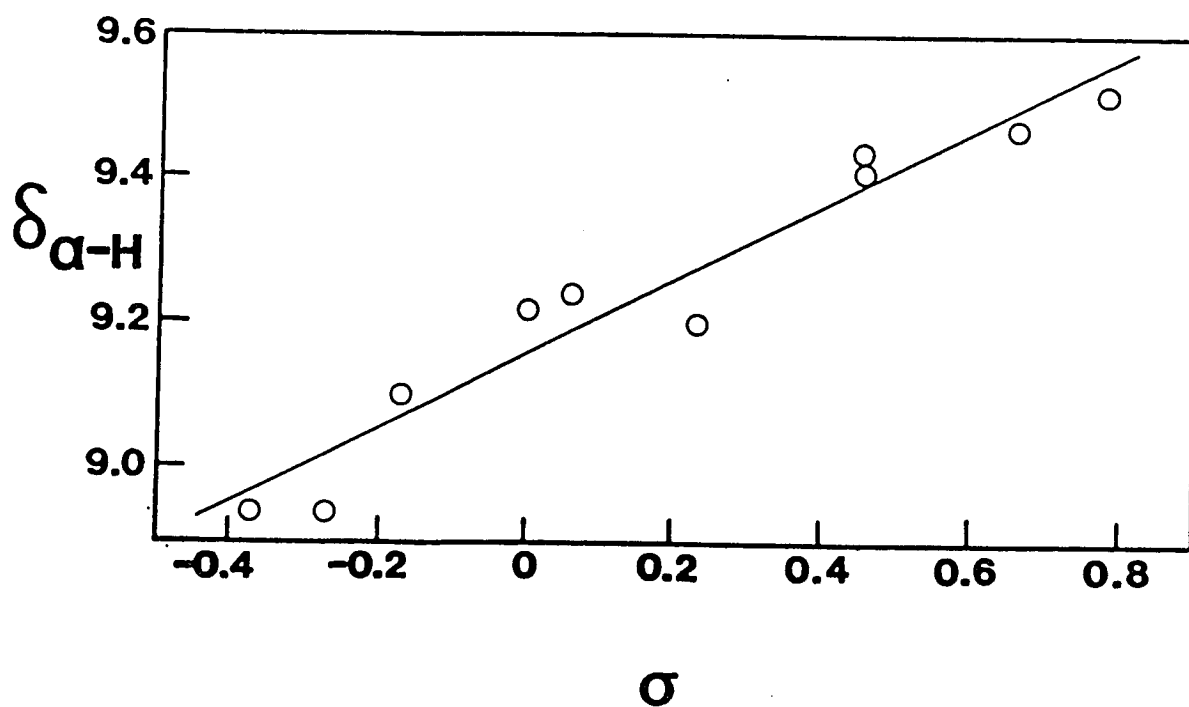
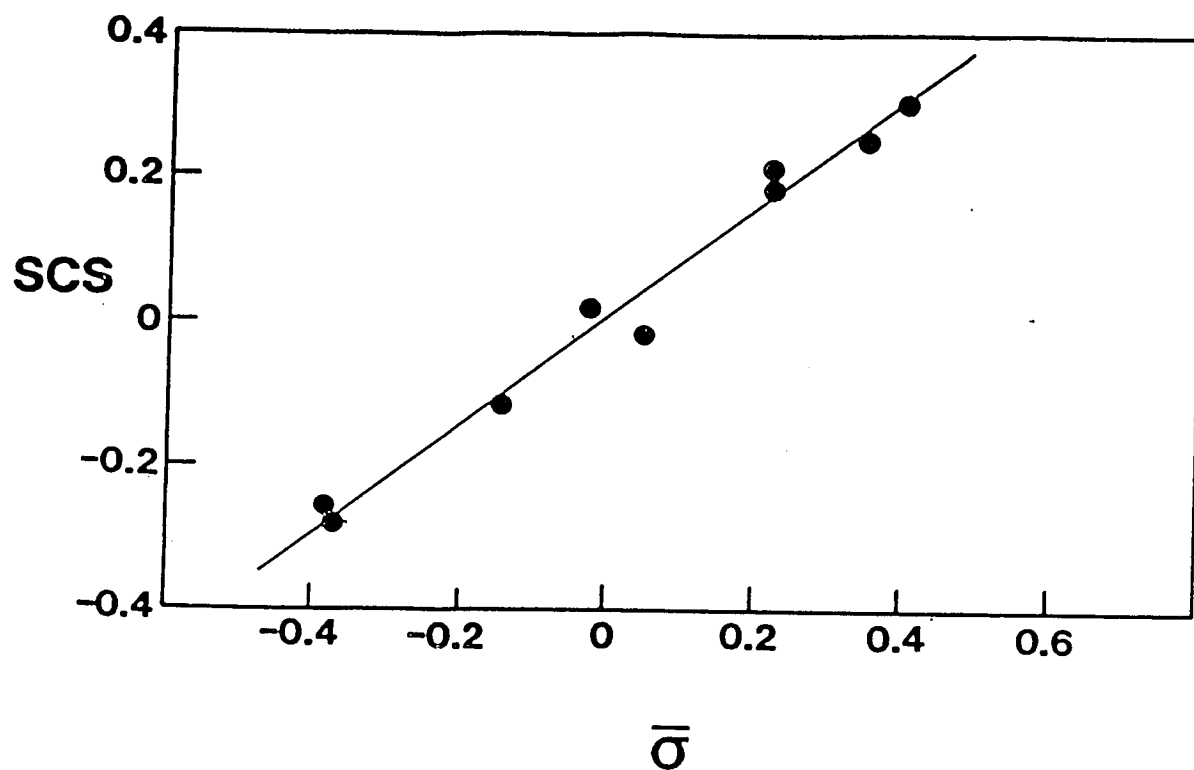


Fig.13. Hammett (o) and DSP (•) plots for $\delta_{\alpha-H}$ for $YC_6H_4CH=NC_6H_5$ in TFA-d.

4.3.2 UV SPECTRA OF POLYMERS AND AROMATIC AZOMETHINES

In order to gain insight into the conformation of the protonated polymers, the UV absorption spectra of the polymers (1 and 2), the monomers (3 and 4), and the model compounds (5-7) were studied in comparison with their spectra in unprotonated form. The UV spectral data are summarized in Tables 12 and 13.

4.3.2.1 UV SPECTRA IN NEUTRAL SOLUTION

The UV absorption spectral results of a series of model compounds(5-7) and the monomers(3 and 4) in methylene chloride are shown in Table 12 . Although it was reported[45] that the π - π^* bands of trans-N-benzylideneaniline are not very sensitive to solvent effects, methylene chloride was chosen as solvent due to its comparable dielectrical constant (9.08) to TFA(8.55) which was employed as a solvent in the study of the effects of protonation on conformation. The compounds(3-7) exhibit four absorption bands all similar to those shown in Fig.14.

Band I is different in its absorption maximum and extinction coefficient for all compounds(3-7) in methylene chloride depending on the substituents and on the substitution pattern

(i.e. para- or meta-substitution on the benzene ring). In (6), a chromophore, PhN=CH-, at the para position of the benzaldehyde ring of trans-N-benzylideneaniline (5), leads to a bathochromic shift from 310 to 345 nm with an increase in its intensity. With substitution at the meta position, i.e. in (7), only a small bathochromic shift from 310 to 318 nm with an even smaller increase in its intensity was found. This band shows slight blue shifts for MPM(3) and MMM(4) while an acetylenic group at the meta position of the aniline rings as in (6) and (7) shows slight blue shifts. These observations can be reasonably understood by considering the fact that the para substitution with a chromophore contributes more to the π - electron conjugation than the meta substitution does. This band is assigned mainly to the π - π^* transition due to conjugation of the whole molecule, corresponding to the intense 295 nm band of fully conjugated trans-stilbene. This assignment agrees with the Brocklehurst model[43] . Akaba et al.[39] also assigned this band mainly to the electronic transition from HOMO to LUMO in trans-N-benzylideneaniline. However, El-Bayoumi and coworkers[40] assigned this band to a benzene $^1B_{2u}$ -type state in the aniline part of the molecule since it was insensitive to the substitution of MeO- and Me₂N- groups in the benzaldehyde ring. This observation does not hold in our case here because the change from (5) to (6) increases both the wavelength and the intensity of Band I. It was generally accepted that the torsion angle around the C-N bond of trans-N-

benzylideneanilines is greatly effected by the substitution in the phenyl ring[39]. Compounds (3) and (6) have higher intensity of Band I than others which is quite similar to that in trans- stilbene. We conclude that (3) and (6) have a smaller torsion angle and a more planar conformation than compound (5). Although an $n-\pi^*$ transition with low intensity would be expected in the long wavelength region, fail to identify this transition is probably due to its low intensity and superposition with Band I.

Band II also depends on the substituents and the pattern of the substitution. This band is interpreted as a transition in the benzaldehyde part of the molecule. From (5) to (6) and (3) , a bathochromic shift from 263 to 298 nm with an intensity increase was observed owing to the longer conjugation in the para -N=CH- Ph-CH=N- chromophore. On the other hand, from (5) to (7), there is only a slight bathochromic shift (from 263 to 265 nm) with an increase in the intensity. In MMM(4), the maximum appears at 256 nm with a shoulder at ca.263 nm. A weak absorption at 263 nm in the spectrum of MPM(3) might be due to some local excitation in N=CHPh chromophore.

Band III remains almost unchanged in all compounds. In (6),(3), and (4), it appears as a shoulder. This band corresponds to the transition to an intramolecular charge-transfer(CT) state in the aniline part of the molecule according to El-Bayoumi's assignment[40].

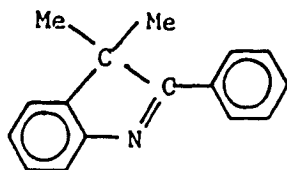
From the above discussion, our results are in favor of the

Brocklehurst model, in which the first band is indicative of the conjugation length in the molecules. All of the evidence supports a nonplanar conformation of aromatic imines and less contribution of the meta-substitution to the conjugation system.

4.3.2.2 UV SPECTRA IN ACIDIC SOLUTION

In this section, the assignments of Bands I-IV are expounded. The assignment of Band I is based on a) the spectral results of the compounds (1-7) in MeSO_3H as summarized in Table 13, b) the information from the addition of water to the acetylenic end group of the monomers and the polymers in MeSO_3H , c) hydrolysis of the polymers in TFA.

Upon protonation, the UV spectra of all compounds(1-7) have a very intense Band I. They seem to be very similar to the spectra of trans-stilbene(Fig.16a) and 3,3-dimethyl-2-phenyl-3H-indole(26) (Fig.16b), an accepted model compound for the planar form of trans-N-benzylideneaniline[47].



(26)

The spectra are shown in Figs.14 and 16. The spectrum of

protonated trans-N-benzylideneaniline(5) falls into the same spectral pattern of trans-stilbene and (26) in neutral solvent. One would conclude that they all have a similar extended pi-conjugated system if Band I is assigned to the transition in the conjugation through the whole molecule.

Band I is in the range 325-396 nm. Comparing with the spectra in methylene chloride (Table 12), the intensity of this band is greatly increased accompanied by a bathochromic shift. Similar to that in methylene chloride, the wavelength of this band depends on the substitution pattern. The para-substitution contributes more to the conjugation than the meta one does. Compounds(5-7) are quite stable in both TFA and MeSO₃H, but the spectra of the monomers(3 and 4) and PMPM(1) change with time in both TFA and MeSO₃H. The spectrum of PMMM(2) does not show such time dependence in MeSO₃H but changes in TFA. In MeSO₃H, the change is due to the addition of water to the acetylenic group to yield an acetyl group in (1), (3) and (4) as discussed before. Stable UV spectra were obtained after ca.30 min. when the reaction was complete. As an example the UV spectrum of MPM(3) are given in Fig.17. Consider Band I, a hypsochromic shift (from 384 to 378 nm) with a little increase of the intensity was observed between the spectra taken at 2 min.(Fig.17a) and at 25 min.(Fig.17c) after the sample preparation. This can be explained by a new transition at a lower wavelength comparing to the original band at

384 nm. An overlapping of two absorptions generates a new band at 378 nm. This new transition might be a charge-transfer(CT) excitation from the aniline-like group to the acetyl group[39,47,72] similar to the CT band at 322 nm of nitroaniline[72]. The spectrum of MM(4) undergoes a similar but more significant change from 331 to 325 nm. An observation of only very little change within 2 nm of this band in the case of PMPM(1) further suggests that the new transition due to acetyl group overlaps with Band I. No change in the spectrum of PMM(2) with time is due to its higher molecular weight which makes the effect of the end group insignificant. Furthermore, Band I of PMM(2) overlaps with a strong absorption of the diethynylene group in the polymer chain. 1,4-diphenyl-butadiyne is known to have five absorption bands with strong intensity at 326, 305, 288, 276, and 255 nm [61,73]. All these bands were found in the spectra of the polymers(1 and 2) in both MeSO₃H and TFA except the 255 nm band in TFA in which it was out of the range of solvent window. This provides solid evidence for the existence of the diethynylene linkage in both polymers. The spectrum of PMPM in MeSO₃H is given in Fig.18 showing all five diethynylene absorption bands at 329.5, 309.2, 292, 276, and 259 nm.

In TFA, the change of the spectra of the monomers(3 and 4) and the polymers(1 and 2) is attributed to the hydrolysis of the imine double bond which has been discussed earlier in the NMR section. Fig.19 shows the change of the UV spectrum of

PMPM(1) with time. Band I gradually shifts to short wavelength accompanied by a decrease in its intensity. At 8 min. after the sample preparation(Fig.19a), the band maximum is at 380 nm; at 25 min.(Fig.19b), the maximum is at 354 nm with some intensity loss; and at 70 min.(Fig.19e), this band almost disappears. The changes of the absorption maximum and the intensity at 380 nm are plotted against time shown in Fig.20a and 20b, respectively.

These observations can be rationalized by the different extent of the hydrolysis reaction. The more imine group hydrolysis, the greater the decrease in the intensity of Band I. The new band maximum formed at each stage of the hydrolysis is a combination of the contributions from long and short conjugated residues until all imine groups are hydrolyzed. From Fig.19a, the hydrolysis seems to slow down after about 40 minutes. At this time the maximum of Band I is hardly visible in the spectrum. Thus, the hydrolysis breaks the conjugation across the whole molecule. The facts of the slow hydrolysis after ca.40 min. and that the intensity at 380 nm never gets to zero show that the hydrolysis could not be complete owing to the limited amount of water molecules available in TFA.

The spectra of MPM(3),MMM(4) and PMMM(2) exhibit the similar changes. In the case of PMMM(2), a gradual receding of the front part of Band I illustrates the hydrolysis because Band I overlaps with the first band of the diethynylene

absorption.

Based on the above discussion, we conclude that Band I corresponds to the π - π^* electronic transition of the conjugated system through the whole molecule. For the monomers and the polymers(1-4) in MeSO_3H , the absorption due to the acetyl substitution is combined into Band I.

Band II in the spectra of all compounds(1-7) in acids is in a narrow range 272-277 nm and is not affected much by the substitution pattern, in contrast to those in methylene chloride. The intensity of this band is generally decreased in comparison with that in methylene chloride. In the spectra of (4) and (7), this band is too weak to be recognized. Band II may still be assigned to the transition in the benzaldehyde part of the molecule. Because of the extension of the π -molecular orbitals of the benzaldehyde part over the aniline ring, only a weak local-excitation transition in PhCH=N chromophore contributes mainly to this band. Band II of the polymers(1 and 2) overlaps with one of the diethynylene bands at ca. 274-277 nm.

Band III did not provide much information about the effect of substitution in the aniline ring in methylene chloride (Table 12) since this band appears weakly as a shoulder. In MeSO_3H , however, the effect becomes very clear. All compounds in Table 13 except (6) exhibit this absorption in the range 242-249 nm. From (5) to (7), the wavelength of this band remains essentially the same but the intensity increases owing

to the introduction of one more aniline moiety. Substitution of acetylenic group to the aniline ring of (7) generating (4) causes a bathochromic shift from 242 to 249 nm. Actually, Band III in the spectra of MMM(4) and MPM(3) changed within 30 min. in MeSO_3H . As an example, the change of Band III of MPM(3) is shown in Fig.17. At 2 min.(Fig.17a), there is an absorption maximum at 233 nm. This absorption is generated from superposition of two separated bands at ca.224 and 243 nm which appears as two shoulders in the spectrum. At 10 min.(Fig.17b), the intensity of 233 nm band and the two shoulders decreases, and a new absorption band at ca. 247 nm appears as a shoulder. At 25 min.(Fig.17c), the 233 nm band and 243 nm shoulder disappear completely, and two well separated bands at 217nm (Band IV) and 247nm (Band III) are observed. After 30 min. no more change takes place. Such change is obviously caused by the effect of the substituent changing from an acetylenic to an acetyl group by addition of water to the acetylenic triple bond. Therefore, Band III is related to the aniline moiety of the molecule and can be interpreted as a transition to the local-excited(LE) state like a $^1\text{B}_{1\text{u}}$ -type state or to a CT state in the aniline moiety [40]. The disappearing band at 243nm corresponds to the transition in $-\text{Ph}-\text{C}\equiv\text{CH}$ group while the increasing band at 247 nm corresponds to the transition in $-\text{Ph}-\text{COMe}$ group.

The monomer MMM(4) also shows significant change of Band III with time (Fig.21). A band at 243 nm disappears as the

249 nm band increases. Band III in the polymers appears at 246 and 247 nm, and corresponds to the transition related to the $\text{-PhC}\equiv\text{CC}\equiv\text{C-}$ group. The change caused by the reaction of the acetylenic end group is either submerged into this band or too weak to be observed. Band III in (6) is too weak to be identified owing probably to the strong resonance across the whole molecule.

