

Electrical/Mechanical Properties and Activation Energies of Some Poly(2-vinylpyridine)-Metal Complexes

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ABSTRACT: Poly(2-vinylpyridine) (P2VP) and its metal-based complexes have been synthesized and characterized through analytical measurements, such as thermal analysis and IR- spectroscopy. The electrical conductivity of these complexes was studied as a function of temperature. The conductivity of P2VP is seen to increase by many orders of magnitude on complexation with some metal chlorides such

as BaCl₂, ZnCl₂, NiCl₂, or CoCl₂. The activation energy for electrical conductivity of either of these complexes is found to be lower than that of the host polymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3537–3549, 2006

Key words: poly(2-vinylpyridine); analytical studies; electrical and mechanical properties

INTRODUCTION

Besides their traditional use as insulators, organic polymers are being extensively studied with a view of employing them as semiconductors or conductors. Initially, composites based on polymers along with some conductive fillers (metal powder, etc.) were prepared to achieve these objectives.¹ Electrically conducting polymers have excited considerable interest because many applications can be envisioned for electroactive materials. Conductive polymers offer many advantages, compared to classic materials (metal, wood, etc.), such as facilities of processing, cost effectiveness, low density compared to metals, preservation from corrosion, low hardness, and varied mechanical properties.

Naturally, the introduction of metallic materials allows them to envisage the elaboration of polymers possessing the conductive properties of metals and the varied properties of polymers. The role of the metal in the electron transport property of metal polymers may be related to polarizability, ionization potentials, size of the metal ion, distances between the neighboring metal ions, and the rotational/vibrational dynamics of the metal ion.²

Studies were made on the electrical conductivity of oligomers and polymers prepared from aromatic compounds containing nitrogen. Examples of these compounds are phthalocyanine³ (a chelated compound),

poly-*N*-vinylcarbazole,⁴ polypyrrole,⁵ and poly(2-vinylpyridine) (P2VP).⁶ Chohan and coworkers^{7,8} studied the electrical behavior of some polymeric charge-transfer complexes that were prepared by the complexation of P2VP with metal salts. P2VP and its metal-based derivatives were also synthesized and studied by Rafique et al.² The electrical conductivity of these materials was studied as a function of temperature.

The present work attempts to explore the possibility of designing a polymer backbone, which will be embedded, so to say, in an electron cloud not only of the delocalized π -electrons of carbon–carbon multiple bonds, but also of the nonbonding electrons of heteroatoms, such as nitrogen. That is, we focus on the chemical synthesis and the investigation of the electrical conductivity of P2VP after its complexation with a number of metal chlorides, such as BaCl₂, ZnCl₂, NiCl₂, or CoCl₂. The study of the activation energy for electrical conductivity of P2VP and its complexes with the various metal chlorides has also been carried out.

EXPERIMENTAL

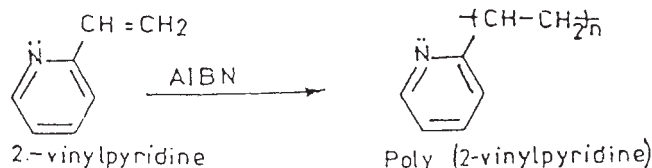
Materials and methods

About 140 mL of 2-vinylpyridine (97%) obtained from Aldrich Chemical Company was put in a round-bottomed flask. 2 g of anhydrous sodium carbonate was added to it and kept for 24 h. The mixture was then distilled under vacuum.

Polymerization of 2-vinylpyridine

105.14 g (1.0 mol) equivalent to 107.8 mL of distilled 2-vinylpyridine dissolved in chloroform (200 mL) was

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Scheme 1

stirred with azoisobutyronitrile (1.0 g) in a round-bottomed flask fitted with a water condenser and refluxed for 4 h at 60°C. The resulting polymer was separated by adding *n*-hexane, washed with alcohol, and dried in an air oven at 100°C. The general equation for the synthesis of the polymer is represented in Scheme 1.

Preparation of semiconducting polymers

For preparation of semiconducting polymers, P2VP was complexed with BaCl_2 , ZnCl_2 , NiCl_2 , or CoCl_2 , (Scheme 2) by the following general procedure:

A saturated solution of P2VP in chloroform and of metal chloride in ethyl alcohol was prepared. The metal chloride solution was added dropwise to the P2VP solution while stirring. A precipitate was formed, which was allowed to stand for half an hour, filtered, and washed several times with water and alcohol until free from reactants, and dried at 60°C. The polymer complex was dissolved in acetonitrile from which a thin film was made.

Analytical measurements

TGA spectra

The thermal stability of the polymers has been studied using a thermogravimetric analyzer (TGA). All TGA spectra were recorded under a nitrogen atmosphere using a program rate of 10°C/min. The thermal stability of the P2VP and its complexes with the metal chlorides studied using the TGA thermogram shows that the metal complexes of P2VP are stable with no weight loss up to 100°C. The degradation in P2VP and its complexes with BaCl_2 , ZnCl_2 , NiCl_2 , and CoCl_2 starts above 100°C and continues up to 454.8, 464.08, 489.29, 594.86, and 602.15°C, respectively. At these temperatures, the percentages of degradation are 97.974, 96.727, 92.231, 90.452, and 82.903%, respectively. It could be concluded from Figures 1(a) and 2(a) that the degradation in P2VP continues up to 454.8°C whereas it continues up to 602.15°C in case of Co-P2VP complex. Figures 1(b) and 2(b) also show that the percentage of degradation in P2VP at 454.8°C (97.974%) decreases to 82.903% at 602.15°C in case of Co-P2VP complex. Furthermore, the derivatograms obtained suggest

that the degradation takes place at different stages in the various complexes. The increase in the environmental stability of P2VP on complexation with the various metal chlorides may be due to the resonance effect of nitrogen in the pyridine ring, which in turn acts to stabilize a carbenium ion on the polymer chain.²

IR spectra

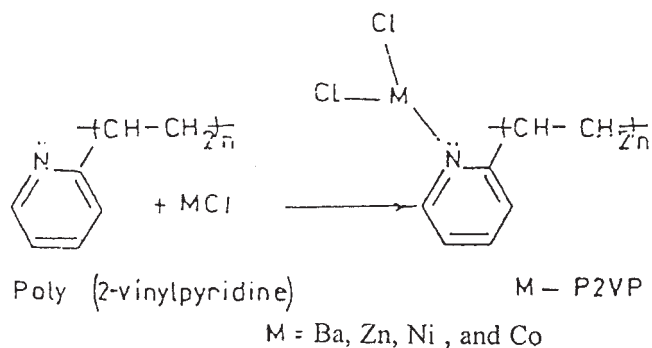
IR spectroscopy of P2VP and its metal complexes has been used to confirm the chemical reaction between P2VP and the metal chloride where a strong broad band appears at 3339.0 cm^{-1} in the spectrum of Ni-P2VP complex for example (Figs. 3 and 4). This band is due to a single bridge compound polymeric association, which results from the overlap of the *d*-orbitals of the nickel element with the π -electrons.

Dielectric measurements

The permittivity (ϵ') and dielectric loss (ϵ'') for the prepared samples were measured at different frequencies ranging from 100 Hz to 100 kHz. An LCR meter (type AG-4311B) Ando electric LTD with an NFM/5T test cell was used. The capacitance *C* and the loss tangent ($\tan \delta$) were obtained directly from the bridge from which ϵ' and ϵ'' were calculated. The samples were in the form of disks with a 58 mm diameter and 3 mm thickness. Calibration of the apparatus was carried out using standard samples (Trolitul, glass, and air) of 3 mm thickness; the accuracy for ϵ' was $\pm 1\%$ and for ϵ'' was $\pm 2\%$. The measurements were carried out at temperatures from 20 to 60°C using an ultrathermostat.

