Effects of Some Solvents on the Thermal and Free-Volume Properties of Poly(4-vinylpyridine) Complexes

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ABSTRACT: Modified poly(4-vinylpyridine) (P4VP) and its complexes were prepared with different solvents such as benzene, toluene, and xylene as well as potassium chloride (KCl) and copper chloride (CuCl₂). Fourier transform infrared spectroscopy, thermal analysis, and positron annihilation spectroscopy were used to investigate the properties of the modified P4VP and its complexes. It was concluded that complexes were formed between the polymer and solvents via quaternization of nitrogen in the ring with the solvents and also with KCl and $CuCl_2 \cdot 2H_2O$. Furthermore, the modified P4VP–CuCl₂ complexes were more stable than the modified P4VP–KCl complexes, and these complexes were more stable than the P4VP–solvent complexes. *Ortho*-positronium components (τ_3, I_3) were used to estimate the nanoscale free-volume hole size (V_f) and the free-volume fraction (f %). The free-volume hole size and its fractions depended on the addition of solvents and metals to the polymer. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 331–340, 2008

Key words: FTIR; NMR; stabilization; thermal properties

INTRODUCTION

Polymer–metal complexes are now of great interest. Different polymers are commonly used in industry to produce a large variety of useful items for everyday personal and industrial uses as well.[1,2] It has been demonstrated that the thermophysical properties of polymeric ligands can be modified by coordination to transition-metal complexes.[3–6] $CuCl_2 \cdot 2H_2O$ salt is an attractive candidate for forming coordination complexes with the pyridine moieties of poly(4-vinylpyridine) (P4VP), such as a soluble copper–pyridine complex of the $CuCl_2(Py)_2$ type.[7] On the other hand, octahedral divalent ruthenium is an attractive candidate for forming coordination complexes with the lone nitrogen pair of pyridine in the side group of P4VP or copolymers containing 4-vinyl repeat units.[8]

Poly(2-vinylpyridine) (P2VP) and its metal-based derivatives have been synthesized and characterized through analytical measurements, molar mass measurements, and thermal analysis.[9] These complexes have been prepared[10–13] by the complexation of P2VP with metal salts. The conductivity of 2-vinyl-pyridine (2VP) has been found to increase by many orders of magnitude on combination with transition metals such as copper, cobalt, and platinum. The nitrogen atom of the pyridine groups of the organic polymer is coordinatively bonded to the copper center as suggested by X-ray photoelectron spectroscopy, ultraviolet spectroscopy, differential scanning calorimetry, and Fourier transform infrared (FTIR) techniques.[14] It has also been found that a P2VP–cobalt complex has the highest conductivity values among the complexes that have been studied.[13] The reaction of poly(2-vinyl pyridine) with cobalt chloride and zinc chloride produces compounds with the stoichiometry of $[Co(2VP)_{2.5}(H_2O)Cl_2]_n$ and $[Zn(2VP)_{2.5}Cl_2]_n$. In the cobalt complex compound, the cobalt ion exists in both octahedral and tetrahedral environments, whereas in the zinc ion, it is in a tetrahedral environment.[15]

P2VP and P4VP have been partly complexed with Co(II), Ni(II), and Zn(II) transition-metal ions. Thermal degradation is initiated at a low temperature, and the complexes decompose even near the threshold temperature for weight loss.[16]

It is known that thermal treatment might influence the free-volume properties of a polymer. The free-volume hole size (V_f) is defined as a space that is not occupied by the macromolecules, and its value is equal to the difference between the specific and occupied volumes of the polymeric system.[17] The free volume, which may influence the physical and chemical properties of the polymer, can be detected with a positron used as a probe.[18,19]

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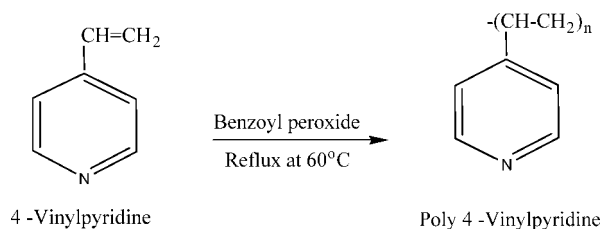
Scheme 1

Positron annihilation spectroscopy is a technique with high sensitivity for probing the nanoscale size and fraction of free-volume holes through measurements of the positron annihilation lifetime (PAL) and momentum distribution of annihilation positron–electron pairs.[20,21] When a positron with a kinetic energy of several kiloelectronvolts from a radioactive source is injected into a polymer, it quickly reaches thermal energies. The thermalized positron can annihilate with an electron from the material in a free or trapped state, or it may form with an electron a bound state called positronium (Ps), and then annihilation from the bound state takes place. The Ps atom has two ground states, *para*-positronium (*p*-Ps) and *ortho*-positronium (*o*-Ps), which depend on whether the spins of the electron and positron are antiparallel or parallel, respectively. *In vacuo*, the lifetime of *p*-Ps is 0.125 ns, and the *o*-Ps lifetime is 140 ns. In a polymer, this long *o*-Ps lifetime may be considerably reduced to 1–5 ns by the pick-off process.[22,23]

In this work, modified P4VP was prepared with different solvents such as benzene, toluene, and xylene. It was interesting to check if the properties of the polymers were stable or if they changed with the addition of the aforementioned solvents. Positron annihilation spectroscopy as a nondestructive method, thermal analysis, FTIR, and nuclear magnetic resonance (NMR) were used to investigate the properties of this polymer. Also, the effect of adding $CuCl_2 \cdot 2H_2O$ and potassium chloride (KCl) to modified P4VP was studied.