Band IV of trans-N-benzylideneaniline(5) is essentially unchanged on protonation except some decrease in the intensity as shown in Table 13. It displays a minor hypsochromic shift from 219 to 217 nm for (5) to (6) due to substitution in the benzaldehyde ring. Substitution in the aniline ring does not lead to a change, e.g. 217nm for both (6) and (3). Band IV is interpreted as the perturbed $^1\text{B}_{1u}$ band of the benzaldehyde part of the molecules [40]. In (7) and (4), this band might be too weak to be identified or to shift to further short wavelength direction.

The UV spectrum of PMPM(1) has also been examined in concentrated H_2SO_4 . The spectrum is stable after 5 min. from the sample preparation, and exhibits an intense absorption band at 391 nm ($\log \epsilon = 4.5$) and a weak band at 284 nm ($\log \epsilon = 3.9$) in a remarkable contrast to those in MeSO_3H and TFA. Disappearance of the five diethynylene absorption bands supports the conclusion that not only the acetylenic but also the diethynylene triple bonds in the polymer chain reacted rapidly in concentrated H_2SO_4 .

Table 12 ULTRAVIOLET SPECTRA OF THE MODEL COMPOUNDS (5-7)
AND THE MONOMERS (3 & 4) IN CH_2Cl_2

Compound	No.	Band I		Band II		Band III	
		λ nm	$\log \epsilon$	λ nm	$\log \epsilon$	λ nm	$\log \epsilon$
	5	(308)	(3.94)	264	4.27	(238)	(4.23)
	6	348	4.34	298	4.34	(235)	(4.25)
	7	318	4.26	265	4.45	239	4.23
	3	343	4.41	298	4.43	(238)	(4.24)
				263	4.26		
	4	316	4.27	(263)	(4.5)	(238)	(4.24)
				256	4.81		
				250	4.80		

Table 13 ULTRAVIOLET SPECTRA OF THE POLYMERS, MONOMERS AND THE MODEL COMPOUNDS
IN ACIDIC MEDIA ^a

Compound No.	Solvent	Band I		Band II		Band III		Band IV	
		λ nm	log ϵ	λ nm	log ϵ	λ nm	log ϵ	λ nm	log ϵ
5	EtOH	(310)	(3.95)	262	4.22	238	3.98	218	4.18
	MeSO ₃ H	332	4.36	273	3.83	243	3.50	219	3.94
	TFA	336	4.4	276	3.8	-	-	-	-
6	MeSO ₃ H	386	4.52	276	3.97	-	-	217	4.17
	TFA	396	4.6	275	4.2	-	-	-	-
	MeSO ₃ H	342	4.65	-	-	242	4.28	-	-
3	TFA	349	4.5	-	-	-	-	-	-
	MeSO ₃ H	378	4.55	272	4.18	247	4.25	217	4.28
	TFA	352	4.41	277	4.22	-	-	-	-
4	MeSO ₃ H	325	4.69	-	-	249	4.60	-	-
	TFA	338	4.4	-	-	-	-	-	-
	MeSO ₃ H	379	4.43	276	4.21	246	4.33	(216)	(4.41)
2	TFA	370	4.50	274	4.23	-	-	-	-
	MeSO ₃ H	335	4.66	-	-	247	4.44	(216)	(4.38)
	TFA	328	4.6	-	-	-	-	-	-

a. The log values for the compounds (1-4) were measured at 30 min. after sample preparation. The absorption bands of diethynylene group in (1) and (2) are listed in a table on next page.

The absorption bands of diethynylene group in (1) and (2) are:

Compd.	Solvent	λ nm	(log ϵ)
PMEM (1)	MeSO ₃ H	329.5 (4.34)	309 (4.29) 292 (4.23) 276 (4.21) (259) (4.28)
	TFA	327 (4.28)	307 (4.25) 288 (4.15) 274 (4.23)
PMEM (2)	MeSO ₃ H	335 (4.66)	312 (4.60) 294 (4.45) 277 (4.37) 259 (4.36)
	TFA	328 (4.5)	307 (4.3) 288 (4.2) 274 (4.2)
PhC $\equiv$ CC $\equiv$ CPh	EtOH	326 (4.48)	305 (4.48) 288 (4.34) 276 (4.10) 255 (4.50)

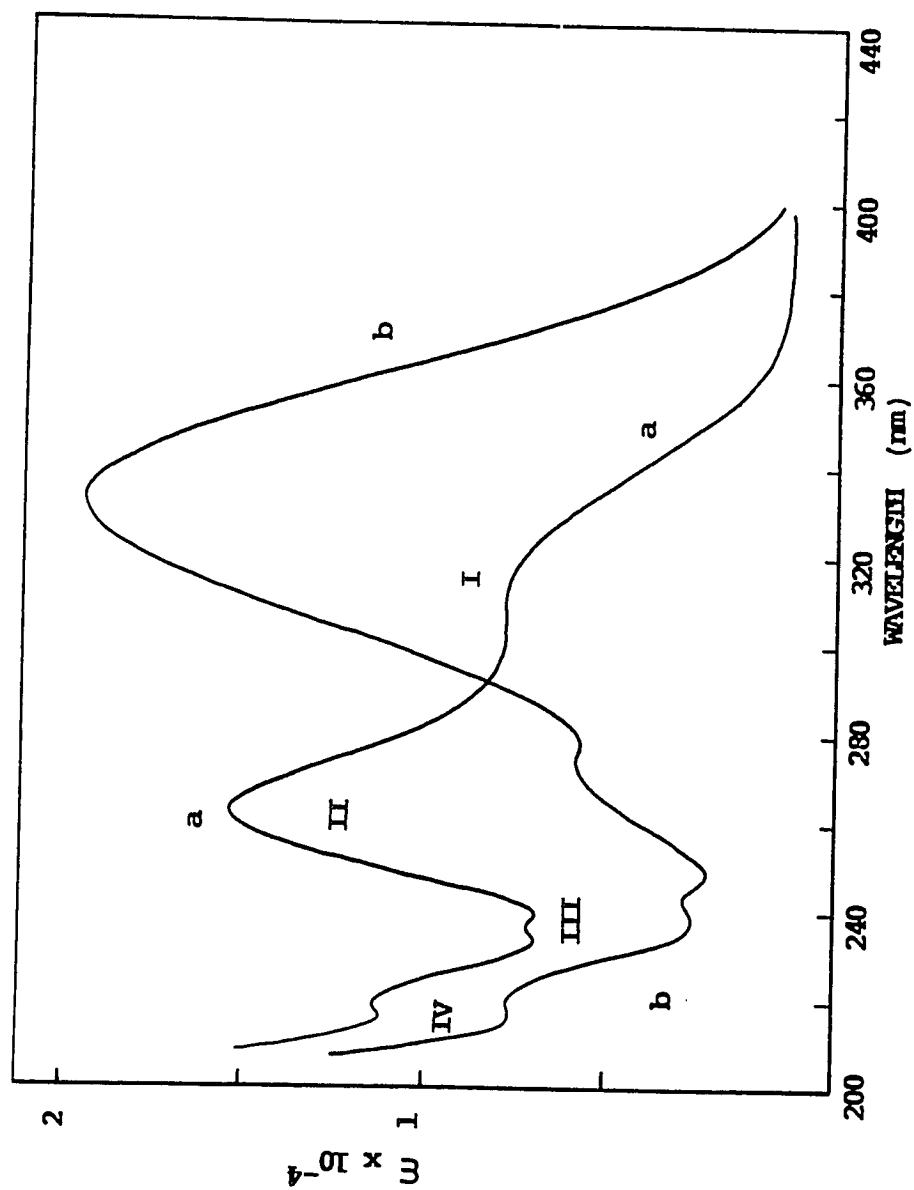


Fig.14. UV spectra of *trans*-N-benzylideneanilines in a) methylene chloride and b) MeSO_3H

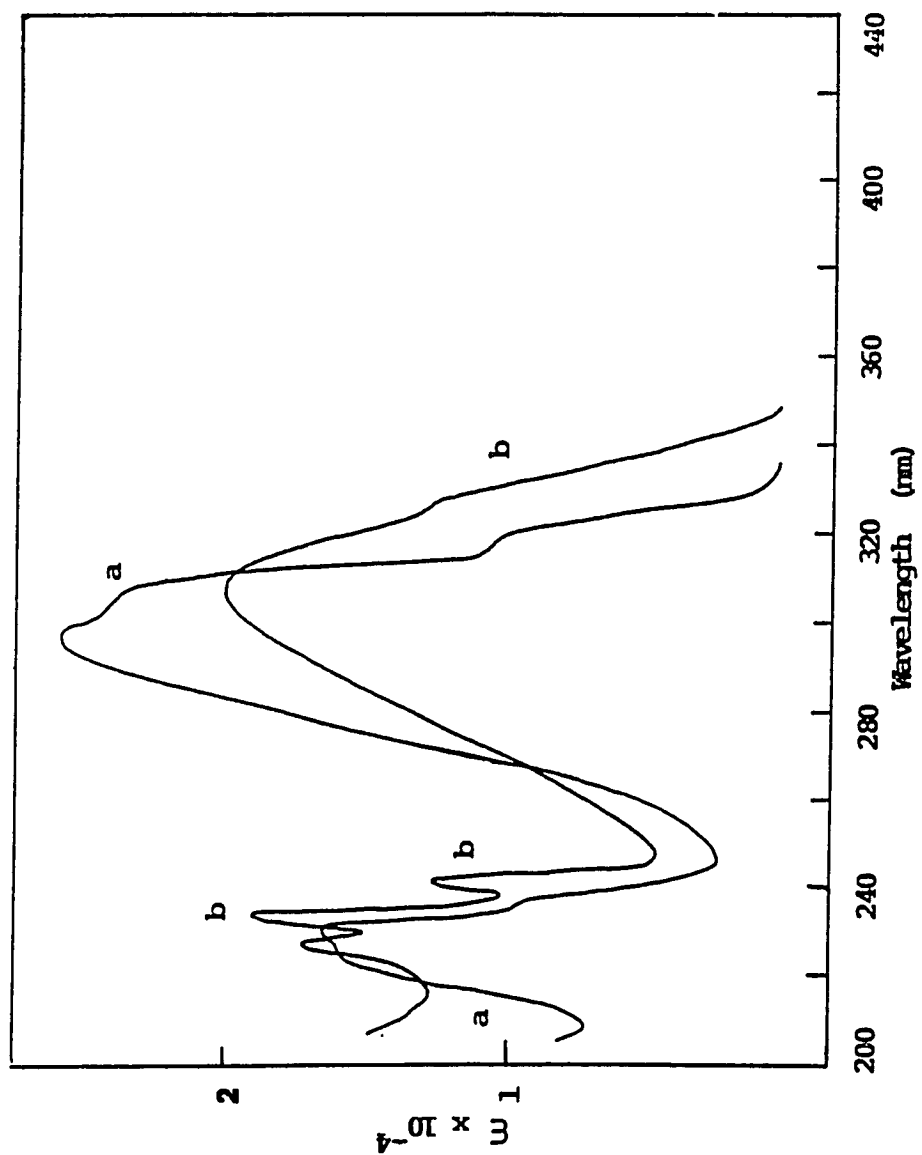


Fig.16. UV spectra of a) trans-stilbene and b) 3,3-dimethyl-2-phenyl-3H-indole in cyclohexane

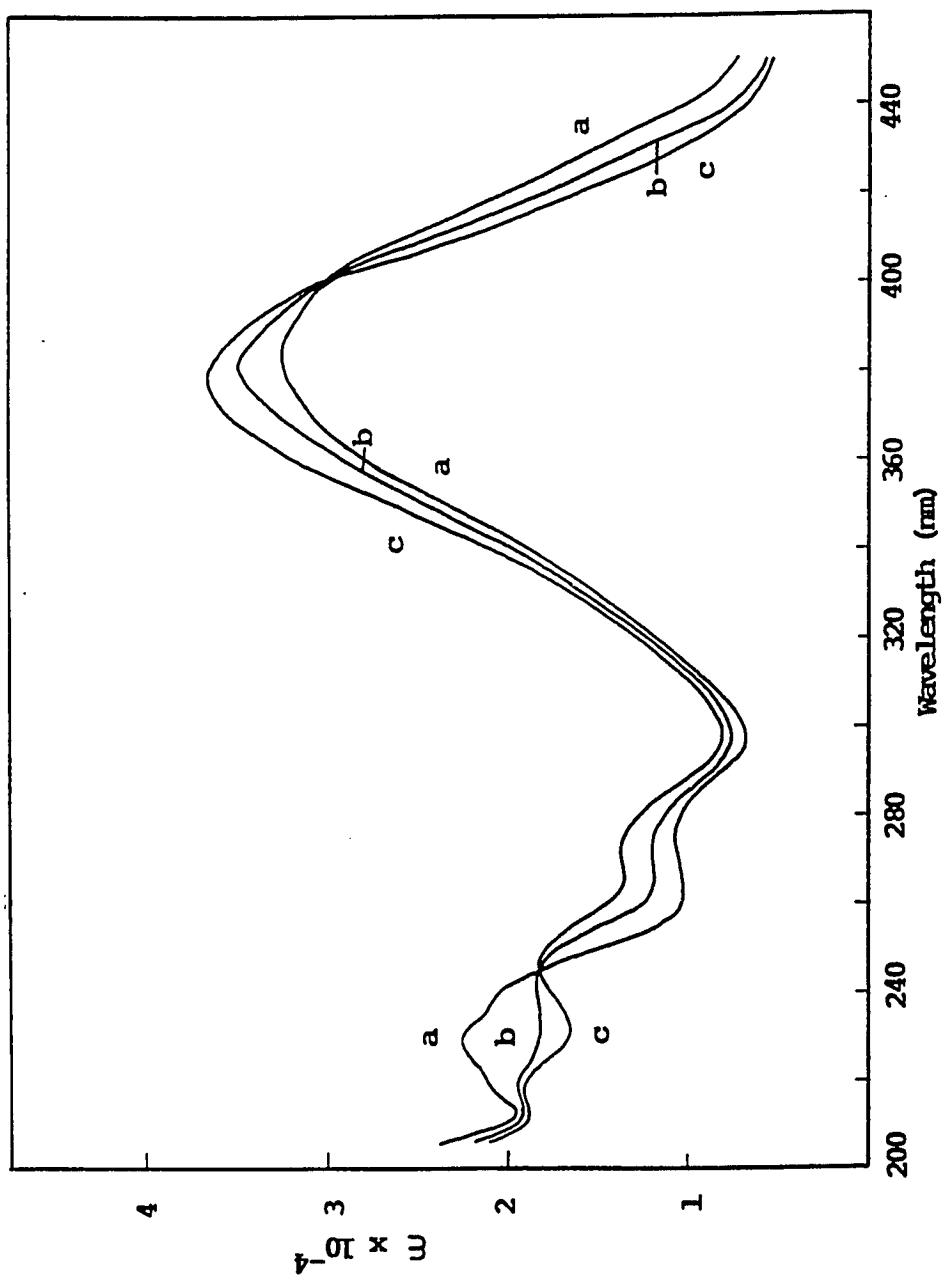


Fig.17. UV spectra of MPM in MeSO₃H recorded at a) 2 min., b) 10 min. and c) 25 min. after sample preparation.