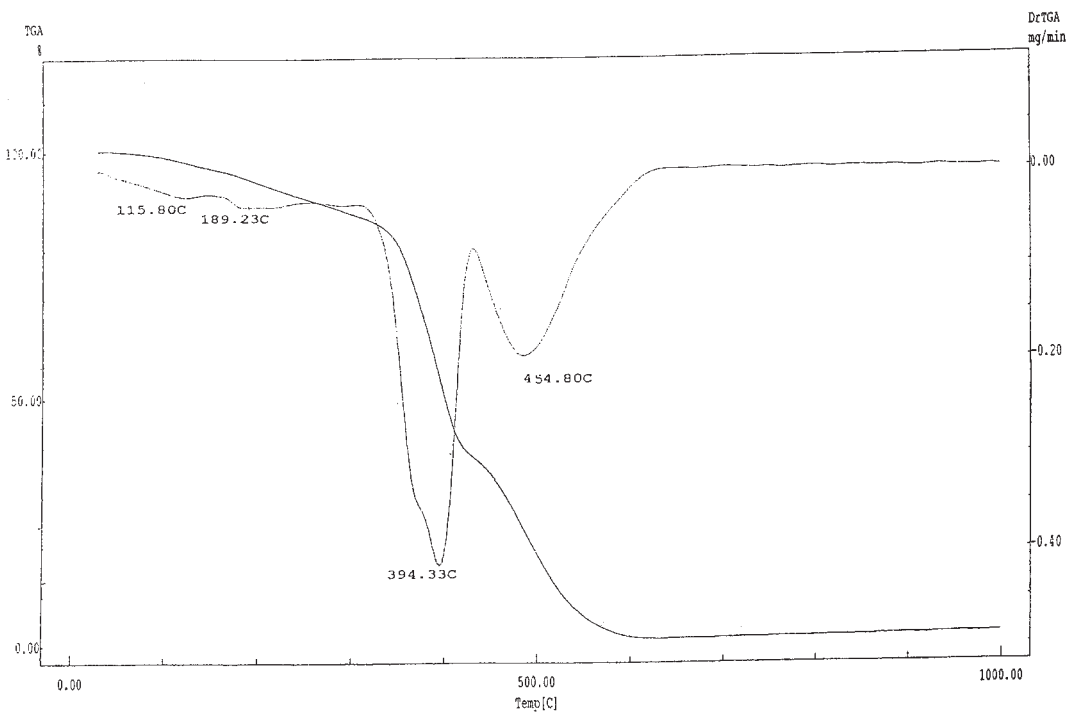
Electrical conductivity measurements

The electrical conductivity (σ) of the investigated samples was measured by the application of Ohm's law



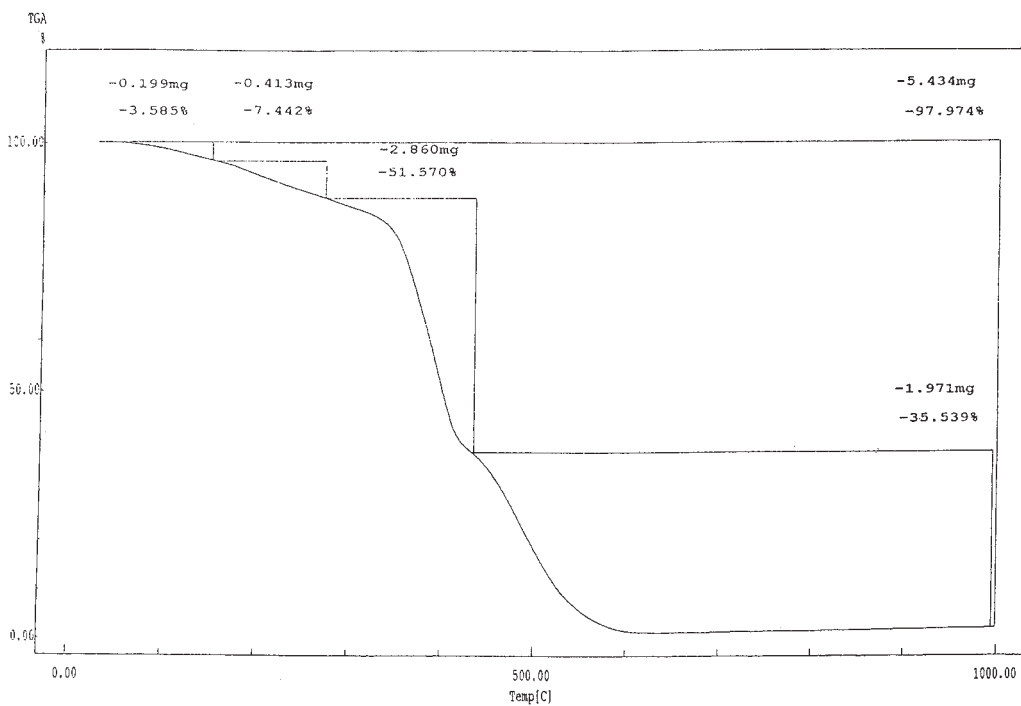
Scheme 2

Detector Type:	Shimadzu TGA-50H	Temp Program	
Acquisition Date:	10/07/09	Rate	Hold Temp Hold Time
Acquisition Time:	09:00:28	[C/min]	[C] [min]
Sample Name:	P2VP	10.0	1000.0 0.0
Weight:	5.547 [mg]		
Cell:	Platinum		
Atmosphere:	Nitrogen		
Rate Flow:	30.00 [ml/min]		
Operator:	IZ		



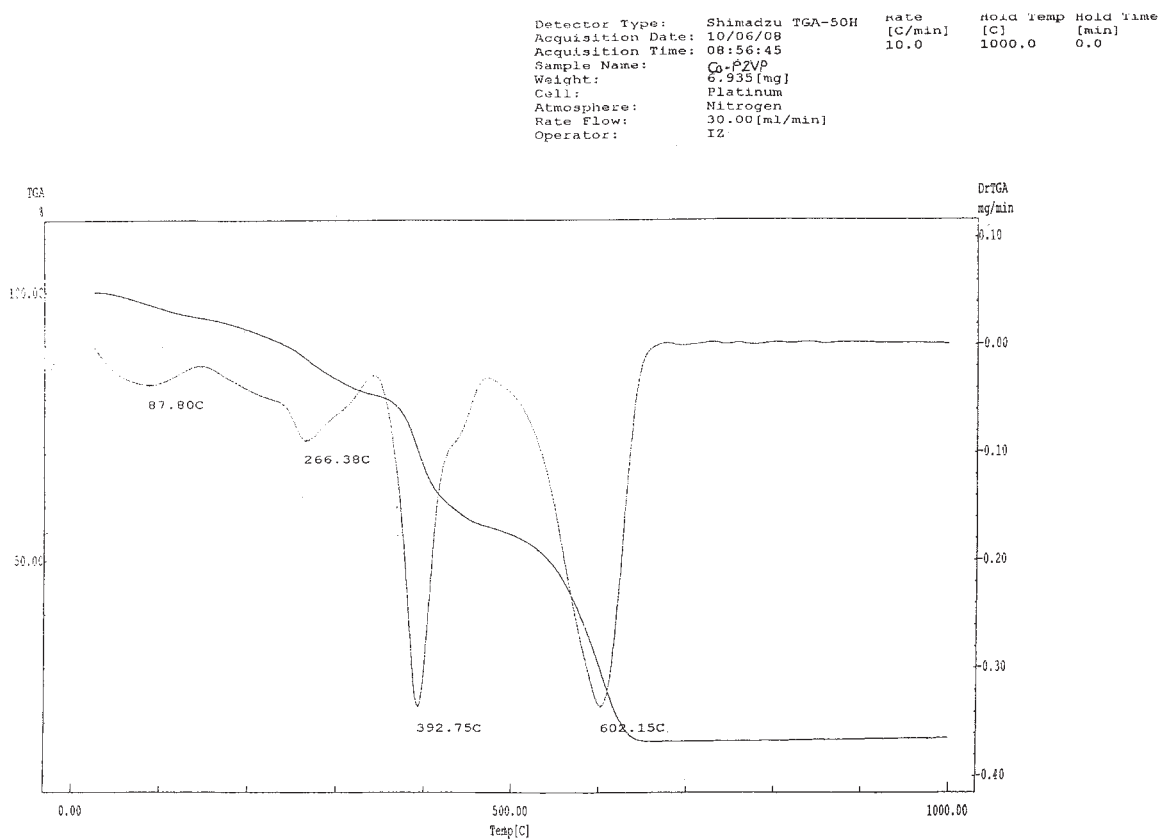
(a)

Detector Type:	Shimadzu TGA-50H	Temp Program	
Acquisition Date:	10/07/09	Rate	Hold Temp Hold Time
Acquisition Time:	09:00:28	[C/min]	[C] [min]
Sample Name:	P2VP	10.0	1000.0 0.0
Weight:	5.547 [mg]		
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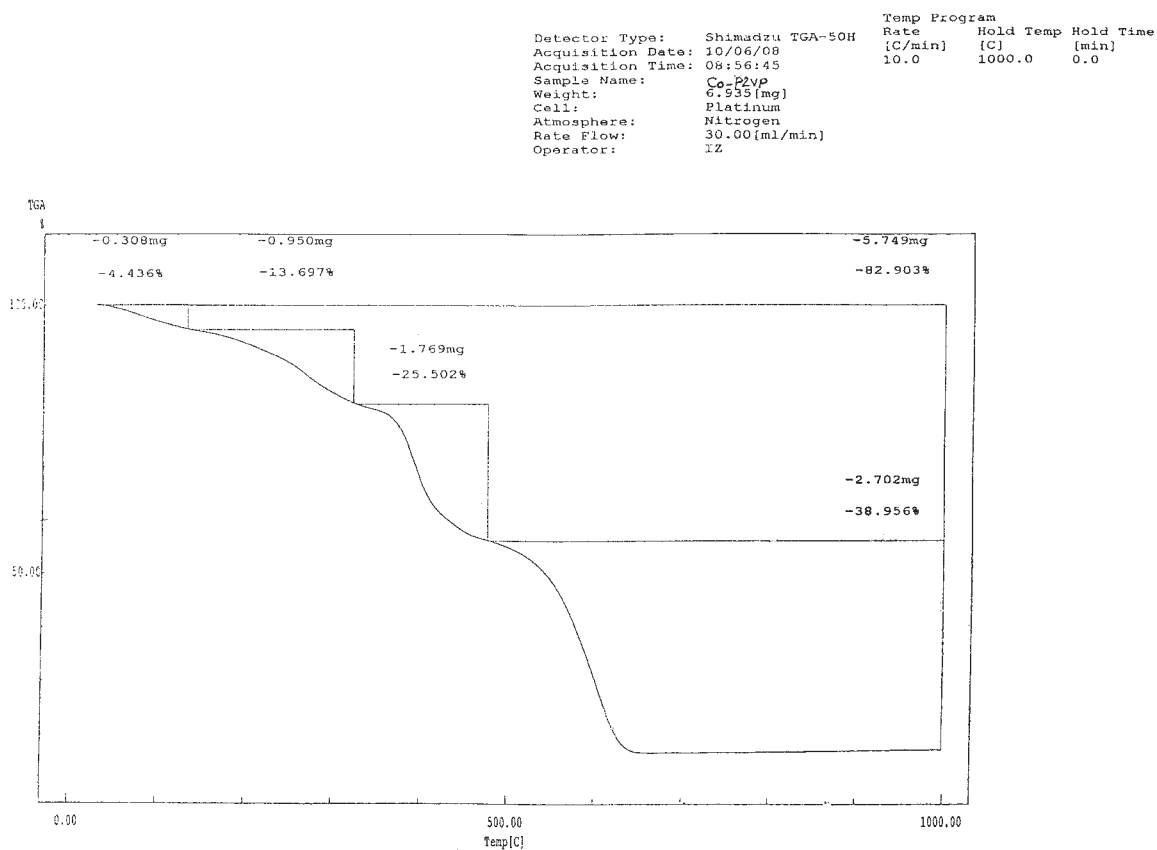


(b)

Figure 1 TGA spectrum of P2VP.



(a)



(b)

Figure 2 TGA spectrum of Co-P2VP.

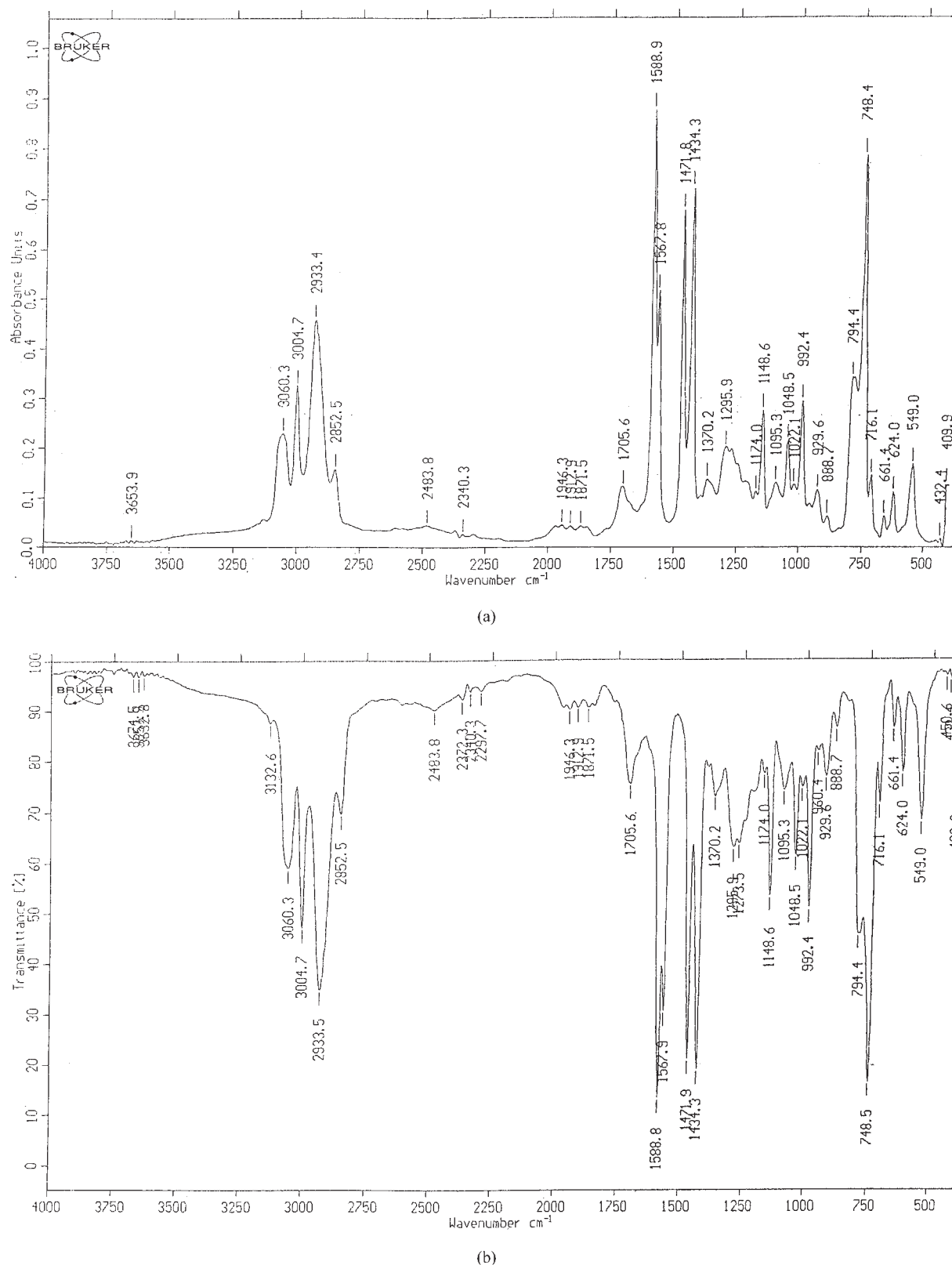
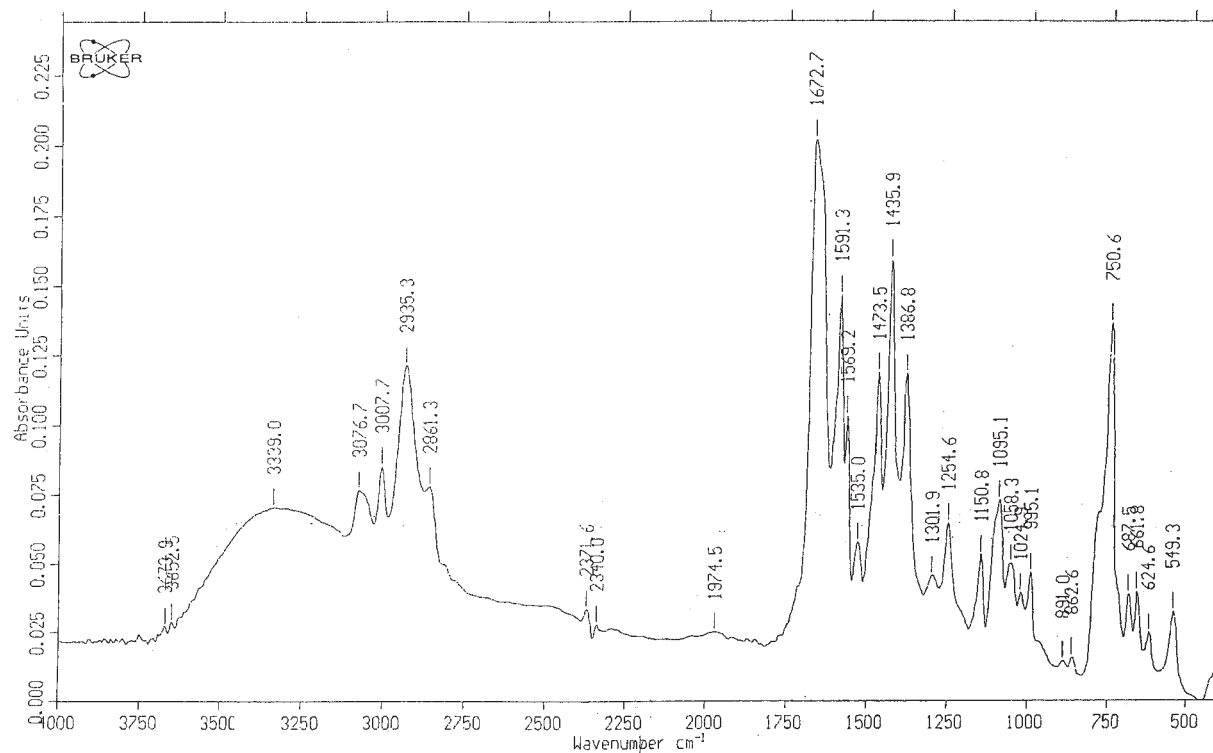