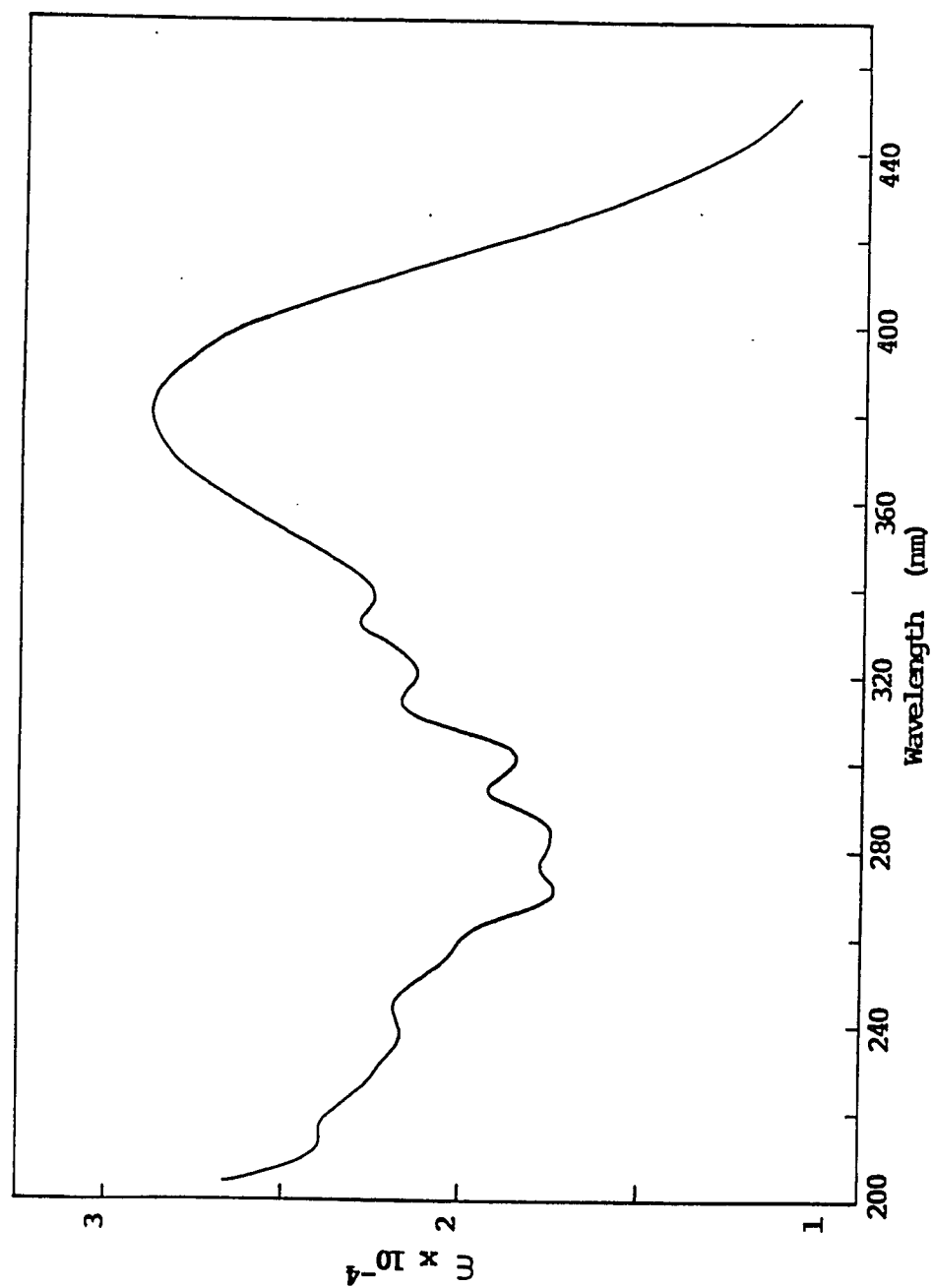


Fig.18. UV spectrum of PMEM in MeSO₃H at 5 min. after sample preparation

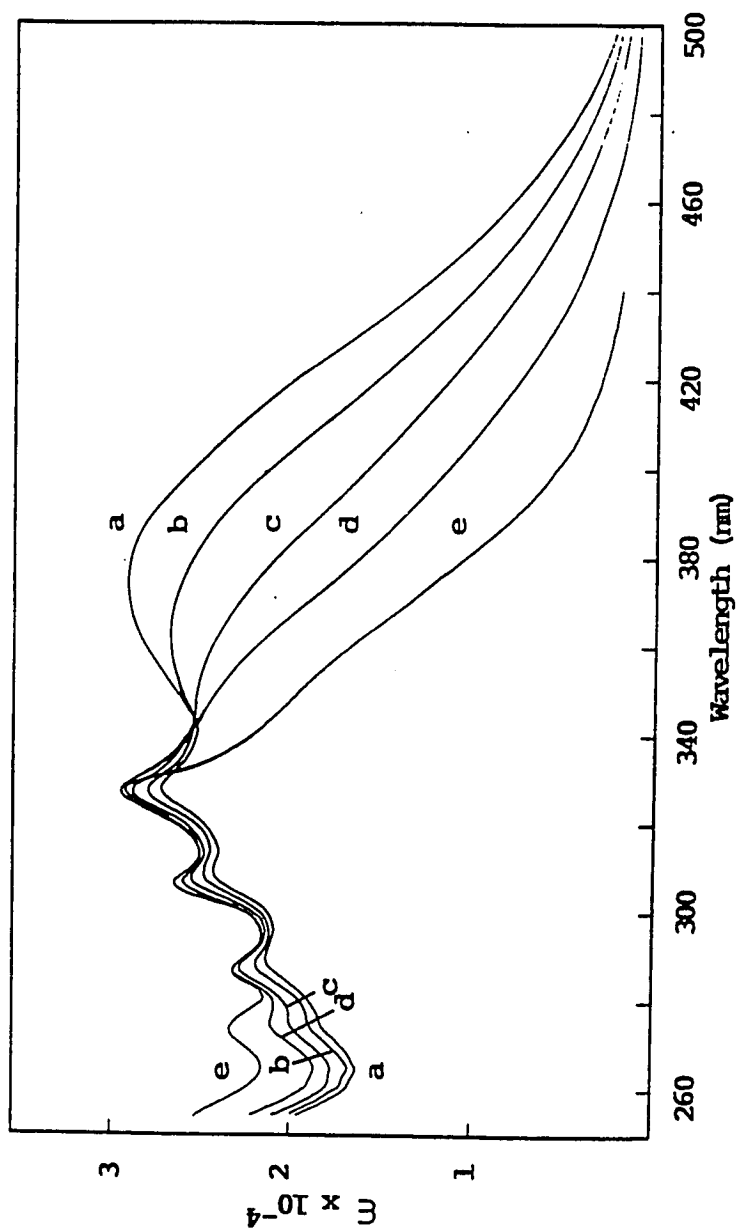


Fig.19 UV Spectra of PMPM (1) in THF (99%) at a) 8 min., b) 15 min., c) 25 min., d) 40 min., and e) 70 min. after sample preparation.

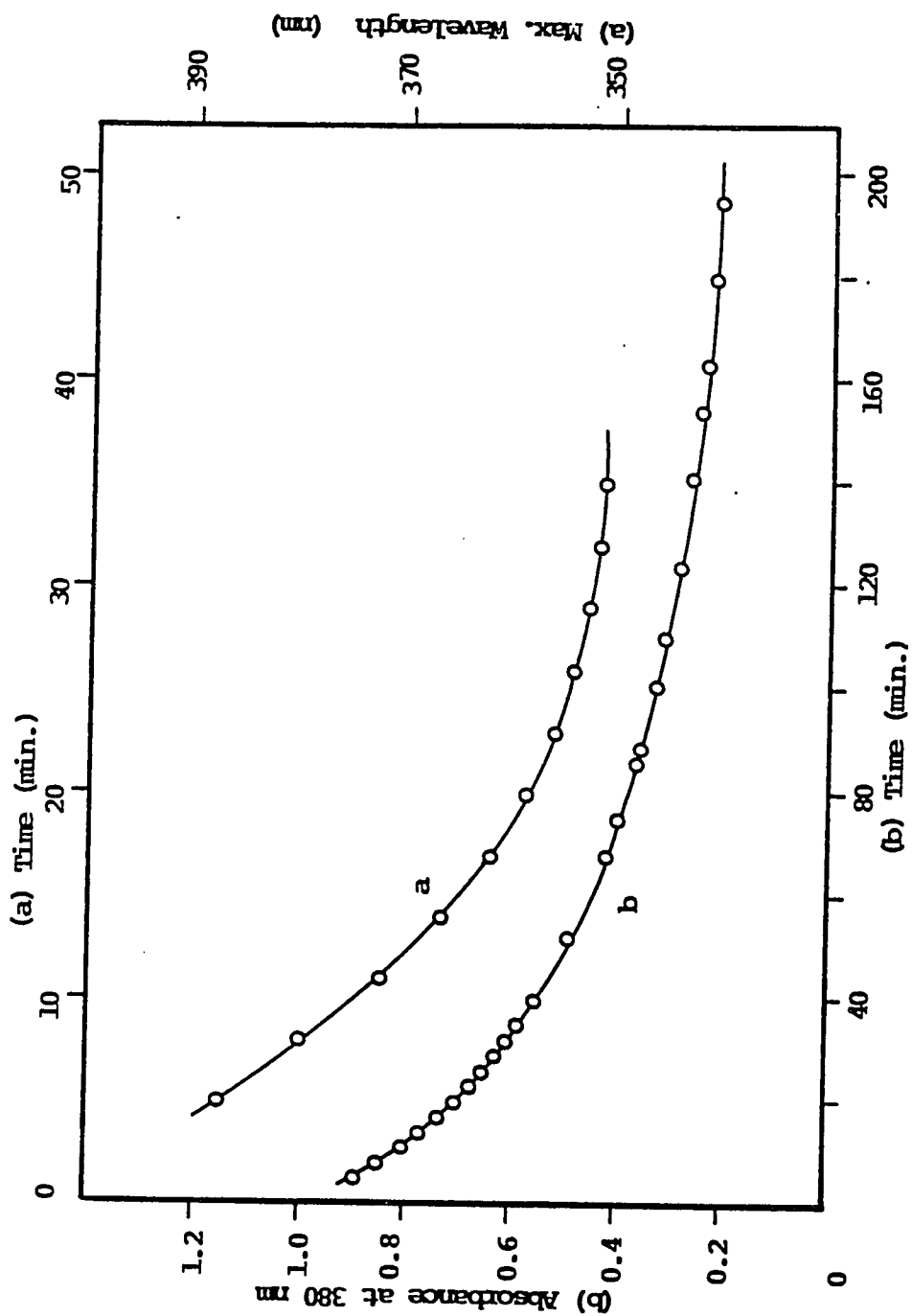


Fig.20. The change of a) maximum wavelength and b) intensity at 380 nm of PMPM UV-absorption with time in TFA.

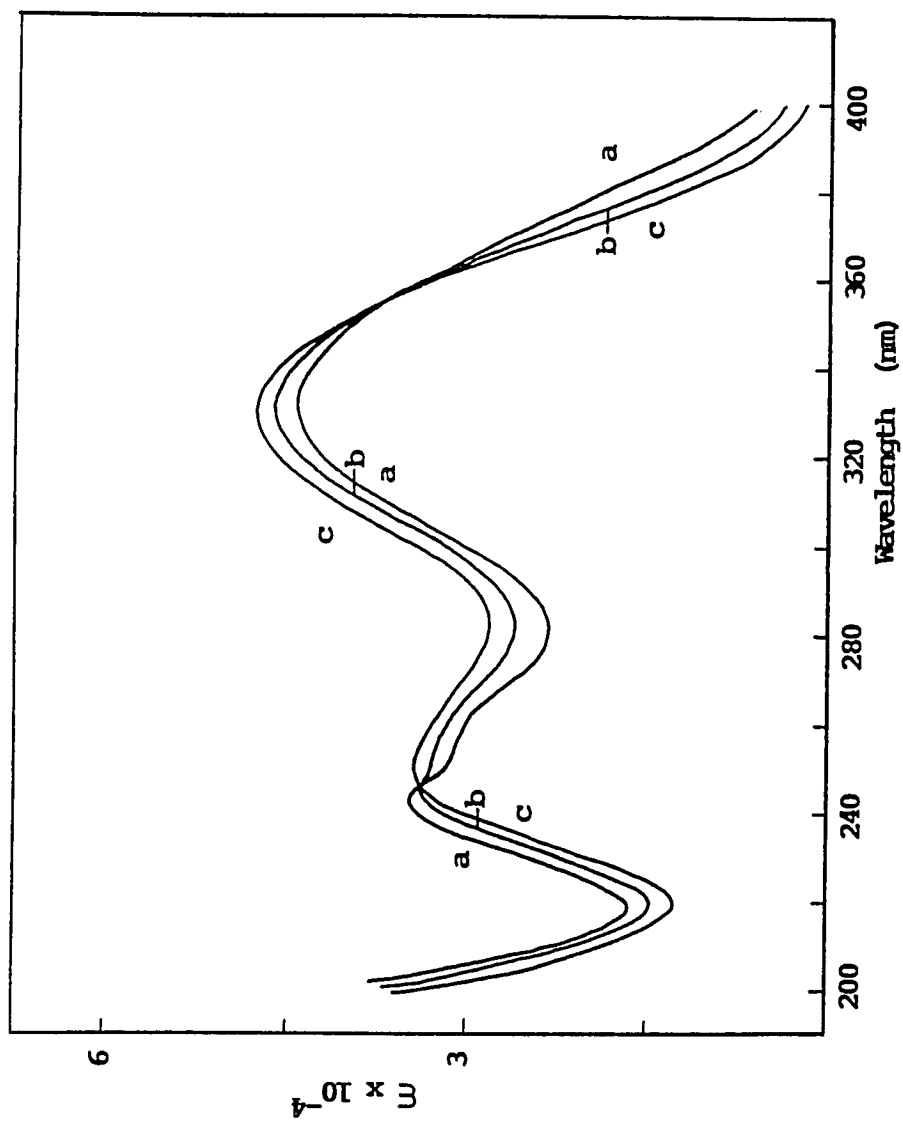


Fig.21. UV spectra of MM in MeSO₃H recorded at a) 5 min.,
b) 15 min. and c) 30 min. after sample preparation.

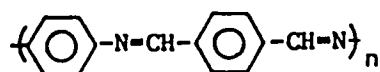
4.4 PROPERTIES OF POLYMERS

The polymers, PMPM(1) and PMMM(2) exhibit interesting thermal, paramagnetic and electronic properties.

4.4.1 TGA, DSC AND IR STUDIES OF THERMAL REACTIONS AND PROPERTIES

Both PMPM and PMMM exhibit superior thermal stabilities in the TGA measurements (Fig.22). The percentage weight loss of the polymers at various temperatures in nitrogen and air are summarized in Table 14. Under nitrogen atmosphere, the weight loss at 900°C is only 31% for PMPM and 27% for PMMM. The onset temperatures of decomposition are 420 and 500°C for PMPM and PMMM, respectively. In air, PMPM and PMMM begin to decompose at about 350 and 450°C, respectively. Then, a rapid decomposition occurs for both polymers, which is indicated by a great weight loss over a narrow temperature range. The higher decomposition temperature of PMMM may be due to the higher flexibility of the PMMM polymer chain leading to easier crosslinking of the triple bonds in PMMM than that of PMPM. The thermal stabilities of PMPM and PMMM in air are quite similar to most of the aromatic polyazomethines[2a]. As a comparison, TGA data of a typical aromatic polyazomethine, PNB(27), are listed in Table 14. The PNB(27) was obtained from a solution condensa-

tion of terephthalaldehyde with 1,4-diaminobenzene in our laboratory.



(27)

Both PMPM and PMMM show some weight gain at about 300°C just before decomposition commences in both nitrogen and air. In nitrogen, the weight gain is less than that in air, e.g. the maximum weight gain for PMPM in air is 1.8% while in nitrogen it is about 0.5%. Considering the fact that the polymer with only aromatic and imine groups, such as PNB(27), shows no such effect, the triple bonds in the polymer chains must be mainly responsible.

Infrared spectra of the polymers at different heating stages were recorded and are illustrated in Figures 23 and 24. In Fig.23a the IR spectrum is given for PMPM upon heating to 225°C in air. Almost no weight loss was found at this temperature in TGA. Comparing Fig.23a with the IR spectrum of PMPM without heat treatment, Fig.2b (in Section 4.2.2), no significant difference is found except that the acetylenic C-H stretching absorption at 3290 cm⁻¹ from the polymer end group has disappeared.

When the PMPM sample was heated to 295°C in air, and the

weight gain reaches its maximum value of 1.8% in the TGA measurement, a new intense absorption was found at ca. 1670 cm^{-1} which is in the range of carbonyl stretching absorptions in the IR spectrum (Fig.23b). This absorption band is quite broad and consists of many absorptions, indicating formation of several kinds of carbonyl groups in the polymer chain. Since the strong N=C stretching absorption remains in the spectrum, the new band must be due to the diethynylene triple bonds in the polymer. This is further supported by the fact that no such new band has been observed in the IR spectrum of PNB(27) after heating to 295°C . When PMPM is heated to 295°C in nitrogen, in contrast to the results in air, the intensities of the carbonyl absorptions are greatly reduced as shown in Fig.23c, in line with the lower weight gain in the TGA measurement.

Similar changes were also observed in the IR spectra of PMMM (Fig.24) after various heat treatments. It should be noted that the N=C stretching absorption appears at 1670 cm^{-1} in the spectra at all temperatures. In the spectrum of PMMM heated to 310°C in air (Fig.24a), only weak absorption bands were found around 1650 cm^{-1} . When the polymer was heated to 310°C in air, the intensity of the carbonyl stretching absorptions in the IR spectrum (Fig.24c) increased greatly. When heated to 310°C in nitrogen, the intensity of the absorption at 1670 cm^{-1} decreased as shown in Fig.24b.

Newkirk and Hay [52] studied the IR spectra of poly(m-

diethynylene benzene)(13) after various heat treatments under a nitrogen atmosphere. They also observed a new carbonyl absorption at 1670 cm^{-1} . This band starts to appear at about 170°C and its intensity increases with an increase in the temperature until it reached a maximum at ca. 300°C . Then the intensity of the band decreases with increase of the temperature. They concluded [52] that the chemical events which occurred below 500°C produced chemically active groups. These groups were prevented from reacting with each other by the three-dimensional crosslinked polymer network which holds them in position. These active groups in this case reacted with atmospheric H_2O , O_2 , or both at room temperature, during transfer of the specimen from oven to spectrometer, to form several kinds of carbonyl groups.

However, this explanation is not satisfactory for the present results for PMPM and PMMM. First of all, it can not explain the weight gain of PMPM and PMMM in the TGA measurements under either nitrogen or air atmosphere if the reactions between the chemically active groups and atmospheric moisture and/or oxygen only occurs during the sample transfer. Secondly, it can not explain why the amount of carbonyl groups was reduced above 300°C when the three-dimensional crosslinked polymer network is not decomposed yet and can still hold the chemical active groups in position. Further discussion will be given later.

Table 14 TGA DATA OF THE POLYMERS ON HEATING IN N₂ OR AIR^a

Polymer	# Atmosphere	% weight loss at (°C) ^b										Max. wt. gain ^c		Temp. of Decomposi- tion, °C
		125	225	295	350	450	550	650	900	Temp. °C	%			
PMPM	1 N ₂	0	0.5	0	0.1	2	6	12	31	310	0.1			420
	Air	0.6	0	-1.8	11	90				295	1.8			345
PMMM	2 N ₂	0	0.3	-0.3	-0.6	-0.6	5	11	27	345	0.6			500
	Air	0	-0.3	-1.9	-3.0	9	90			330	3.0			450
PNP	27 Air	0	2	3	4.8	10	50	89	-	-	-			440

a. Heating rate, 20 °C/min.

b. A negative %wt. loss means % wt. gain.

c. In comparison to the weight of the polymers before heating.