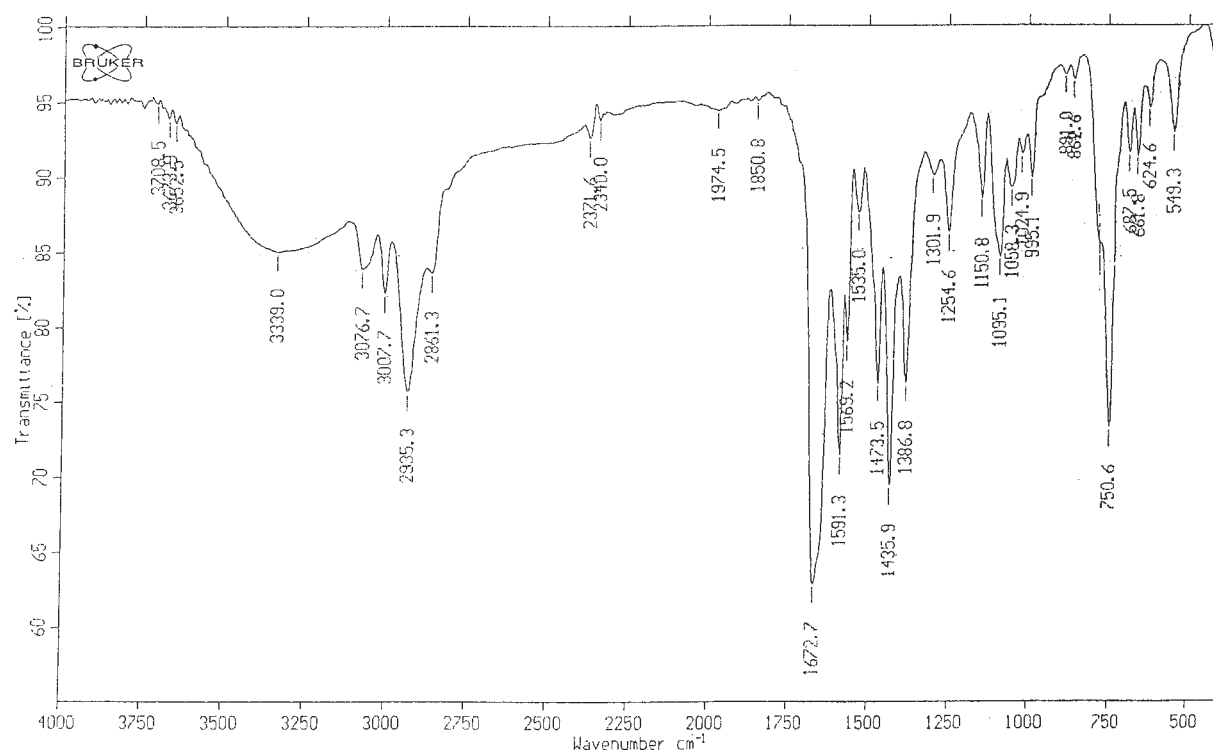
Figure 3 IR spectrum of P2VP.

using the NFM/5T test cell. A power supply unit (GM 45,161/01) from Philips was used. The potential difference (V) between the plates holding the sample and the

current (I) flowing through it was measured by a multimeter (type URI 1050) from Rohde and Schwarz. The electrical conductivity is calculated using the equation:



(a)



(b)

Figure 4 IR spectrum of Ni-P2VP.

$$\sigma = \frac{dL}{AV} \text{ mho m}^{-1}$$

where d is the thickness of the sample in meters and A is its surface area in square meters.

Mechanical measurements

Shore-B hardness was determined using a Shore B Durometer, according to DIN 53505 ASTM D2240

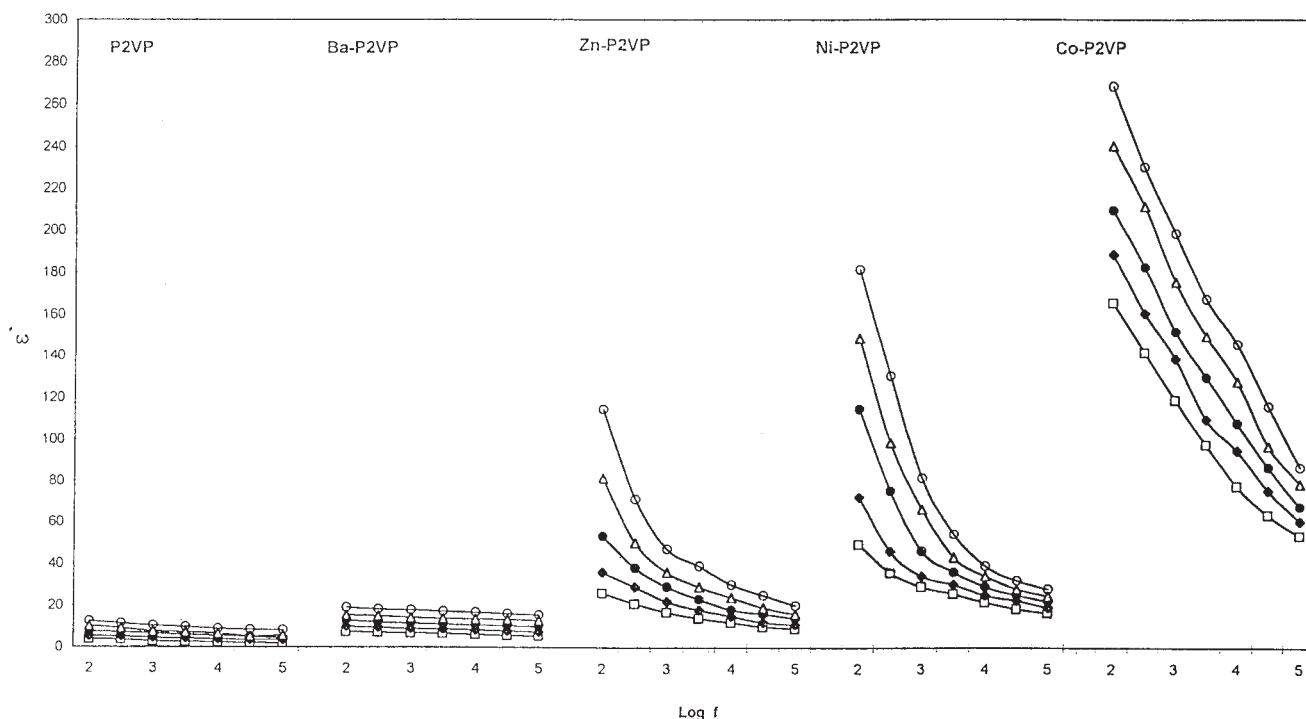


Figure 5 The permittivity (ϵ') versus frequency at (\square) 20, (\blacksquare) 30, (\circ) 40, (Δ) 50, and (\circ) 60°C for P2VP and Ba-P2VP, Zn-P2VP, Ni-P2VP, and Co-P2VP complexes.

(1983). The shore hardness value was taken as an average of five readings from different points.

RESULTS AND DISCUSSION

Vinylpyridine reacts both as tertiary amines and as olefins.^{9,10} As amines, the vinylpyridine forms salts and complexes. P2VP structure is thermally stable due to nitrogen, which is covalently bonded to the neighboring carbons to form heterocycles. It is argued¹¹ that the compound 2-vinylpyridine should be able to form coordination compounds through the nitrogen atom (in the manner of pyridine), through the double bond (in the manner of styrene), or through both at the same time. Variation in the choice of the complexing metal in the preparation of the conducting polymer of P2VP clearly has several effects.

Effects of complexing metal on properties of P2VP

Electrical properties

Dielectrics. The ϵ' and ϵ'' for the various complexes were studied over the frequency region from 100 Hz to 100 kHz at different temperatures from 20 to 60°C. It is evident from Figure 5, which represents the variation of ϵ' with frequency at different temperatures, that the value of ϵ' increases with increasing temperature and decreases with increasing frequency. Similar behavior was noticed before in the literature.¹²⁻¹⁶ The

increase of ϵ' with temperature can be explained by the increase in the mobility of polar groups, the decrease in density, and hence, a decrease in the effect of the environment that facilitates the orientation of the mobile groups. The decrease of ϵ' with frequency may be caused by dielectric dispersion.

It is apparent from Figures 6 and 7, which represent the variation of ϵ'' with frequency at different temperatures, that the value of ϵ'' is greatly increased at higher temperatures, especially in the lower-frequency region. The increases in ϵ'' in the very low-frequency region may be caused by either the Maxwell-Wagner effect¹⁷ as a result of an alternating current (ac) in phase with the applied potential or the direct current (dc) conductivity,^{18,19} or both. To confirm this, the dc conductivities of the investigated samples were measured by application of Ohm's law to the dc flowing through the samples at 200 V and at temperatures from 20 to 60°C. All investigated samples showed appreciable dc conductivity. The dielectric loss caused by the dc conductivity (σ) at the different frequencies (ω) are calculated using the equation:²⁰

$$\epsilon''_{dc} = \frac{9 \times 10^{11} \times 4\pi\sigma}{\omega}$$

and subtracted from the values of ϵ'' in the low-frequency region. The data of ϵ'' after subtracting ϵ''_{dc} are

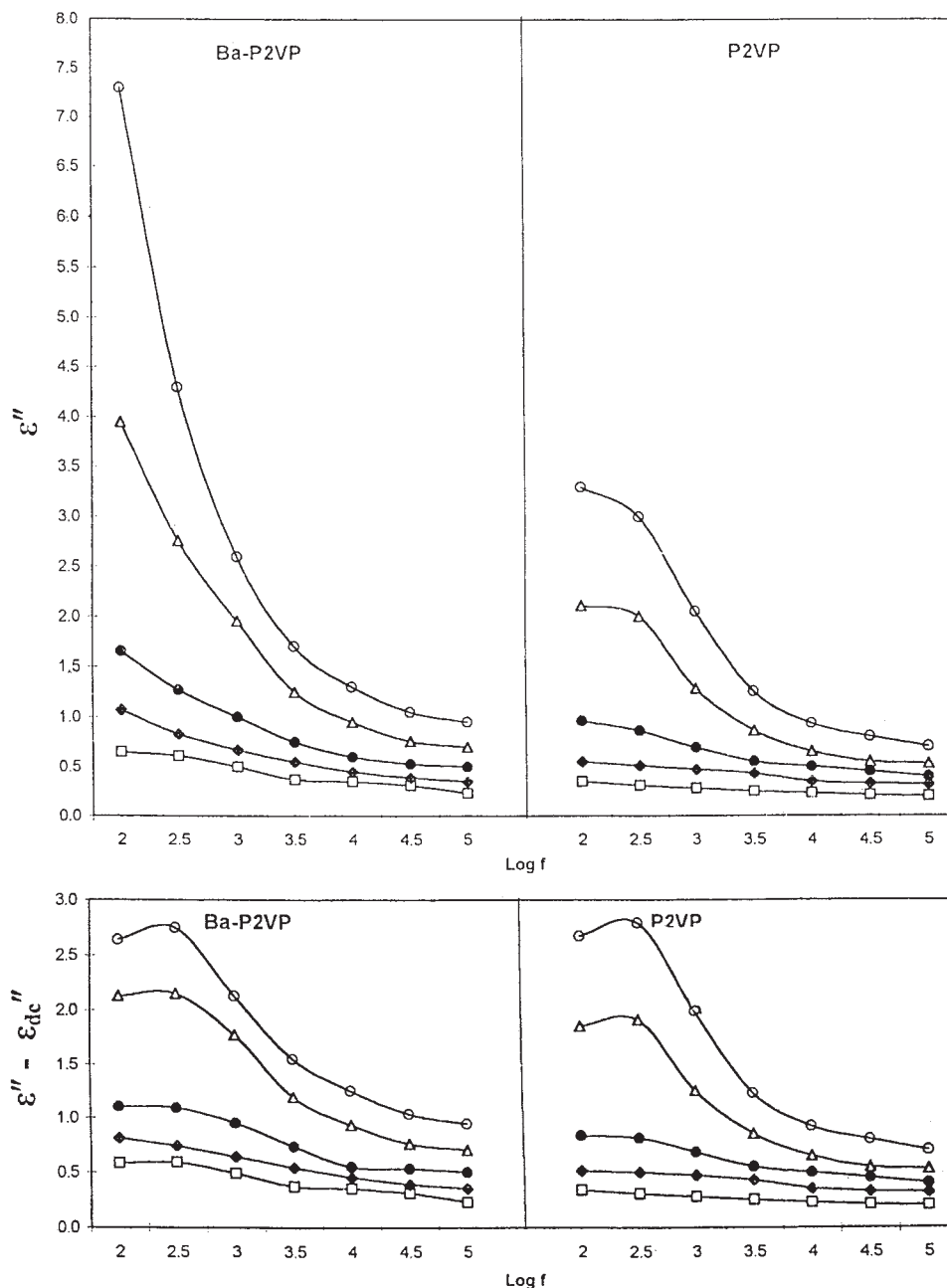


Figure 6 The dielectric loss (ϵ'') and $\epsilon'' - \epsilon''_{dc}$ versus frequency at (□) 20, (◆) 30, (●) 40, (Δ) 50, and (○) 60°C for P2VP and Ba-P2VP complexes.

plotted versus $\log f$ and are represented in Figures 6 and 7. From these figures, it is clear that there is an absorption region at the different temperatures. As the temperature increases, the maximum loss peak increases and becomes clear and is shifted to higher frequency.