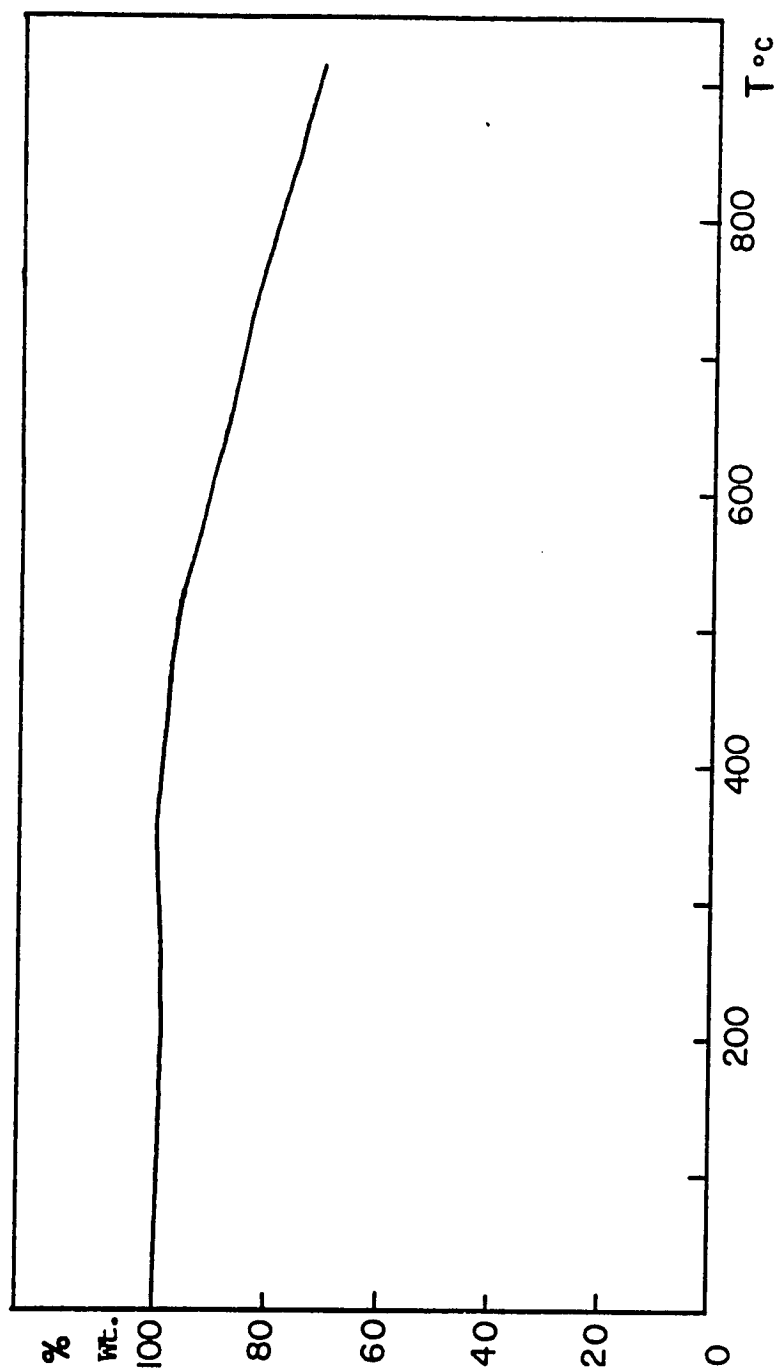


Fig.22a. TGA thermogram of EMPM in nitrogen.

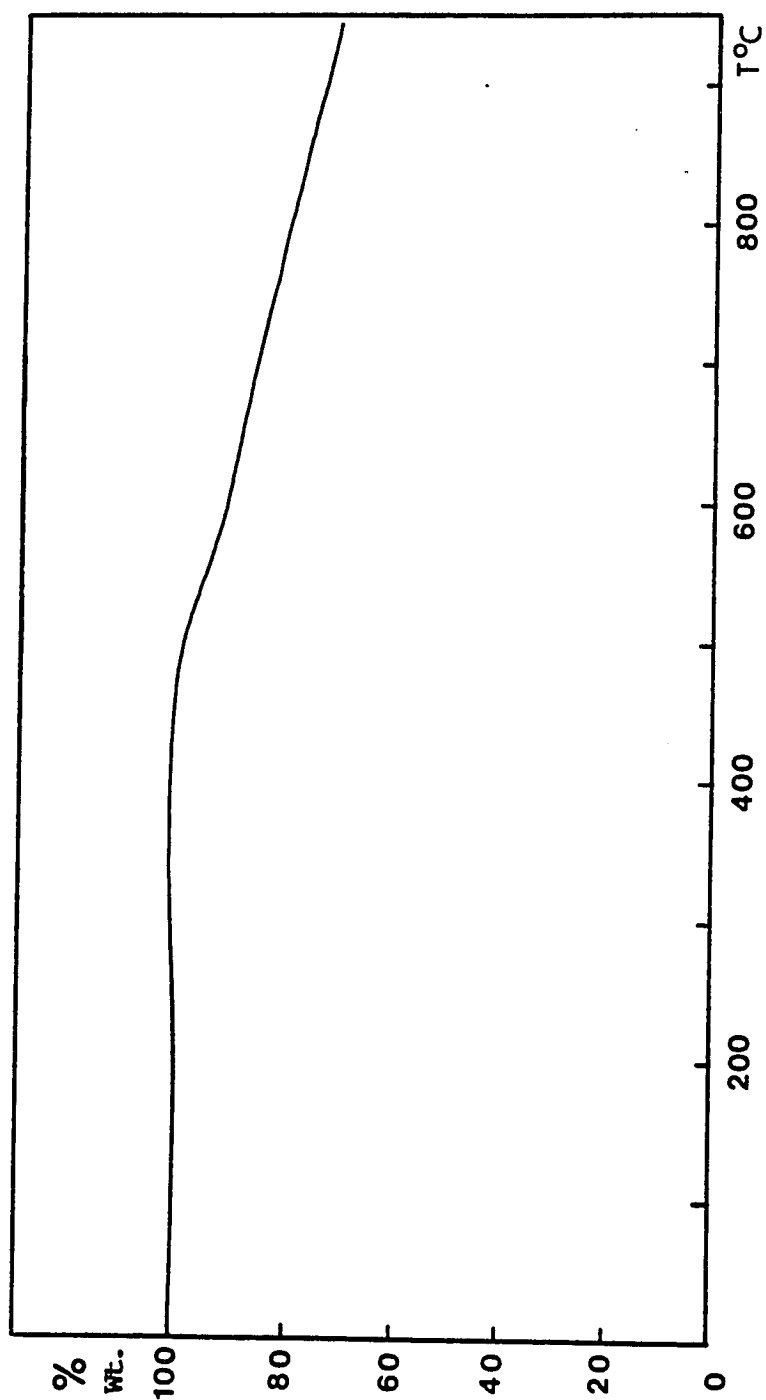


Fig.22b. TGA thermogram of PMAM in nitrogen.

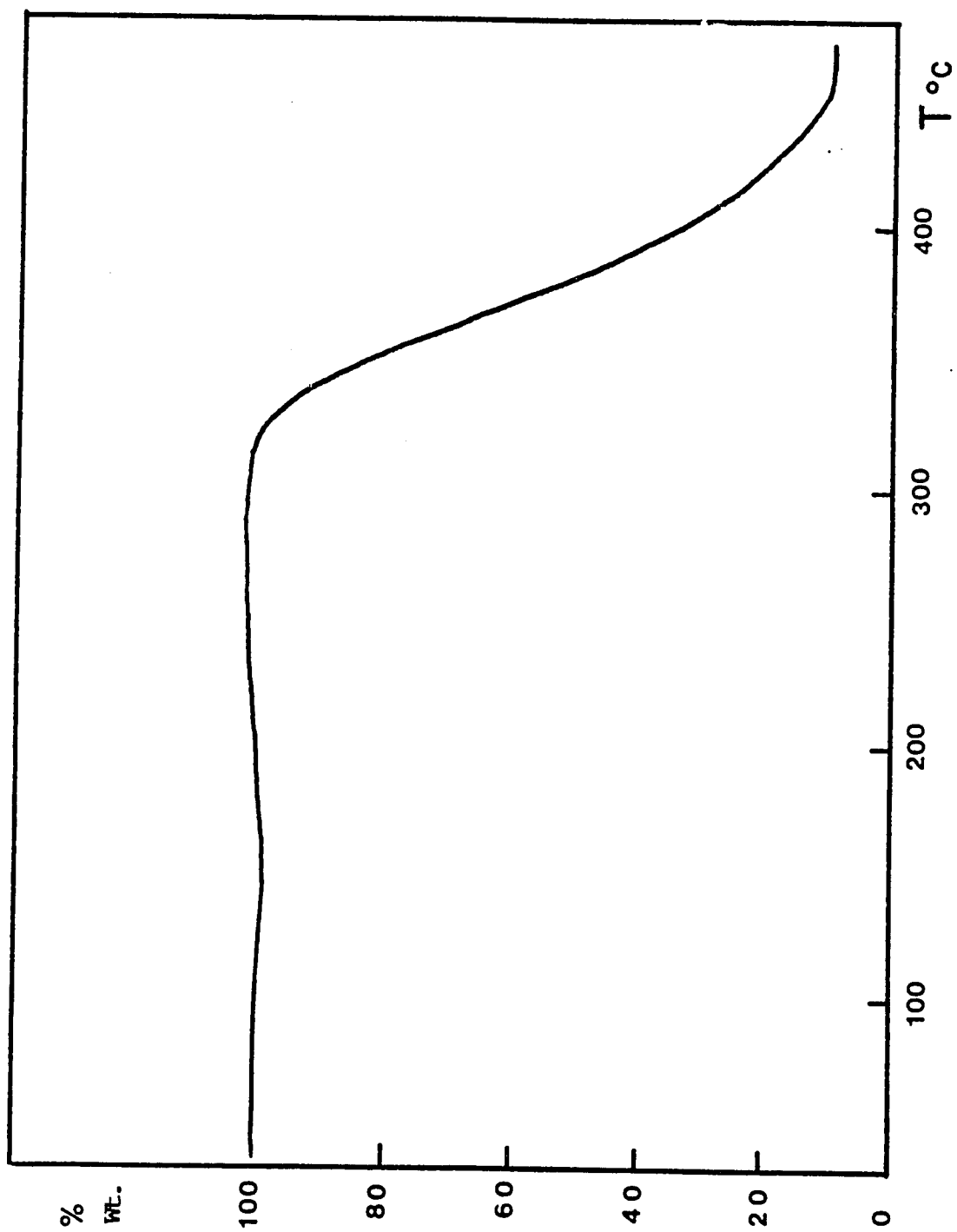


Fig.22c. TGA thermogram of PMPM in air.

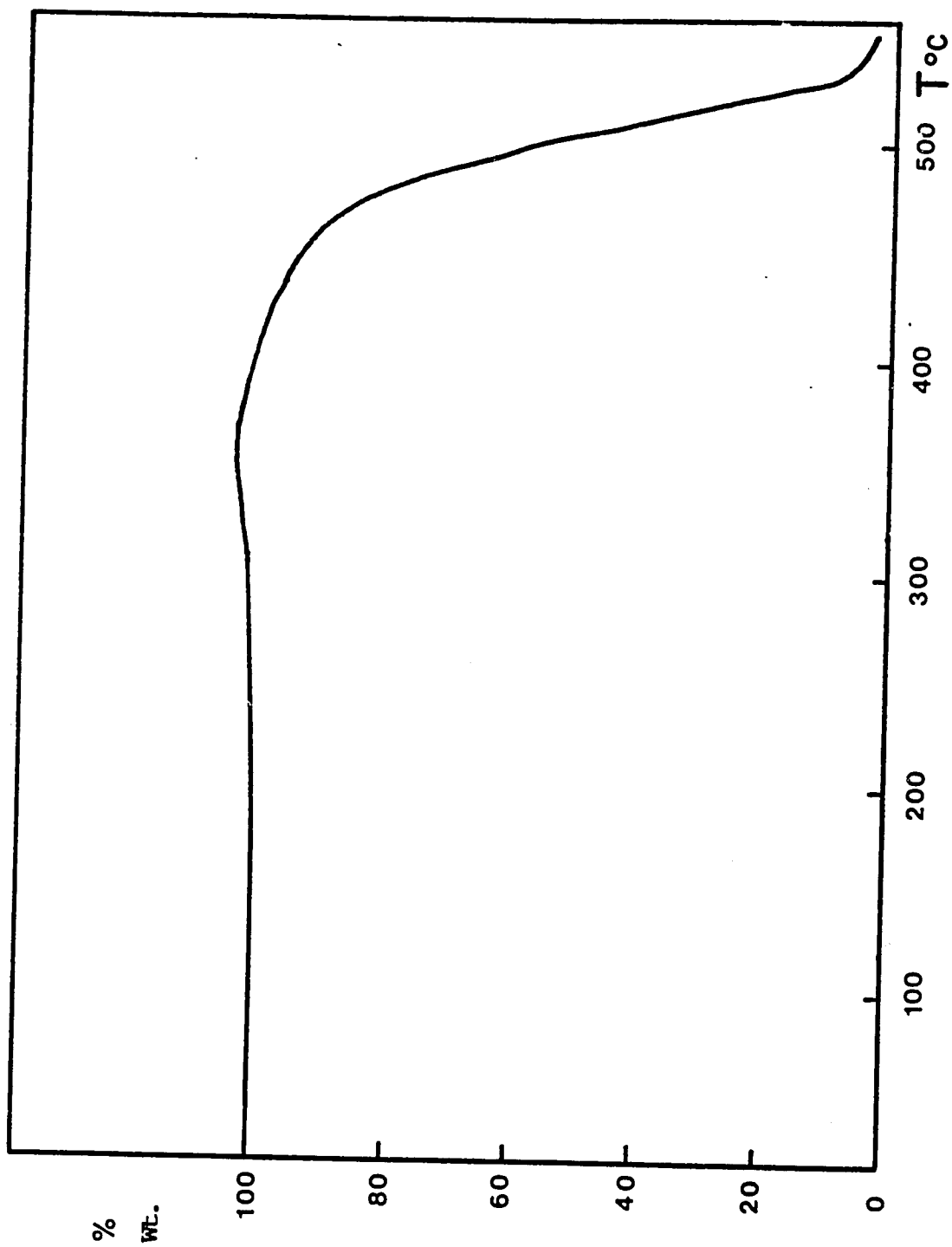


Fig.22d. TGA thermogram of PMMA in air.

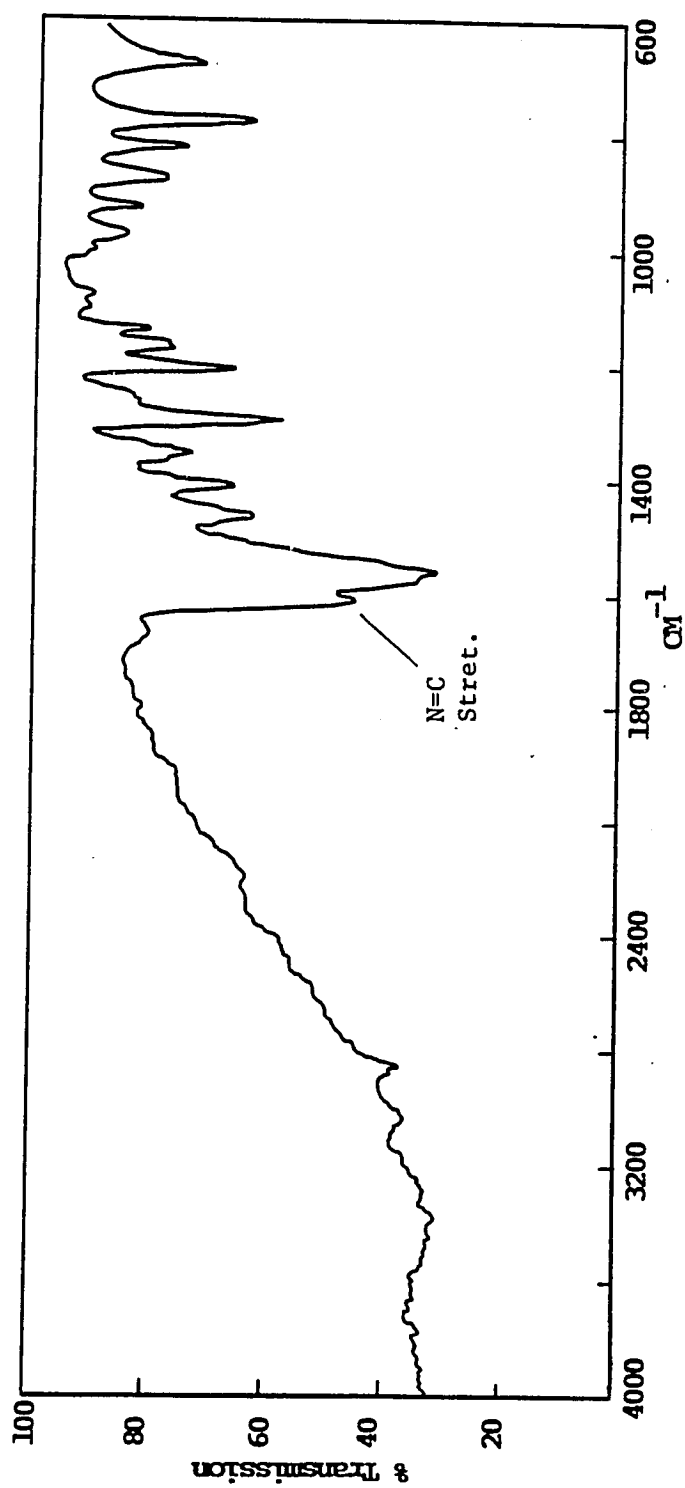


Fig. 23a. IR spectrum of PMPM sample after heated to 225°C in air (KBr).