It may be concluded that the low-frequency losses are not totally dc losses and that they may comprise Maxwell-Wagner losses, because the differences between the permittivities and conductivities of the different ingredients in the investigated samples are relatively large.

Electrical conductivity. On the addition of an electrically conductive additive to a polymer matrix, the specific electrical conductivity of the latter will be increased due to the formation of ionic charges on excitation by heat or light. These charged species become mobile when an electric field is applied, and hence, the electrical conductivity in the host polymer increases. One of the interesting features of conductivity is its temperature dependence, which allows one to understand conduction mechanisms in materials. Figure 8 shows such a behavior in P2VP and its complexes with Ba, Zn, Ni, and Co. It is evident from this

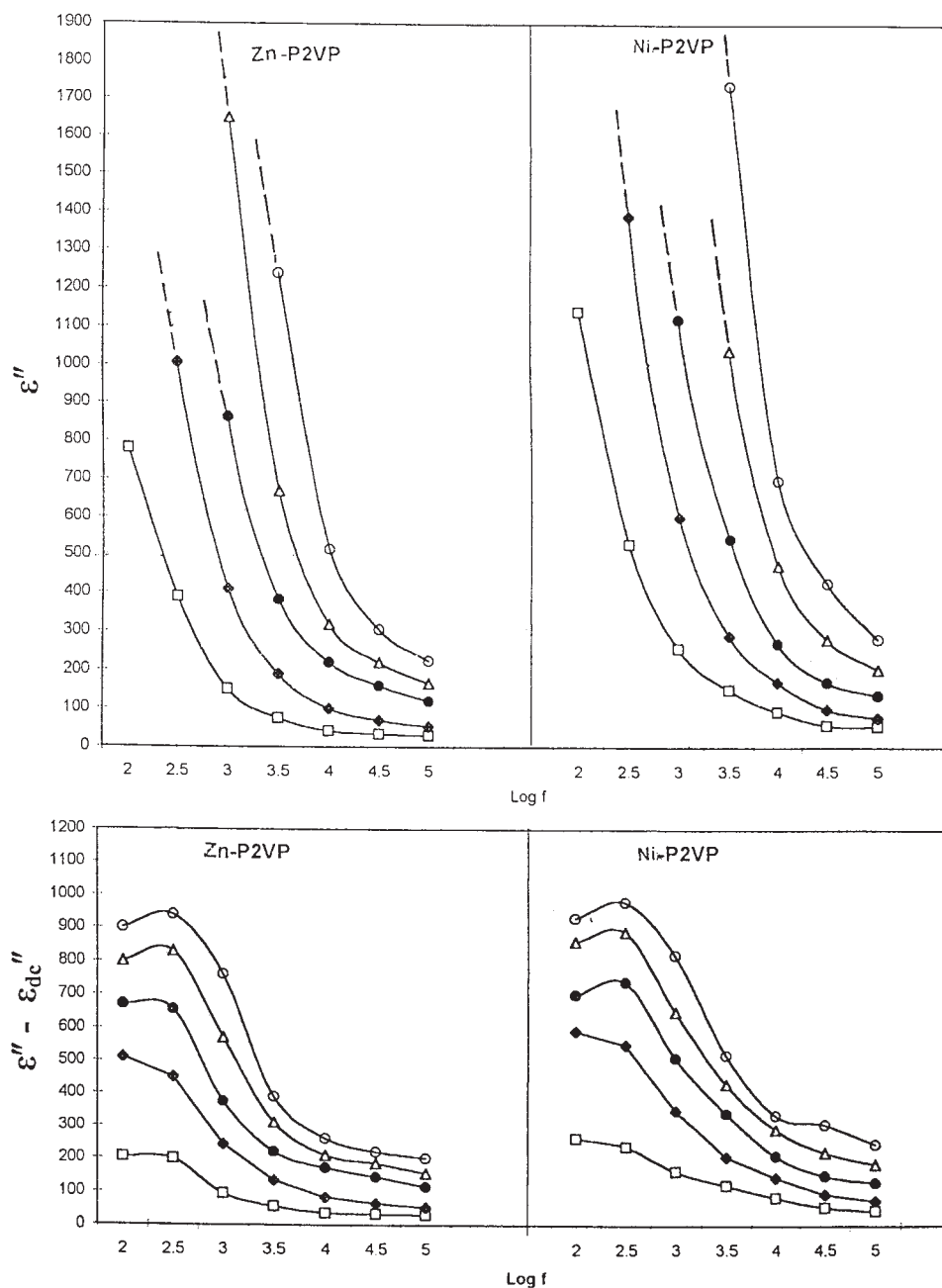


Figure 7 The dielectric loss (ϵ'') and $\epsilon'' - \epsilon''_{dc}$ versus frequency at (□) 20, (◆) 30, (●) 40, (Δ) 50, and (○) 60°C for Zn-P2VP and Ni-P2VP complexes.

figure that the conductivity (σ) of the base P2VP polymer and its Ba, Zn, Ni, and Co complexes drops on cooling. This characterizes semiconductor-like conduction in these polymers. Furthermore, σ of P2VP increases by the addition of the various metal chlorides in the sequence $\text{BaCl}_2 < \text{ZnCl}_2 < \text{NiCl}_2 < \text{CoCl}_2$, especially at the lower frequency region and higher temperatures; thus indicating the role of metal ions in the conduction mechanism. The data in Table I show that the values of σ of the metallic complexes increase by 10 to 10^6 orders of magnitude than those of pure P2VP, which is of the order of $10^{-12} \Omega^{-1} \text{ cm}^{-1}$. These

values are between the two extremities of those of semiconductors (10^{-10} to $10^{+2} \Omega^{-1} \text{ cm}^{-1}$).²¹ The increase in σ on the introduction of metal atoms into the polymer matrix may be due to (i) improved intermolecular orbital overlap of the more diffuse metal d -orbitals and (ii) extension of the intramolecular conduction path by conjugation of the d -orbitals of the metals with the π -electron system of the polymer, thereby facilitating the conduction path through the metal-atoms.²¹ The presence of nitrogen in the pyridine ring should enhance intrachain coupling through d -orbital overlap, and thereby improve the interchain