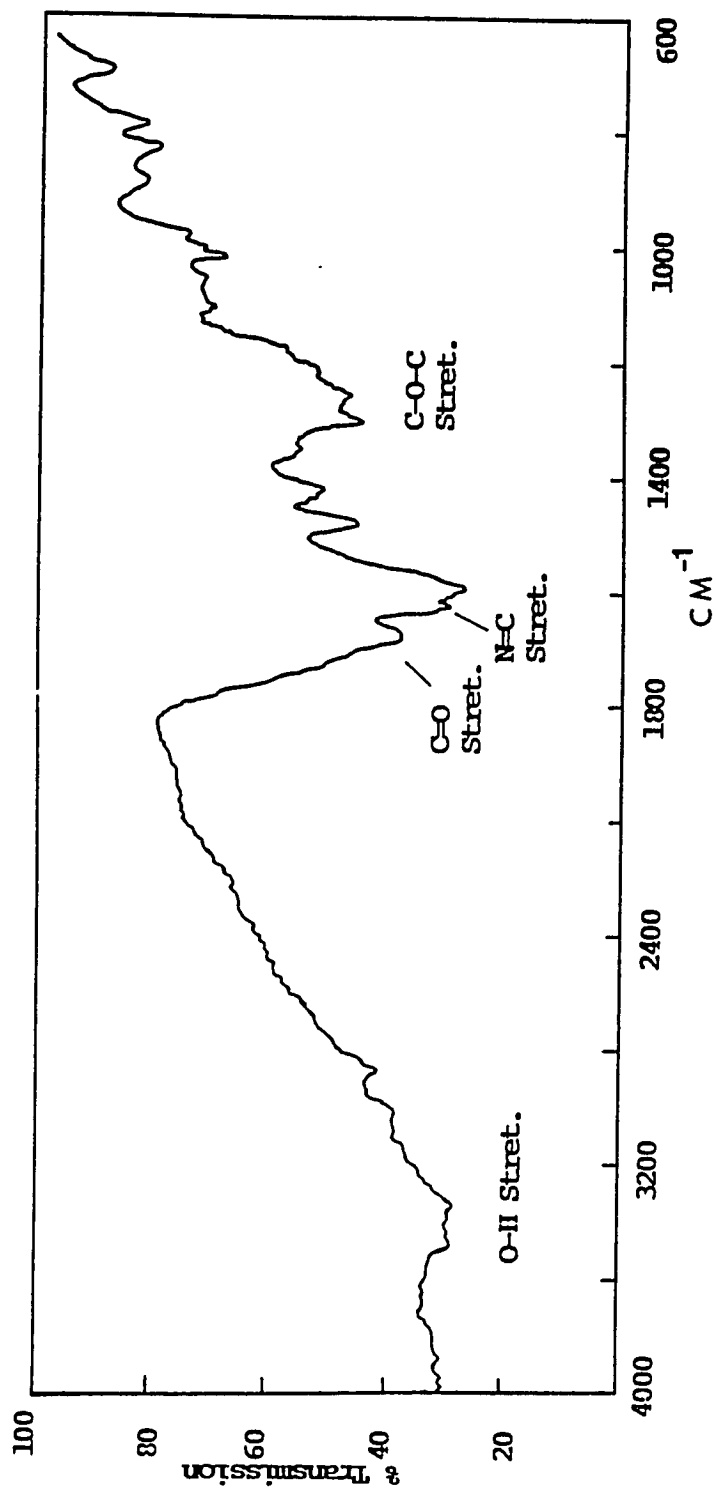


Fig.23b. IR spectrum of PMPM sample after heated to 295°C in air (KBr).

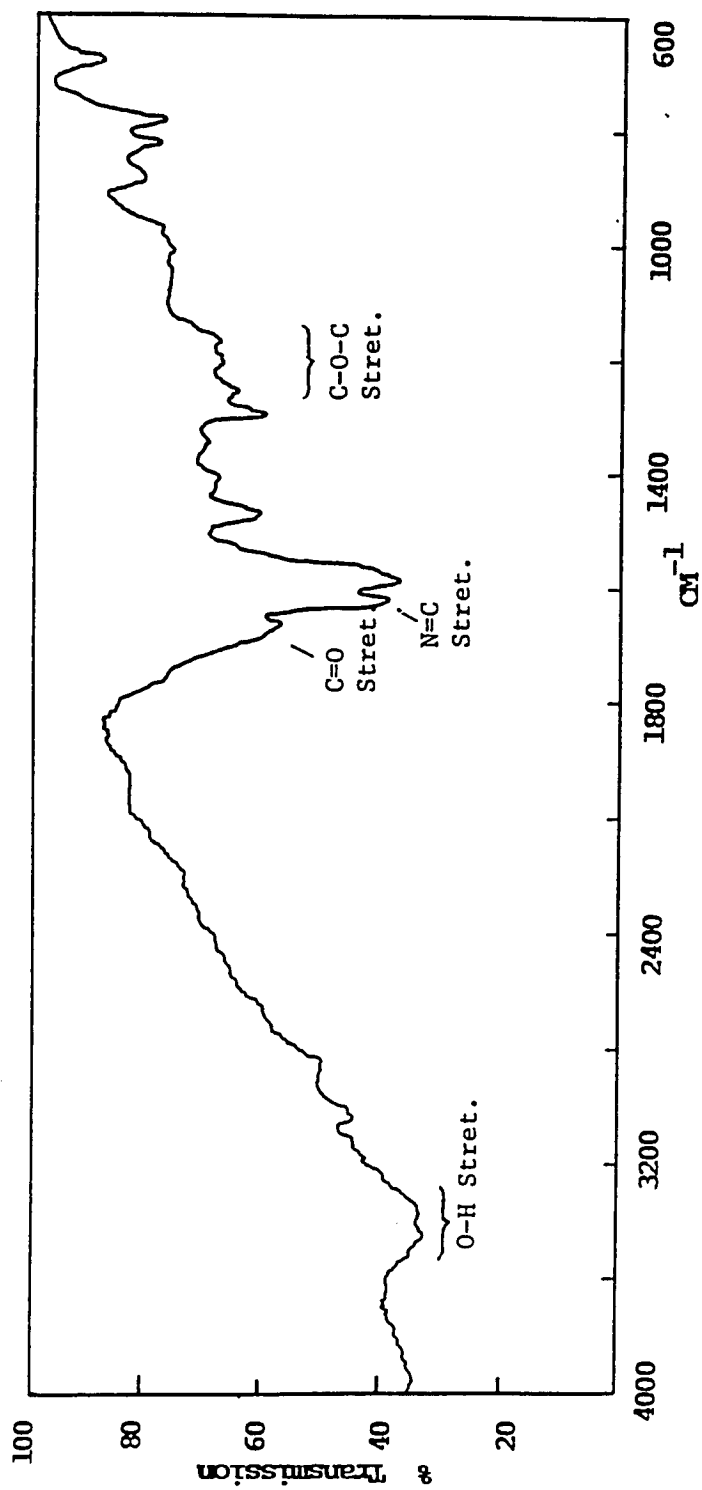


Fig. 23c. IR spectrum of FMPM sample after heated to 295°C in N₂ (KBr).

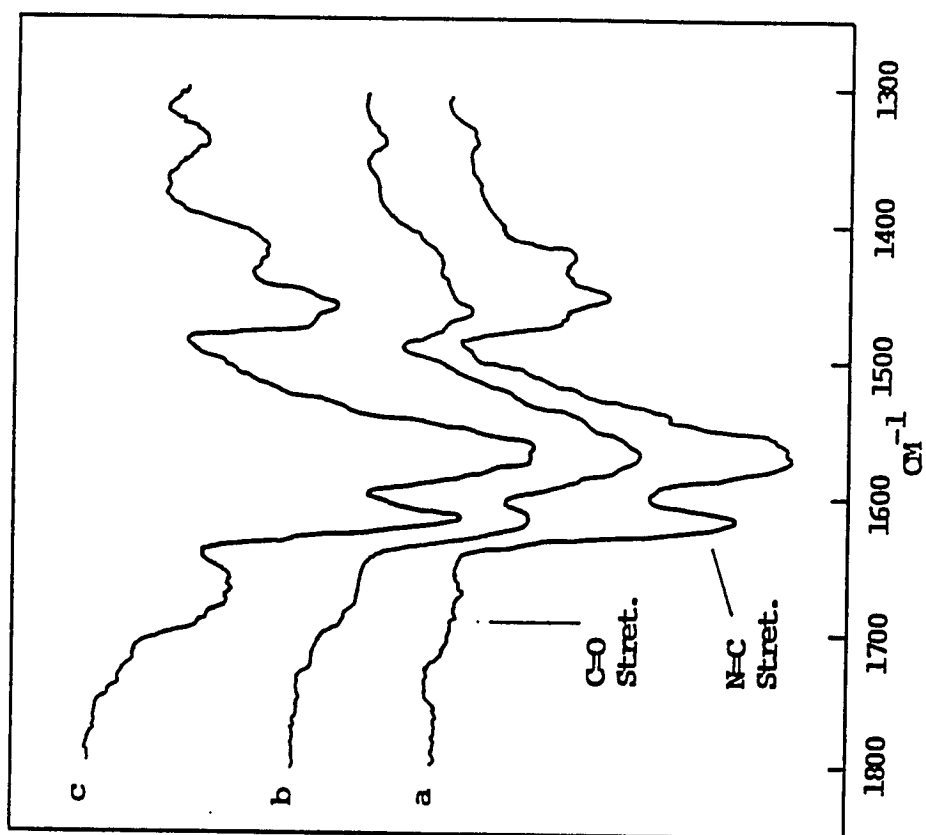


Fig.24. IR spectra of PMM samples after heated to a) 245°C in air, b) 310°C in N₂ and c) 310°C in air.

Differential scanning calorimetric results are summarized in Table 15 and are in good agreement with TGA and IR observations.

The monomer, MPM, demonstrates one endotherm and two exotherms in its DSC thermogram in nitrogen as shown in Fig.25. The endothermic peak at 139°C is very sharp corresponding to the melting transition of MPM. The first exothermic peak at 225°C is also strong and fairly sharp with a reaction window of ca. 40°C . (The reaction window is defined as a temperature range between the onset and final temperatures of an exotherm.) A separate experiment shows that MPM melts at 140°C followed by a solidification at ca. 225°C . The solidification process of MPM is apparently related to the first exotherm in the DSC measurement. The second exothermic peak appears at ca. 442°C and is very broad.

The polymer PMPM does not melt in the temperature range of the experiment, therefore there is no endotherm in its DSC thermogram(Fig.26). No glass transition was observed for this polymer under the present experimental conditions. In N_2 , the DSC thermogram (Fig.26a) shows two exotherms at 225 and 298°C , and a very broad exotherm covering a temperature range from ca.355 to 500°C . The first exotherm starts at ca. 160°C and displays a maximum at 225°C which is exactly the same temperature of the first exotherm of its monomer, MPM. This suggests that it is caused by the same process in MPM and PMPM. However, there are some differences. For example, for PMPM this

exotherm is weaker and broader (reaction window 90°C) than that for MPM. Under an air atmosphere, there is no noticeable change of the first exotherm of MPM, and the intensity of the first exothermic peak of PMPM also has no significant difference (Fig. 26b) in comparison to those under a nitrogen atmosphere. The TGA results of PMPM show no significant weight loss at 225°C . Re-heating the PMPM sample which has been heated to 250°C and cooled to room temperature in nitrogen, generates a DSC curve without the first exotherm around 225°C .

From the above observations, it is concluded that the first exotherm is caused by a thermal crosslinking of the acetylenic end groups in both PMPM and MPM. The IR spectrum of PMPM after heating to 225°C (Fig. 23a) showing disappearance of the acetylenic end group further supports this conclusion.

The polymer, PMPM, has fewer end groups on a per weight basis than its monomer, MPM. Thus, the intensity of the first exothermic peak of PMPM is smaller than that of MPM. Between the melting point and the thermal crosslinking temperature, MPM exists in the liquid state while PMPM exists in the solid state at all temperatures. The molecular mobility of MPM is much higher than that of PMPM when crosslinking takes place. Therefore the first exothermic peak for MPM is sharper than that of PMPM.

The uses of terminal acetylenic groups as a crosslinking site for the preparation of high molecular weight polymer networks are well documented[8,53,54]. The thermal crosslinking

of the acetylenic groups were found to take place at a similar temperature, i.e. 225°C [54b,53]. The structure of the crosslinked polymers and the mechanism of the reaction are still not well understood. In some of the initial work in this area, it was generally assumed that the crosslinking reaction involved the trimerization of three acetylene groups into a benzene ring[74]. However, Kovar and coworkers[75] and Hergenrother[76] indicated that the trimerization reaction is probably minor and that the crosslinking reaction occurs by a number of simultaneous, complex reaction mechanisms. It is generally believed now that most of these reactions produce aromatic or condensed aromatic rings, and conjugated linear chains which are probably further converted to aromatic systems at elevated temperatures. Thus the structures of the polymer networks can be depicted in only general terms. The thermal crosslinking reaction of the acetylene end groups in PMPM is thus illustrated in Scheme 6 where the circles represent some undefined aromatic ring or conjugated chain formed from the reacting acetylenic groups. The lack of a significant weight loss at 225°C in the TGA data of PMPM indicates that such thermal crosslinking of the acetylenic groups most likely involves only an inter or intramolecular rearrangement of chemical bonds without gaining or losing any atom from the original polymer molecules. Because the thermal crosslinking reaction converts the acetylene end groups into conjugated rings or into chains which should further stabilize the system

through the resonance effect, an exotherm in the DSC thermograms for PMPM and MPM could be expected.

Observations similar to those for PMPM and MPM were made in DSC studies of PMMM and its monomer, MMM. The DSC thermogram of MMM (Fig.27) shows a melting endotherm at 93°C , and a maximum of the first exotherm at 237°C with a reaction window of about 50°C . Both the temperature and the value of the reaction window of the first exothermic peak for MMM are higher than those for MPM. A reason for this might be that the molecular chain of MMM is less linear than that of MPM, resulting in a reduced chance for the collision of acetylene groups in MMM. Thus the thermal crosslinking of the acetylenic groups in MMM would be more difficult than that in MPM.

The DSC thermograms of PMMM are presented in Fig.28. In the DSC curves at about 180°C just before the first exothermic peak, a downward slope begins to appear. In a separate experiment, a PMMM sample pre-heated to 310°C and then cooled to room temperature in N_2 shows a DSC curve without such a slopping baseline. This baseline deviation might be due to the glass transition of the original polymer. Since PMMM is a more flexible polymer than PMPM, it would be reasonable to assign this change in slope to T_g for PMMM. Fig.28a shows the DSC curve of a low molecular weight PMMM sample (obtained with a polymerization time of 30 min.) in which the first exothermic peak appears at 245°C . In comparison with MMM (Fig.27), the intensity of the first exothermic peak decreases greatly due to

its lower acetylenic group content. The temperature of the maximum of the exothermic peak is slightly higher than that of MMM owing possibly to the difficulty of collision of the acetylenic end groups in the relatively longer PMMM chains. A high molecular weight PMMM sample (obtained with a polymerization time of 1 hour, $M_n=16000$) gives a DSC curve in nitrogen (Fig.28b) with the intensity of the first exothermic peak further reduced in comparison to the low molecular weight PMMM. This further confirms the conclusion that the first exotherm is caused by the thermal crosslinking of the acetylenic end groups. In air, the first exotherm of the high molecular weight PMMM can hardly be identified because it is almost submerged into the second exothermic peak. In the TGA measurement, the weight loss of PMMM under N_2 atmosphere is less than 0.3% at $245^{\circ}C$, while in air, the weight gain has already started at that temperature.

The second exotherm in the DSC thermograms for the polymers occurs at temperatures where the weight gains are around their maximum values in the TGA measurements (see Tables 14 and 15). Since the first and the second exothermic peaks overlap to a certain extent, the onset temperatures of the second exotherms measured and listed in Table 15 do not necessarily represent the actual ones which should be somewhat lower than the listed values.

The polymer PMPM in nitrogen has its second exotherm (Fig.26a) with an onset temperature of $250^{\circ}C$ and a maximum at

298°C, which is very close to the temperature of the maximum weight gain in the TGA measurement. In air, the second exothermic peak appears as a shoulder at ca. 325°C. In comparison to that in N₂, the intensity of this peak considerably increased corresponding to the larger weight gain in the TGA results(Table 14). The intensity of the carbonyl absorptions in its IR spectrum (Fig.23b) is considerably higher than that in N₂(Fig.23c).

For either high or low molecular weight PMMM in N₂ (Fig.28), the second exotherm occurs at 293°C, at which temperature a significant weight gain in the TGA measurement is observed. The maximum weight gain is reached at a somewhat higher temperature. The peak area of the high molecular weight PMMM seems to be slightly larger than that of the low molecular weight one. With a heat treatment in air, the high molecular weight PMMM gives a shoulder at ca.295°C.

The monomers, MPM and MMM, exhibit only a very small second exotherm appearing as a shoulder at near 295°C (Figs.25 and 27).

Based on results from TGA and DSC measurements and IR spectroscopy , it is concluded that the diethynylene triple bonds in the polymers, PMPM and PMMM, react with H₂O, O₂ or both to form carbonyl groups and other oxygen-containing groups in a broad temperature range, ca. 200-450°C with a maximum around 295°C. Since these reactions start before or during the thermal crosslinking process of the acetylenic end groups,

some of acetylenic triple bonds might also undergo these reactions. However, the amount of the acetylenic units involved in such reactions must be very small because there is only a very small exothermic peak appearing as a shoulder after the first exotherm in the DSC thermogram of the two monomers, MPM (Fig.25) and MMM (Fig.27).

Thus, the heat treatment of the diethynylene triple bonds in the polymer samples produces the chemically active species which start to form at about 200°C. As the temperature goes higher, the more of these species are produced. Because these chemically active species are extremely reactive, even a trace amount of oxygen and/or moisture in the nitrogen gas flow through the samples will react. As soon as they are formed, some of them react with O₂ and/or H₂O from the atmosphere to yield carbonyl groups and other oxygen-containing groups causing the weight gain in TGA and the second exotherm in DSC. Some of them react with other unactivated groups in the polymer chains or even react with each other. (This explains why the weight gains and second-exotherm intensities of the polymers in N₂ are smaller than those in air.) Some of them may be trapped inside the polymer networks and remain unreacted.

Since the chemically active species have not been observed directly from the IR spectra, their identities are open to speculation. Newkirk and Hay[52] suggested that these chemically active groups might be free radicals.

There are two possible contributing processes for the ap-

pearance of the maximum weight gain in the TGA curves and the maximum of the second exothermic peak in the DSC thermograms. One is that all of the active species available on the surface of the polymer networks have been exhausted at the temperature of the maximum weight gain; the other is that the weight gain at higher temperatures is compensated by the weight loss due to the polymer decomposition. Those carbonyl and other oxygen containing groups may accelerate the thermal decomposition process. The formation of the maxima of the second exotherm, implies that the first process plays a more important role. The polymer samples for the DSC measurement were tightly compressed and have, therefore, lower surface area in comparison to the powder samples used for the TGA measurement. There are less chemically active species available to react with H_2O and/or O_2 , therefore the maximum of the second exothermic peaks occur generally at lower temperatures (ca. 293-325°C) than the temperatures of the weight gain maxima (ca. 295-345°C). However, the second process can not be excluded, particularly at higher temperature before the polymer decomposes.

The third exotherms in the DSC thermograms for all of the polymers and monomers are very broad as shown in Figs.25-28. For MPM and MMM, the third exothermic maxima at 442 and 480°C, respectively, are quite small and are caused by the thermal decomposition of the polymer networks because the intensities

of the peaks increases as the atmosphere is changed from N_2 to air. For PMPM and PMMM(both the high and low molecular weight ones) in N_2 , the third exotherms cover the temperature ranges 350-525°C and 355-550°C, respectively, and are attributed to a combination of the thermal crosslinking of the diethynylene triple bonds which survived the previous thermal reactions and the thermal decomposition. A small maximum at 375°C is mainly due to the crosslinking of the diethynylene triple bonds. It was reported [53] that the thermal crosslinking of diethynylene triple bonds occurs at higher temperatures than that of the acetylenic triple bond. Similar to PMPM, a small shoulder at ca. 350°C in the DSC curves of PMMM(Fig.28) can be identified and is also attributed to the thermal crosslinking of the remaining diethynylene triple bonds. In air, both PMPM and PMMM exhibit an intense exotherm covering a large temperature range. The polymer PMMM seems to have two stages of decomposition in air as indicated by the shoulder at ca. 340°C (Fig.28c).

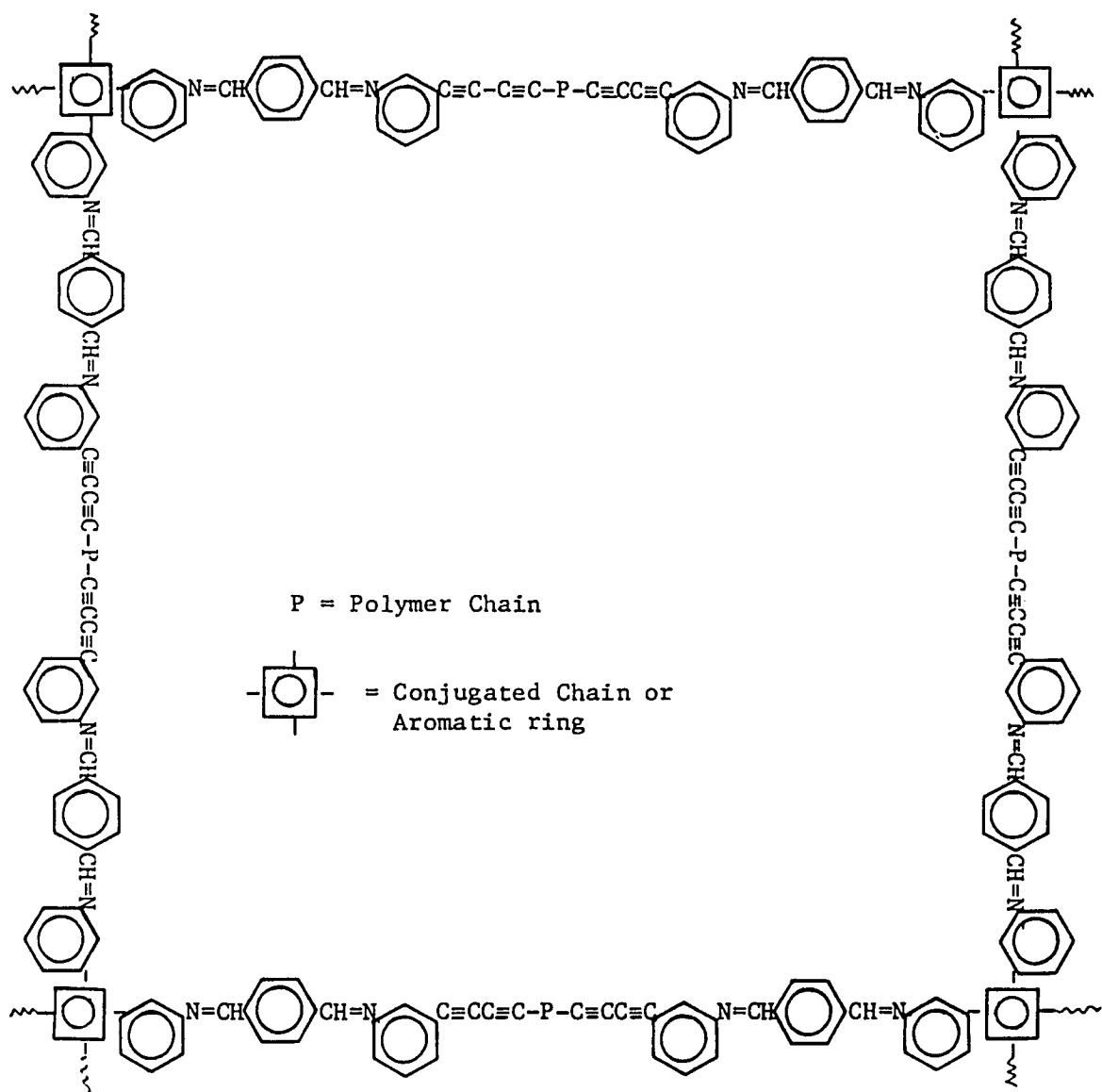
Table 15 DSC DATA OF THE POLYMERS AND THE MONOMERS IN AIR OR N₂ (HEATING RATE, 20°C/MIN.)

Compd.	No.	Atm.	T _m (°C)	T _g (°C)	Exotherm 1 (°C)		Exotherm 2 (°C)		Exotherm 3 (°C)	
					Onset Max.	Reaction Window	Onset Max.	Reaction Window	Onset Max.	Reaction Window
PMPM	1	N ₂	-	-	160	225 90	250	298 105	350	(375) -
		Air	-	-	180	230 70	250	325 105	355	485 -
PMMM ^a	2	N ₂	-	180	200 (245)	65	265	293 95	355	- -
		Air	-	180	-	- -	220	295 -	-	- -
PMMM ^b	2	N ₂	-	180	200	245 65	265	293 95	355	- -
MPM	3	c	139	-	185	225 40	-	- -	360	442 140
MMM	4	c	93	-	190	237 50	-	- -	300	480 -

a. PMMM with high molecular weight(60 min polymerization time)

b. PMMM with low molecular weight (30 min polymerization time)

c. No significant difference has been observed in the thermograms under N₂ and air.