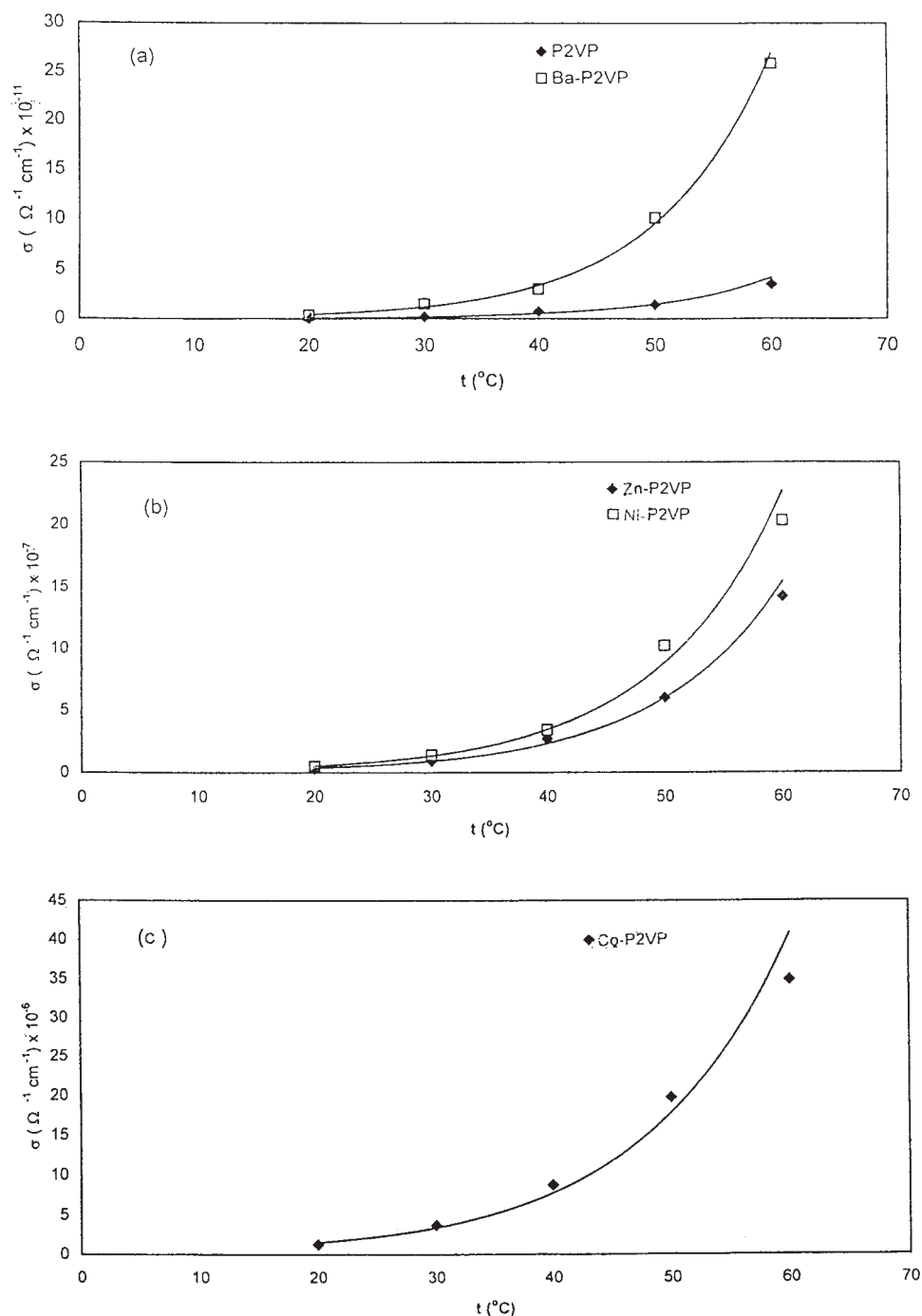
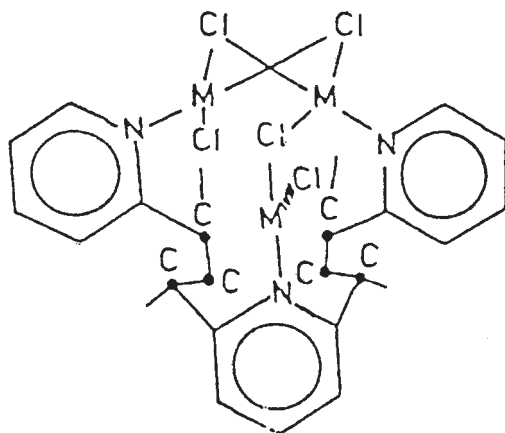


Figure 8 The relation between conductivity (σ) and temperature (t) for: (a) P2VP (♦) and Ba-P2VP (□); (b) Zn-P2VP (♦) and Ni-P2VP (□); and (c) Co-P2VP (♦).

electron transfer necessary for the conductivity. The lone pair of electrons on the ring nitrogen plays an important role in the electrical conductivity. On complexation with a metal salt, the lone pair of electrons on the nitrogen is given to the metal d -orbital, which overlaps with the π -orbitals of the ligand, thus forming a conduction path in the polymer backbone chain. The formation of a bridge structure² also greatly facilitates the occurrence of conduction. The lone pair of

TABLE I
Electrical Conductivity of P2VP and Its Complexes with the Various Metal Chlorides

Polymer	$\sigma (\Omega^{-1} \text{cm}^{-1})$ at temperatures ($^{\circ}\text{C}$)				
	20	30	40	50	60
P2VP	0.51	2.22	8.0	14.34	35.21×10^{-12}
Ba-P2VP	0.38	1.92	5.53	12.0	23.84×10^{-11}
Zn-P2VP	0.32	0.93	2.71	6.0	10.43×10^{-7}
Ni-P2VP	0.47	1.42	4.0	10.21	21.50×10^{-7}
Co-P2VP	1.12	3.78	8.84	17.0	28.91×10^{-6}



Scheme 3 Structure of P2VP metal complex showing the metal-chlorine-metal bridge and the distorted C-C chain.

electrons on the nitrogen is denoted to a metal atom through the $p-\pi$ system and enhances the ability of the metal to form a metal-chlorine-metal bridge structure, resulting in distortion of the otherwise linear polymer backbone chain. The resulting distortion will bring the chlorine atoms closer, giving intramolecular metal-chlorine-metal bridging as shown in Scheme 3.

Mechanical properties

Shore-B hardness was measured for P2VP and its complexes with BaCl_2 , ZnCl_2 , NiCl_2 , and CoCl_2 and the obtained data are given in Table II. From these data, it is clear that shore hardness of P2VP decreases by the addition of the various metal chlorides in the sequence $\text{BaCl}_2 > \text{ZnCl}_2 > \text{NiCl}_2 > \text{CoCl}_2$. It is also clear from Tables I and II that as the electrical conductivity of P2VP increases, its shore hardness decreases successively on the addition of BaCl_2 , ZnCl_2 , NiCl_2 , or CoCl_2 .

Activation energies

The activation energy (E) for electrical conductivity (σ) of P2VP and its complexes with BaCl_2 , ZnCl_2 , NiCl_2 , or CoCl_2 was calculated by plotting the logarithm of the conductivity against the reciprocal of the absolute temperature where a straight line was obtained, as shown in Figure 9, showing that the P2VP complexes tend to behave as semiconductors. From the slope of the straight line, E was calculated using the equation.²²

$$\sigma = \sigma_0 e^{-E/RT}$$

It has been found that the period of excitation depends on the activation energy needed to make the substance conducting. If the activation energy is low, i.e., the system is easily excited the P2VP com-

plexes become semiconducting at room temperature or in the presence of indirect light. Hence, it can be used for electronic devices working at normal temperatures. It is apparent from Table III that the activation energy for electrical conductivity of P2VP decreases successively on the addition of BaCl_2 , ZnCl_2 , NiCl_2 , or CoCl_2 . The lowest values of E for Co-P2VP complex (6.89 K cal/mol) indicates that it is easily excited and tends to behave as a semiconductor, and can be better employed for electronic and microwave devices.

CONCLUSIONS

From the studies certain conclusions can be made concerning the environmental and thermal stability and electrical conductivity of the P2VP and its metal complexes:

1. The novel route adopted to synthesize P2VP and its metal complexes provides a convenient and efficient method of preparation, which also excludes the possibility of getting impurities or moisture in the materials.
2. P2VP structure is thermally stable. Its complexation with metals further increases its stability due to the resonance effect of nitrogen in the pyridine ring, which acts to stabilize a carbenium ion on the polymer chain.
3. The electrical conductivity of P2VP is greatly enhanced on its complexation with the various metal chlorides in the sequence $\text{BaCl}_2 < \text{ZnCl}_2 < \text{NiCl}_2 < \text{CoCl}_2$. The temperature dependence of the conductivity shows that, for P2VP and its Ba, Zn, Ni, and Co complexes it is semiconductor-like.
4. The activation energy for electrical conductivity is lower for Co-P2VP complex than that for the other complexes, showing that it is easily excited and tends to behave as a semiconductor and can be better employed for electronic and microwave devices.

TABLE II
Shore-B Hardness of P2VP and Its Complexes with the Various Metal Chlorides

Polymer	Shore-B hardness
P2VP	46
Ba-P2VP	43
Zn-P2VP	33
Ni-P2VP	30
Co-P2VP	23

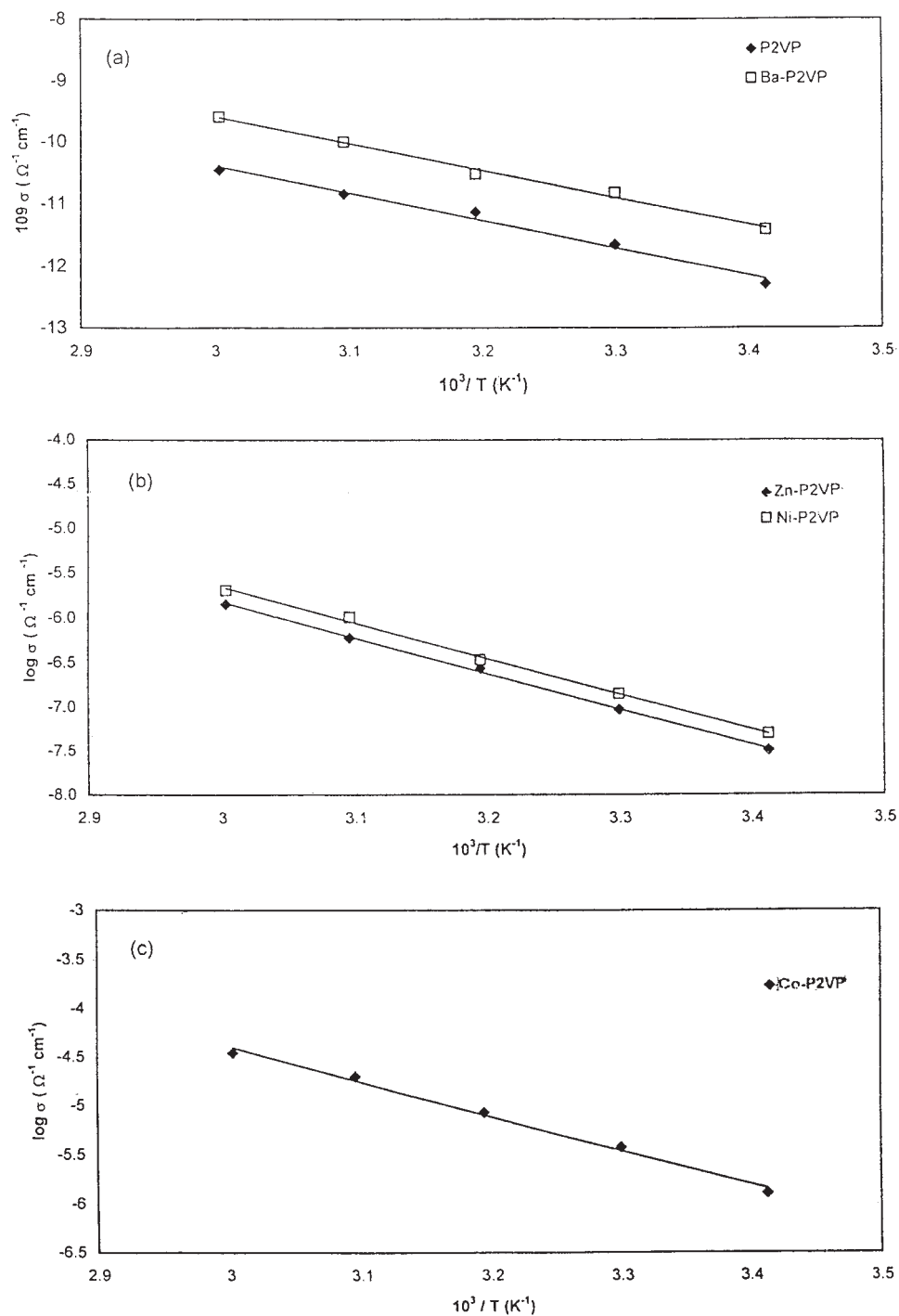


Figure 9 The relation between $\log \sigma$ and $10^3/T$ for: (a) P2VP (♦) and Ba-P2VP (□); (b) Zn-P2VP (♦) and Ni-P2VP (□); and (c) Co-P2VP (♦).

TABLE III
Activation Energy of P2VP and Its Complexes
with the Various Metal Chlorides

Polymer	Activation energy (kcal/mol)
P2VP	9.02
Ba-P2VP	8.74
Zn-P2VP	7.41
Ni-P2VP	7.30
Co-P2VP	6.89

References

1. Kusy, P. R.; Tuner, D. T. *J Appl Polym Sci* 1973, 17, 1631.
2. Rafique, U.; Mazhar, M.; Ali, S.; Khwaja, F. A. *Synth Met* 1996, 78, 73.
3. Eley, D. D.; Parfitt, G. D. F.; Perry, M. J. *Trans Faraday Soc* 1953, 49, 79.
4. Klopffer, W. *J Chem Phys* 1969, 50, 1689, 2337.
5. Simon, R. A.; Ricco, A. J. *J Am Chem Soc* 1982, 104, 2031.

6. Vander Donckt, E.; Noirhomme, B.; Konicki, J. *J Appl Polym Sci* 1982, 27, 1.
7. Chohon, M. H. *J Mater Sci Lett* 1994, 13, 6.
8. Chohon, M. H.; Asghar, M.; Adris, T. *J Mater Sci Lett* 1994, 13, 1426.
9. Tazuke, S.; Sato, N.; Okamura, S. *J Polym Sci Part A-1: Polym Chem* 1966, 4, 2461.
10. Pudvin, J. E.; Mattern, J. A. *J Am Chem Soc* 1956, 78, 2104.
11. Anderson, J. S. *J Chem Soc* 1936, 2, 1042.
12. Saad, A. L. G.; Hassan, A. M.; Gad, E. A. M. *J Appl Polym Sci* 1993, 49, 1725.
13. Saad, A. L. G.; Hassan, A. M.; Youssif, M. A.; Ahmed, M. G. M. *J Appl Polym Sci* 1997, 65, 27.
14. Saad, A. L. G.; Hussien, L. I.; Ahmed, M. G. M.; Hassan, A. M. *J Appl Polym Sci* 1998, 69, 685.
15. Saad, A. L. G.; Sayed, W. M.; Ahmed, M. G. M.; Hassan, A. M. *J Appl Polym Sci* 1999, 73, 2657.
16. Saad, A. L. G.; Aziz, H. A.; Dimitry, O. I. H. *J Appl Polym Sci* 2003, 91, 1590.
17. Hanna, F. F.; Yehia, A. A.; Abou Bakr, A. *Br Polym J* 1973, 5, 83.
18. Davices, J. M.; Miller, R. F.; Busse, W. F. *J Am Chem Soc* 1941, 63, 361.
19. Sasabe, H.; Saito, S. J. *J Polym Sci Part A: Polym Chem* 1969, 7, 1405.
20. Smyth, C. P. *Dielectric Behavior and Structure*; McGraw-Hill: New York, 1955.
21. Goodings, E. P. *Chem Soc Revs* 1976, 5, 95.
22. Eley, D. D.; Parfitt, G. D. *Trans Faraday Soc* 1955, 51, 1529.