Scheme 5 Endgroup Crosslinked Polymer Network

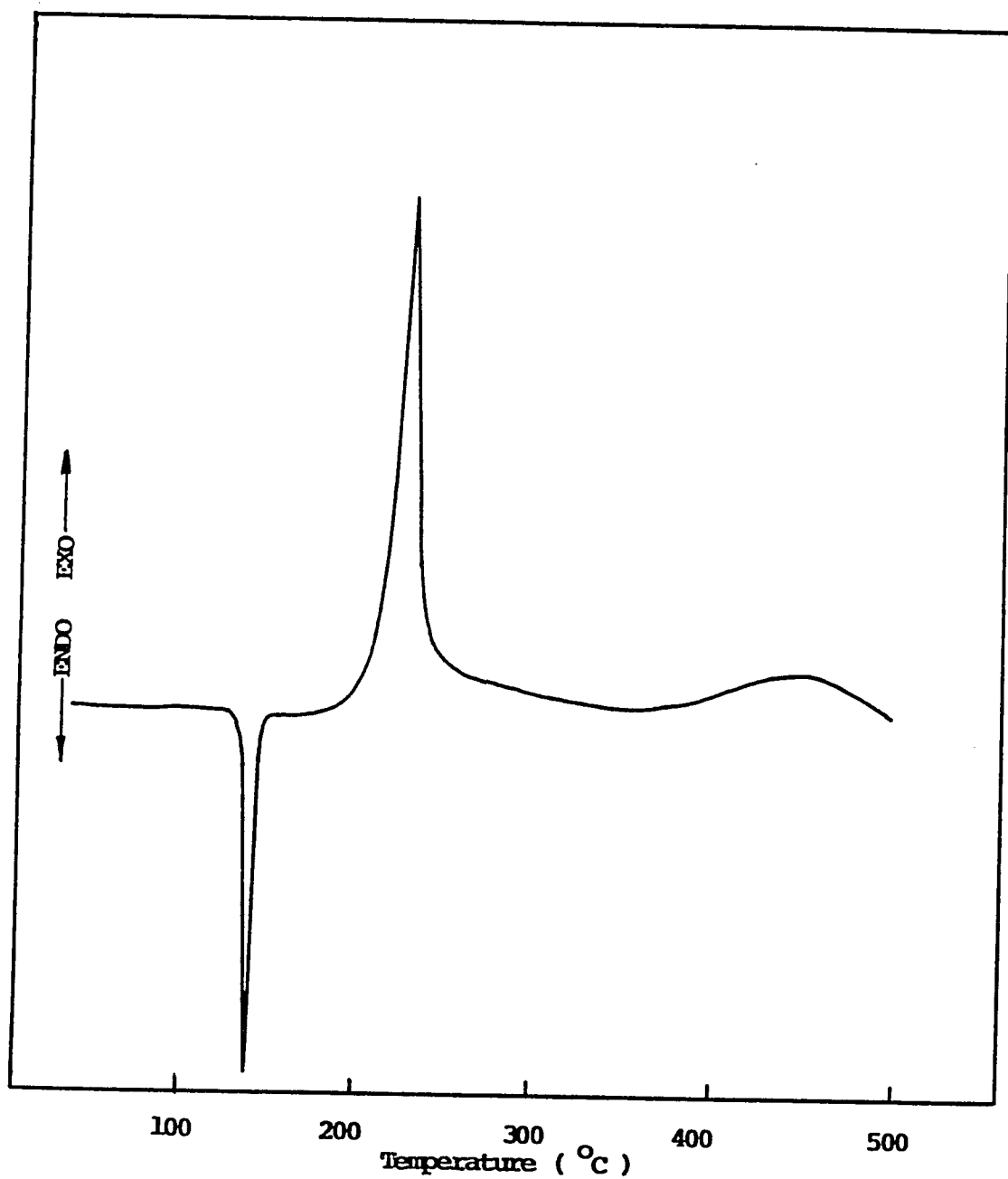


Fig.25. DSC thermogram of MPM in nitrogen

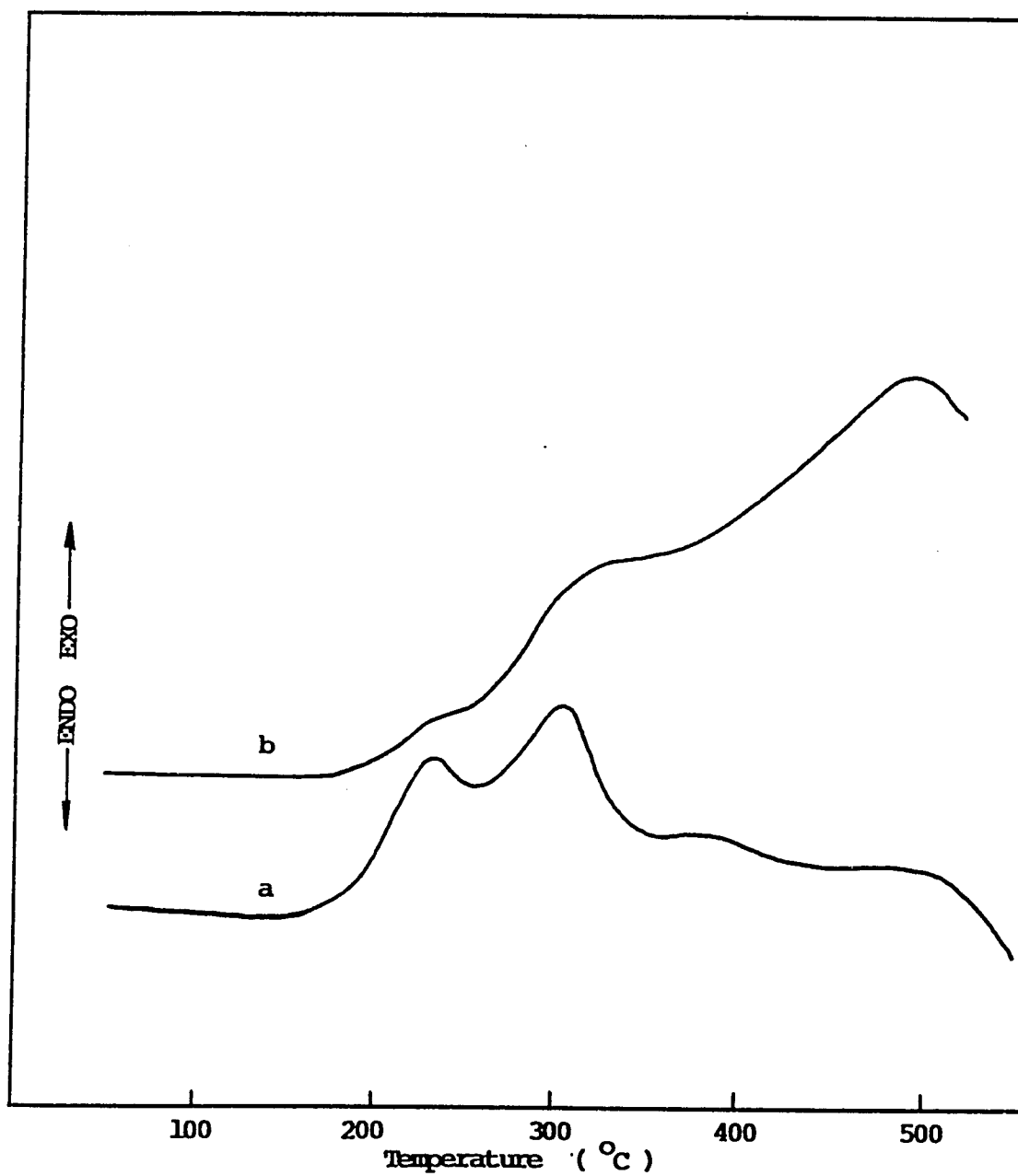


Fig.26. DSC thermograms of PMPM in a) nitrogen and b) air

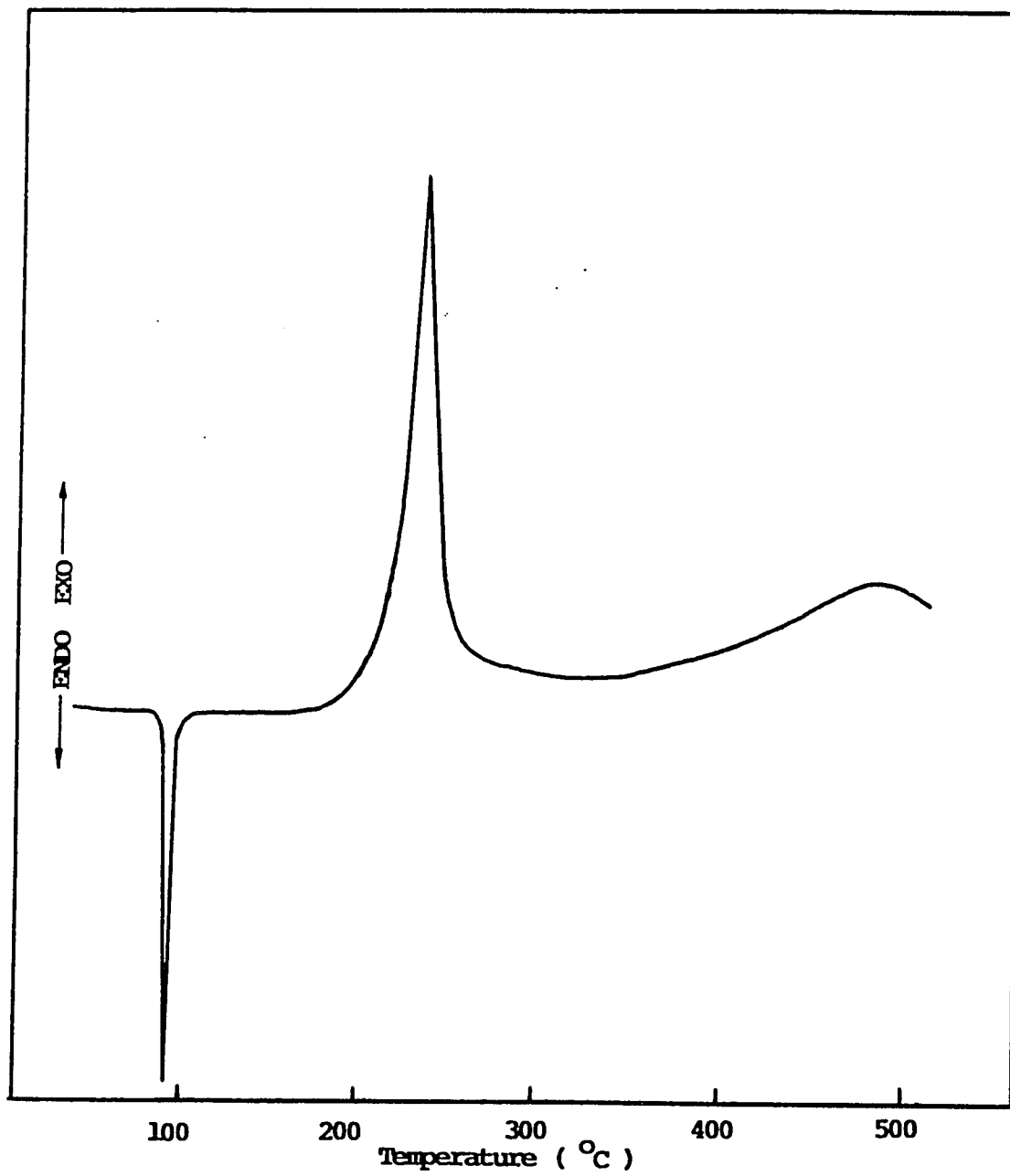


Fig.27. DSC thermogram of MM in nitrogen

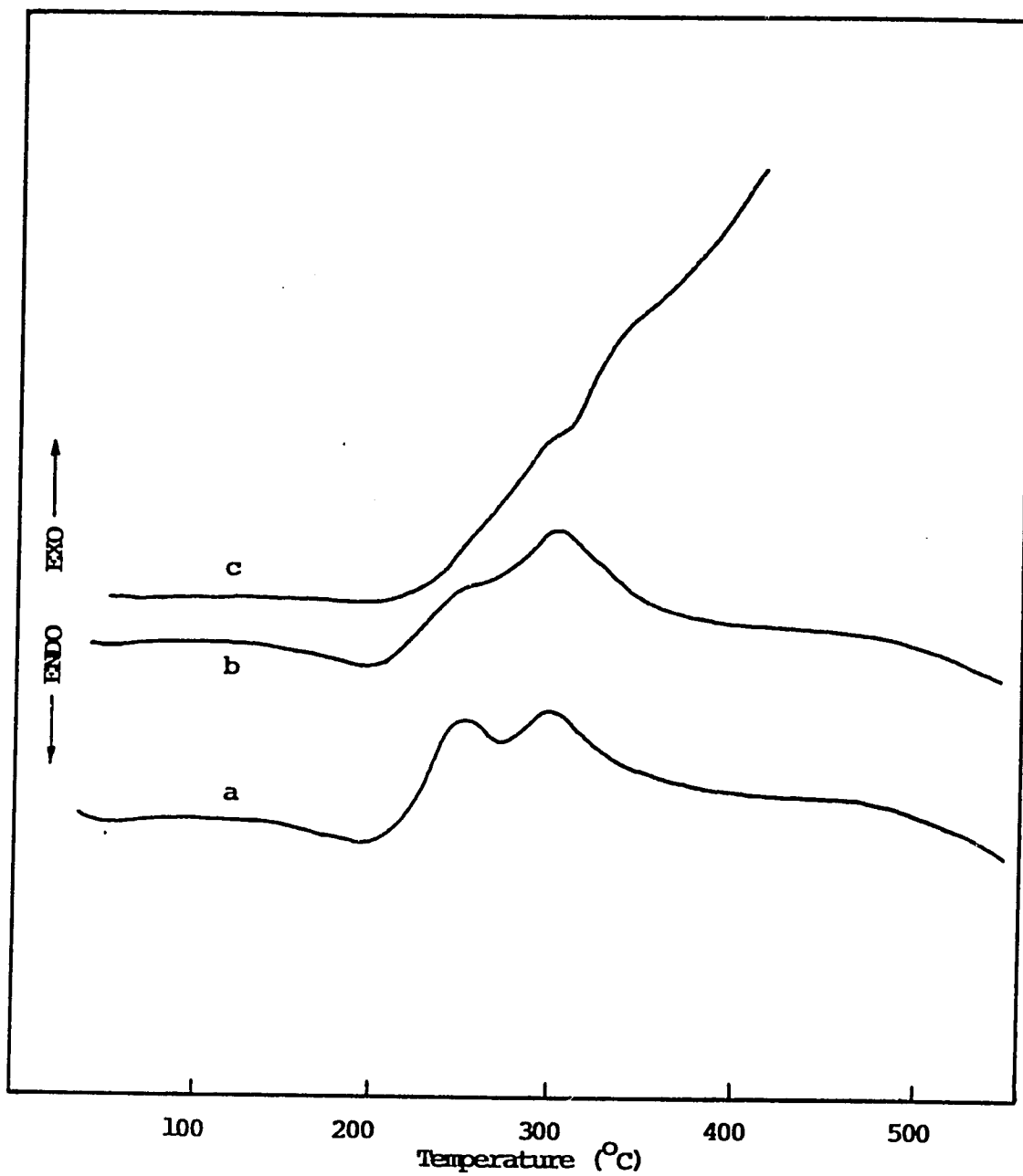


Fig.28. DSC thermograms of a) low molecular weight PMM in nitrogen; high molecular weight PMM in b) nitrogen and c) air

4.4.2 PARAMAGNETISM

The polymer PMPM and its monomer MPM in the condensed phase under various conditions exhibit sharp ESR absorptions (Figs.29-33) between the third and fourth lines of the Mn^{2+} marker where most ESR signals for typical organic free radicals in a doublet ground state appear. The spin densities and the linewidths of the signals are listed in Table 16. In general, all of the ESR signals are structureless narrow singlets indicating that the unpaired electrons are delocalized over a fairly large conjugated system.

The ESR spectrum of MPM in its neutral state (Fig.29) shows a singlet signal with a linewidth 9.0 gauss and spin density 3.0×10^{17} spins/gram.

The polymer PMPM in its neutral state also gives a narrow singlet ESR signal with a linewidth of 7.0 gauss, and a spin density 5.4×10^{16} spins/gram which is lower than that of MPM. The spectrum (Fig.31) appears to consist of a triplet with its central line overshadowed by a strong singlet.

The ESR spectra of protonated MPM and PMPM (Figs.30 and 32, respectively) were measured at room temperature. Tri-fluoroacetic acid (99%) in a quantity about twice of the stoichiometrical amount to insure a complete protonation of all imine groups was added to the PMPM or PMMM sample and well mixed. Then, the excess of TFA were removed by evaporation un-

der vacuum at room temperature to yield a protonated MPM or PMPM sample in the condensed phase. The intensities of the ESR signals of such protonated MPM and PMPM are enhanced. It is well known that the intensity of the ESR signal rises usually with an increase in the dimensions of the system of conjugated bonds[17]. Therefore the protonation of the imine groups in both MPM and PMPM lead to formation of better conjugated systems. This is consistent with the earlier conclusion from the NMR and UV spectral studies that the protonation of imine groups leads to a more planar conformation of the aromatic azomethines. The spin densities of PMPM and MPM increase to 8.0×10^{16} and 5.7×10^{17} spins/gram, respectively, upon protonation. One expects the polymer PMPM to have a more extended conjugation system; therefore, it has a higher ESR intensity than for the monomer MPM in either the neutral or protonated state. However, the results are just opposite to the expectations. These results consists with the observation in the UV spectroscopic studies of PMPM and MPM in acidic solutions (Section 4.3.2 and Table 13) where the first absorption band of PMPM occurs at a similar wavelength (379 nm in MeSO_3H) as that of MPM (378 nm in MeSO_3H). ALL these observations indicate that the conjugation length of the polymer, both in neutral and protonated forms, in the solid phase is shorter than that of its monomer. However, in solution, they are comparable. A reasonable explanation could be that the polymer chains would be twisted more from a planar conformation

than the monomer chains, due to a steric effect of the bulky chain wherein the unpaired electrons are confined to a smaller conjugated system.

After protonation, the ESR spectrum of PMPM changes into a structureless singlet. This suggests that the ESR signal of PMPM in the neutral state consists of two different types of unpaired electrons due to the nonplanar conformation. One is delocalized over the diethynylene phenylene unit with probably some nitrogen lone pair characters, $\text{N-Ph-C}\equiv\text{C-C}\equiv\text{C-Ph-N}$, leading to a triplet hyperfine structure. Another is delocalized over the whole molecule but mainly around the -N=CH-Ph-CH=N- part, which generates the main central ESR singlet absorption. After protonation, the molecule becomes flatter and therefore the unpaired electrons are delocalized through the whole molecule leading to one enhanced structureless ESR signal.

The protonation of MPM and PMPM also causes some increase in the linewidths of their ESR signals (Figs.30 and 32). The linewidth of the PMPM signal increases to 11.0 gauss and the MPM signal to 13.0 gauss. The broadening of the lines can be due to the interaction of the unpaired spins with protons or with molecules of a paramagnetic impurity, such as oxygen [77]. To eliminate the effect of oxygen, the protonated polymer sample was measured under vacuum after repeated treatments by passing N_2 through followed by evacuation. In air, the intensity of the ESR signal is slightly higher than that in vacuo, but there is no difference in the linewidth of the signals in

air and in vacuo. Therefore, the increase in the linewidths of the ESR signals of PMPM and MPM upon protonation is due to the protonation of the imine nitrogen atoms.

Although, the conjugated polymers with imine [16] or diethynylene [12] groups in the backbones were reported to have ESR absorptions respectively, the ESR spectrum of the protonated polyazomethines has not been reported before. In contrast to MPM and PMPM, MMM and PMMM do not display any ESR signal in both neutral and protonated states, probably because of their poor conjugation. The PMPM was doped with iodine generating a singlet ESR signal with a twenty-fold increase in intensity (spin density, 1.7×10^{18} spins per gram of polymer) as shown in Fig.33. The linewidth of the signal is 17.0 gauss.

The MeSO_3H solutions of PMPM and MPM show strong narrow singlet ESR absorptions.

The mechanism of the enhancement of the ESR signals by doping is still not completely understood yet for most of the conducting or semiconducting polymer systems. For polyazomethines, doped with bromine or iodine, the enhanced ESR signals were considered to be caused by the formation of molecular donor (the polymer chains)-acceptor (Br_2 or I_2) complexes [78].

Table 16 ESR DATA AND D.C.CONDUCTIVITIES (AT ROOM TEMPERATURE)

Compound No.	Mol.Wt.	Sample Treatment	Spin Density (Spins/g)	Line-Width (gauss)	D.C. Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	
PMPM	1	1500	None	5.4×10^{16}	7.0	Less than 10^{-8}
		Protonated with TFA	8.0×10^{16}	11.0	4×10^{-6}	
		Doped with Iodine ^a	1.7×10^{18}	17.0	5×10^{-4}	
MPM	3	332	None	3.0×10^{17}	9.0	-
		Protonated with TFA	5.7×10^{17}	13.0	-	

a. Molar ratio of the polymer repeat unit to iodine is 1:4.

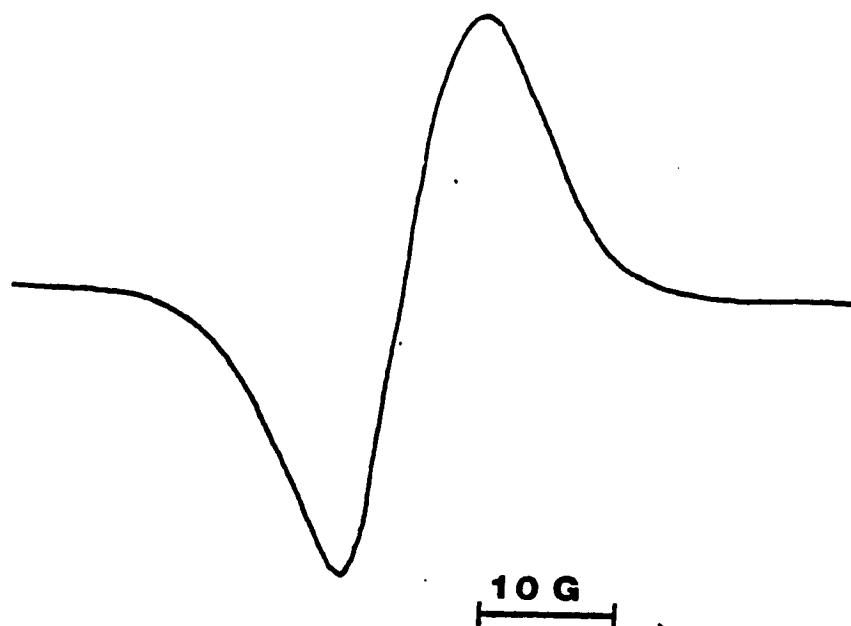


Fig.29. ESR spectrum of MPM

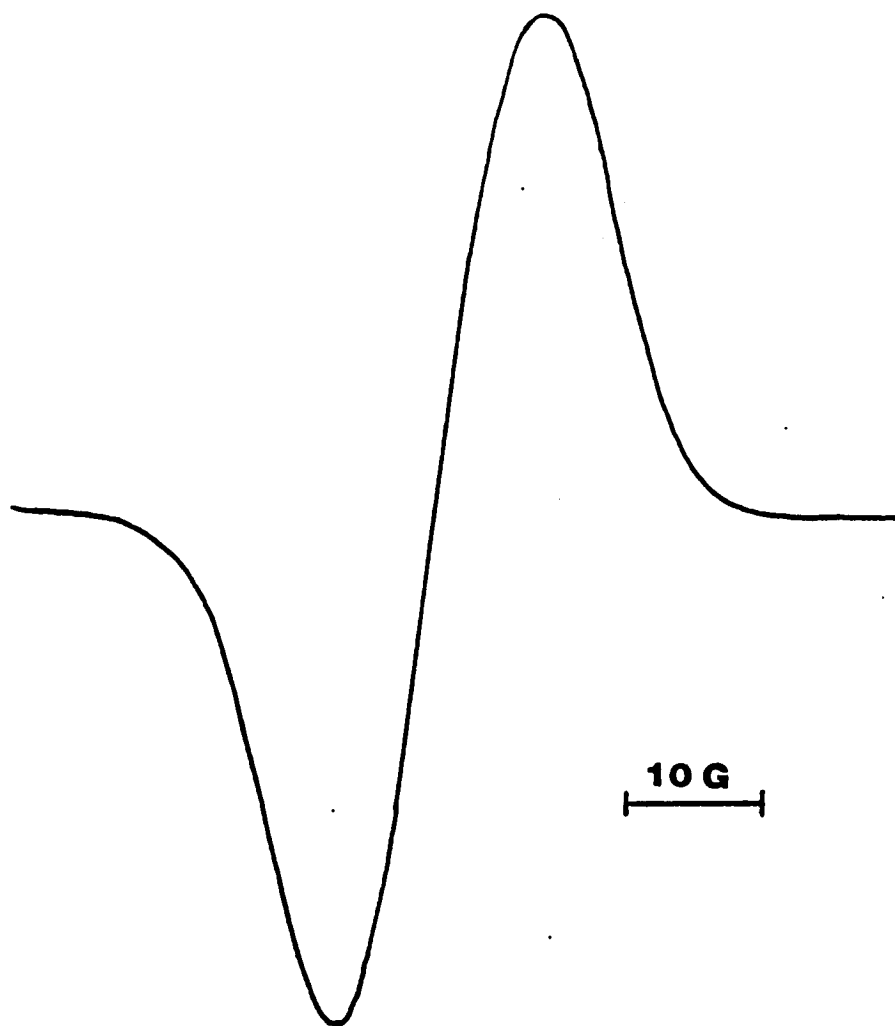


Fig.30. ESR spectrum of MPM protonated with TFA

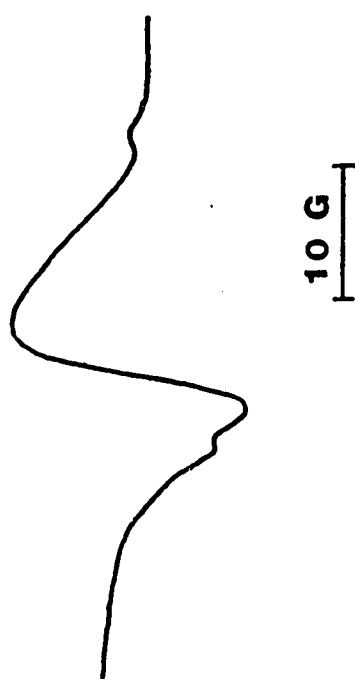


Fig.31. ESR spectrum of PMPM

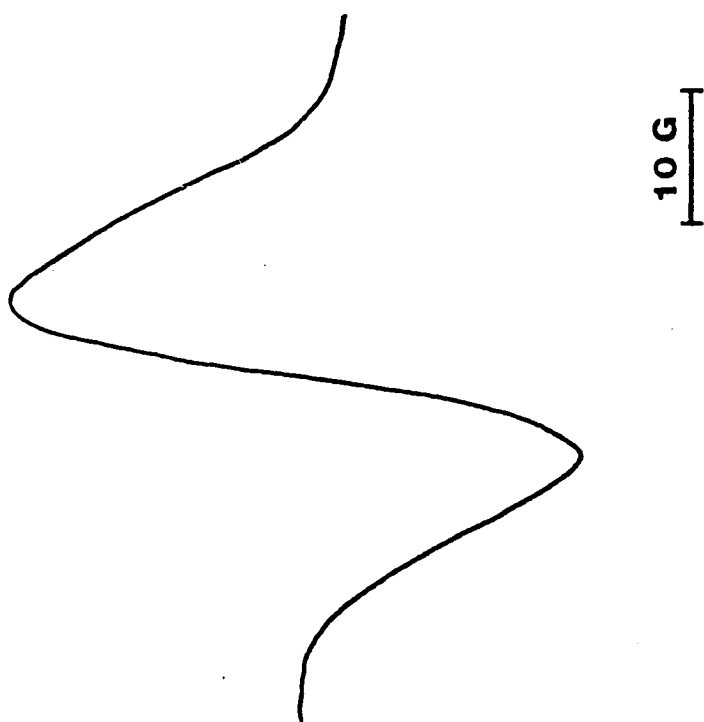


Fig.32. ESR spectrum of EMPM protonated with TFA

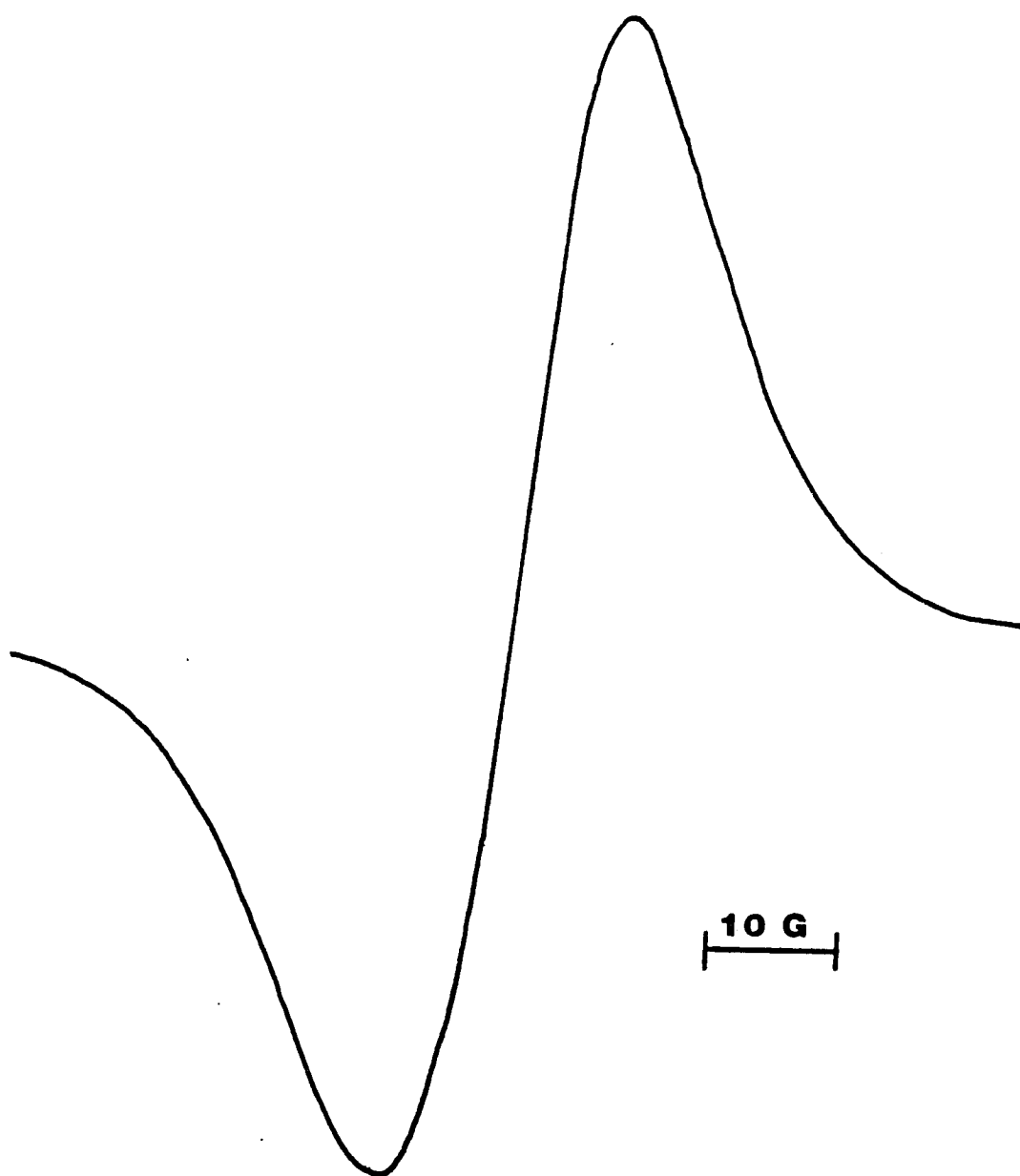


Fig.33. ESR spectrum of PMPM doped with iodine

4.4.3 ELECTRICAL CONDUCTIVITY

Although ESR absorption and the degree of coplanarity of polymers can not be directly correlated with electrical conductivity, the measurements of D.C. conductivities at room temperature on a compressed pellet of PMPM treated under various conditions yield very interesting results, showing good correlation between the ESR spin density and the conductivity as shown in Table 16.

The polymer PMPM in absence of dopant is an insulator at room temperature ($\sigma < 10^{-10} \text{ Ohm}^{-1}\text{cm}^{-1}$), similar to most undoped polyazomethines ($\sigma = 10^{-14} - 10^{-17} \text{ Ohm}^{-1}\text{cm}^{-1}$ e.g. for PNB(5), $\sigma = 2.0 \times 10^{-17} \text{ Ohm}^{-1}\text{cm}^{-1}$) [7] or diethynylene polymers (e.g. for poly-p-diethynylene benzene $\sigma < 10^{-14} \text{ Ohm}^{-1}\text{cm}^{-1}$) [50]. Protonation of PMPM increases the conductivity to a semiconducting level, $4 \times 10^{-6} \text{ Ohm}^{-1}\text{cm}^{-1}$, corresponding to the increase in the spin density. We do not have sufficient direct evidence to conclude that such increase in conductivity is mainly caused by the increase in the degree of coplanarity of the polymer conformation, but the protonation provides the polymer certainly with more unpaired electrons, delocalized through the polymer chain, and probably some types of charge carriers. The effects of the protonation of polyazomethines on their conductivities have not been studied before.

A.G.MacDiarmid and his coworkers recently reported [79] a similar system, the quinoil-benzenoid-diimine form of polyaniline, synthesized by both chemical and electrochemical methods, which was doped, i.e. protonated, by dilute aqueous protonic acids to give the corresponding iminium salt. The conductivity of the polymer increased from an insulator to the metallic regime ($\sigma = 5 \text{ Ohm}^{-1}\text{cm}^{-1}$ compressed pellet) upon doping. The doping was found to be reversible by neutralizing the protonic acid with an aqueous alkali solution. This gives another excellent example of greatly improving the conductivity of the polymers with imine groups in their backbones by protonation.

Although a better understanding of the mechanism of the conductance is still to be developed, any further study on the protonation of the polyazomethines may produce fruitful results in the field of conducting polymer research.

The polymer PMPM doped with iodine in a 1:4 molar ratio turns into a black and brittle solid with some metallic luster. The conductivity increases drastically and reaches $10^{-4} \text{ Ohm}^{-1}\text{cm}^{-1}$ as a fairly good semiconductor corresponding to an ESR spin density of 1.7×10^{18} (spins per gram of polymer). The conductivity of PMPM doped with iodine is comparable to those diethynylene polymers doped with AsF_5 ; as an example, Yang, Odian and Pemawansa reported [12] that poly (biphenylylene-1,3,-butadiynylene) has a D.C. conductivity $2.5 \times 10^{-5} \text{ Ohm}^{-1}\text{cm}^{-1}$ upon doping with AsF_5 . The conductivities of polyazomethines

upon doping with iodine (126% mol.) were reported to be 10^{-6}
 $-10^{-7} \text{ Ohm}^{-1}\text{cm}^{-1}$ [19].

5.0 CONCLUSIONS

We have accomplished the first synthesis of the two conjugated polymers, PMPM and PMMM, through the oxidative coupling polymerization. These polymers incorporate imine and diethynylene groups as repeat comonomer units. The work represents the first thorough characterization of conjugated systems with imine linkages. The conformations of these two polymers and a series of model compounds have been extensively investigated by NMR, ESR, and UV spectroscopies. Results from this broad scope of spectroscopies have been successfully correlated with polymer properties, including D.C. electrical conductivity.

Under the present oxidative coupling polymerization conditions, the imine group in the monomers is not effected and no significant side reaction was observed. Satisfactory elementary analysis results of both the polymers and the monomers were obtained. The polymers are not soluble in any common organic solvent except PMMM is soluble in some extent in pyridine. Strong protonic acids, such as TFA, concentrated H_2SO_4 and MeSO_3H , are generally good solvents for both polymers. The polymers in the acidic solutions are quite sensitive to water leading to a hydrolysis of the imine bond, but in the solid state, they are stable even suspended in aqueous acidic media. A comparison of the IR spectra of the polymers

in KBr pellet with those of the monomers shows that the polymer formation is via the oxidative coupling of the acetylenic groups of the monomers and that the polymer with para-substituted phenyl segments, i.e. PMPM, has a longer conjugation than that with all meta-substituted segments, i.e. PMMM. The solid state ^{13}C NMR spectrum of PMPM shows very similar chemical shifts to that of its monomer, MPM, in neutral solvent. No cis-unit for the imine double bond was found in either the polymers and monomers.

In acidic solution, all imine groups in the polymers and the monomers are protonated to generate the iminium group. The polymers and the monomers have different behaviors in different acids. In MeSO_3H (98%), the acetylenic triple bond in the monomers and in the end group of the polymers reacts with a water molecule to yield an acetyl group as the main addition product. However, the diethynylene triple bonds in the polymer chains remain unreacted. The ^1H NMR and ^{13}C NMR spectra of the polymers, monomers and the model compounds in MeSO_3H have been completely assigned, further confirming the structure of the polymers. The end-group effects on the spectra appear very clear for PMPM but not for PMMM owing to the higher molecular weight of the latter.

In TFA(99%), both polymers and monomers undergo a quick hydrolysis of the imine bond. The percentage of hydrolysis is governed by the amount of water in the solvent. No addition of water to either acetylenic or diethynylene triple bonds takes

place. In concentrated. H_2SO_4 (98%), the acetylenic triple bonds in both the polymers and the monomers react with water generating acetyl groups, while the diethynylene triple bonds in the polymers react with the solvent to give some mixture of furan and ketone products. However, there is no hydrolysis of the imine group in concentrated H_2SO_4 solution. The proposed structures, (1) and (2), for the polymers are supported by all of the IR and NMR results.

Polymer molecular weight has been determined by end-group analysis from ^1H and ^{13}C NMR spectra of the polymers in acidic solutions, and estimated through the intrinsic viscosities of the polymers in MeSO_3H . The PMPM has a number average molecular weight of 1,500 with an intrinsic viscosity, $[\eta] = 20.8$ ml/g, corresponding a semi-rigid chain conformation; while PMMM has a number average molecular weight of 16,000 with $[\eta] = 48.0$ ml/g corresponding probably to a flexible chain conformation.

Twenty-one 4- and 4'-substituted trans-N-benzylideneanilines were synthesized and their ^1H NMR spectra recorded at 30°C in DMSO-d_6 and acidic media, TFA-d and D_2SO_4 . The effects of substituents on the chemical shifts of H- α (proton on carbon of imine group) and H-2' (proton on benzaldehyde ring ortho to the imine group) were analyzed by the Hammett single parameter and Taft dual substituent parameter techniques. In the neutral solvent DMSO-d_6 , there is transmission of the electronic effects of substituents on the benzaldehyde ring to the H- α and H-2' protons, but no electronic

transmission for substituents on the aniline ring. There is a dramatic change in acidic media. Protonation of the imine group results in significant electronic transmission from substituents on the aniline ring to the H- α and H-2' protons, as well as an enhancement in electronic transmission from substituents on the benzaldehyde ring. DSP analysis indicates that both inductive and resonance factors are responsible for the observed electronic transmission effects, with resonance being the major factor. The π -polarization mechanism is mainly responsible for the observed inductive electronic transmission in protonated 4-substituted trans-N-benzylideneanilines. Thus, the protonation of the trans-N-benzylideneanilines leads to an increase of the molecular coplanarity since the electronic transmission by both resonance and π -polarization mechanisms requires the coplanar conformation of the molecules.

The UV spectra of the polymers, monomers and model compounds have been studied extensively both before and after protonation. The absorption bands have been assigned. In neutral solvents, the trans-N-benzylideneaniline-type of compounds take a non-planar conformation with a varying twist angle between the aniline ring and the rest of the molecule. The monomer MPM(3) and N,N'-(1,4-phenylenedimethyldiyl)-bis-aniline(6) seem to have more planar conformation in methylene chloride. The results further support the Brocklehurst model[43]. In acidic solutions, the compounds have more planar

conformation owing to the protonation of the imine group. The UV spectra of all compounds(1-7) become more similar to those of trans-stilbene and 3,3-dimethyl-2-phenyl-3H-indole (26), a model compound generally accepted to have a planar conformation. The first band is assigned to the $\pi-\pi^*$ transition in the whole conjugated molecule or polymer segment, and is indicative of the conjugation length of the molecule. Meta-substitution seems to contribute very little to the conjugated system. The conjugation lengths of the polymers are similar to those of their monomers since Band I for both the polymers and the monomers exhibits quite close values for both the wavelength and the intensity.

The reactions of the acetylenic and the iminium groups with water in different acids can also be monitored by UV spectroscopy. The results support not only the conclusion drawn from the NMR studies but also the assignments of the UV spectral absorption bands. The existence of five diethynylene absorption bands in the UV spectra of the polymers in TFA and methanesulfonic acid further confirms the formation of the diethynylene linkage in the polymers. Lack of these five bands in the UV spectra of the polymers in concentrated. H_2SO_4 indicates that the diethynylene triple bonds have been reacted with the solvent.

Both PMPM and PMMM exhibit superior thermal stabilities under nitrogen atmosphere. The weight losses of PMPM and PMMM are 31% and 27%, respectively, at 900°C . In air, PMPM and PMMM

decompose explosively at ca. 350 and 450°C, respectively. A weight gain was observed for both polymers at the temperatures just before the decomposition in both N₂ and air.

The polymers undergo four types of thermal reactions as the temperature of heat treatments progressively increases either in N₂ or in air.

At ca. 225-245°C, the ethynyl end group of the polymers undergoes a thermal crosslinking reaction to yield polymer networks. This is concluded based on the observations: a) there is no significant weight loss in the TGA measurements; b) the acetylenic C-H stretching absorption of PMPM end group disappears in the IR spectrum; and c) in the DSC thermograms of the polymers as well as the monomers, there is an exotherm with intensity dependent on molecular weight. In the temperature range 295- 345°C, the polymers show maxima of weight gains in the TGA measurements. Such weight gains in N₂ are less than those in air. Infrared spectra indicate that the formation of carbonyl groups and other oxygen-containing groups from the diethynylene triple bonds are responsible for the weight gain. No involvement of the imine group in these reactions was found by the TGA measurement of the pure aromatic polyazomethine(27) since no weight gain was observed. The DSC thermograms displays maxima of exothermic peaks ranging from 293 to 325°C corresponding to the temperatures of the weight gain in TGA. It is concluded that the heat treatment of the diethynylene triple bonds in the polymer chains produces some kinds of extremely reactive

species. Once they form, they undergo a variety of reactions. One of these is the reaction of such species with the atmospheric H_2O and/or O_2 to generate several types of carbonyl and other oxygen-containing groups until all of such species available on the sample surface have been exhausted. The identity of such species is still to be ascertained but they are likely to be some kinds of free radicals. At elevated temperatures (ca. $345\text{--}500^\circ\text{C}$) after formation of the oxygen-containing groups, the polymer decomposition takes place. (Under nitrogen atmosphere, the major weight loss of the polymer samples occurs in this temperature range.) Another thermal reaction which was observed in the DSC thermograms of the polymers appearing as very weak exothermic peaks at ca. 375°C is attributed to the thermal crosslinking of the surviving diethynylene triple bonds.

The polymer, PMPM and its monomer, MPM, in condensed phase show narrow ESR absorption signals. This indicates that the unpaired electrons are delocalized in the molecules over a fairly large conjugated system. Some hyperfine structures observed in the ESR spectrum of PMPM suggests the existence of more than one types of paramagnetic species. Protonation of both PMPM and MPM enhances the intensities of the signals and leads to the disappearance of the hyperfine structures of PMPM. This suggests the increase of the dimensions of the conjugated system owing to the coplanar conformation of the molecules. The interaction between the additional protons and the un-

paired electrons is mainly responsible for the increase of the linewidth of the signals upon protonation. The lower intensity of both protonated and unprotonated PMPM in comparison with MPM indicates that PMPM has relatively shorter conjugation length than MPM in solid state because of twisting or entanglement of the polymer chains wherein the unpaired electrons are confined to a smaller conjugated system. Upon doping with iodine, the intensity of the ESR signal of PMPM is further increased. No ESR absorption was observed for MMM or PMMM.

Pure PMPM was found to be an electrical insulator while upon protonation or doping with I_2 , it becomes a good semiconductor with conductivities equal to 4×10^{-6} or $5 \times 10^{-4} \text{ Ohm}^{-1} \text{ cm}^{-1}$, respectively. These results indicate correlation among conductivity, structure and conformation of the polymers.

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