EXPERIMENTAL

Sample preparation

Polymerization of 4-vinylpyridine (4VP) by different solvents

4VP (0.25 mol ≈ 27 mL) was placed in a round-bottom flask. Benzoyl peroxide (0.5 g) and benzene (100 mL; used as a solvent) were added and refluxed gently for half an hour. The chemical reaction is shown in Scheme 1. The same procedure was performed with toluene and xylene as the solvents instead of benzene.
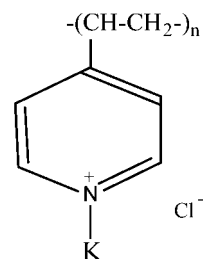
P-4VP-K Complexes

Scheme 2

Preparation of P4VP–KCl complexes (Scheme 2)

A saturated solution of KCl in 50 mL of ethyl alcohol was added dropwise with stirring to a saturated solution of P4VP prepared with different solvents. A precipitate was formed and was allowed to stand for half an hour. The precipitate was filtered, washed with water and methyl alcohol, and dried at 60°C. The P4VP–KCl complexes were dissolved in acetonitrile, and a thin film was prepared.

Preparation of P4VP–$CuCl_2$ complexes (Scheme 3)

The same procedure was performed with $CuCl_2$ instead of KCl. The number of modified P4VP samples is given in Table I.

Analytical measurements

Molecular weight

Molecular weight determination was performed by gel permeation chromatography. The number-average molecular weight was 400.

Thermogravimetric analysis (TGA)

A Shimadzu TGA-50 systems in a nitrogen atmosphere (30 mL/min) was used. The temperature range was from the ambient temperature to 600°C. The rate of heating was 10°C/min.
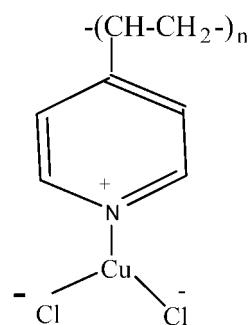
P-4VP-Cu Complexes

Scheme 3

TABLE I
Coding of the Modified P4VP Samples

Number	Sample
A	P4VP + benzene
A1	P4VP + benzene + KCl
A2	P4VP + benzene + $CuCl_2$
B	P4VP + toluene
B1	P4VP + toluene + KCl
B2	P4VP + toluene + $CuCl_2$
C	P4VP + xylene
C1	P4VP + xylene + KCl
C2	P4VP + xylene + $CuCl_2$

FTIR spectra

IR spectra were recorded on a Jasco (Tokyo, Japan) 300E FTIR spectrometer. They were used to confirm the chemical reaction between P4VP and the metal chlorides and the effects of different solvents in the preparation of P4VP.

NMR

NMR spectra (Ex-270 NMR spectrometer, JEOL, Tokyo, Japan) were used to confirm the chemical reaction between the polymer and the metal chloride and the effects of the different solvents in the polymerization of 4VP to P4VP.

PAL measurements

The PAL spectra were collected with a conventional fast–fast coincidence spectrometer, which measured the time difference between the positron birth indicated by the 1.27-MeV γ-ray emitted from the [22]Na source and the annihilation γ-ray emitted from the sample. Two plastic scintillations coupled to photomultiplier tubes were used, one with an energy window set for 1.27 MeV to provide a start signal and the other with an energy window set for 0.511 MeV to provide a stop signal.

The PAL spectra were analyzed with the computer program LT 9.0,[24] which allows both discrete and long normal distributions of the annihilation rate ($\lambda = 1/\tau$, where τ is the lifetime of positron). From the distribution of the o-Ps annihilation rate ($\lambda_3 = 1/\tau_3$, where τ_3 is the o-Ps lifetime of the longest component), the mean size and size distribution of free-volume holes can be calculated. In finite lifetime analysis, the shortest components (τ_1, I_1) are related to p-Ps annihilation, and the intermediate components (τ_2, I_2) are indicating annihilation of the free positron in the polymer matrix as well as amorphous–crystalline interfaces. The longest components (τ_3, I_3) represents pick-off annihilation of the o-Ps in free volume. Consequently, the o-Ps component can provide infor-

mation on free-volume properties that markedly affect microstructural changes.

The o-Ps lifetime (τ_3) can be correlated with the mean radius (R) of the free-volume holes in the polymer material by the following semiempirical equation:[25,26]

$$\tau_3 = 0.5\left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right]^{-1} \quad (1)$$

where $\Delta R = 0.1656$ nm is the fitted empirical electron layer thickness.

On the other hand, positron lifetime measurements of polymers allow the estimation of the fractional free-volume parameter [f (%)], which is defined as follows:

$$f = (V - V_o)/V = V_f/V \quad (2)$$

where V is the total macroscopic volume of the polymer, V_o is the volume occupied by molecules, and V_f is the free-volume hole size of the polymer. Wang
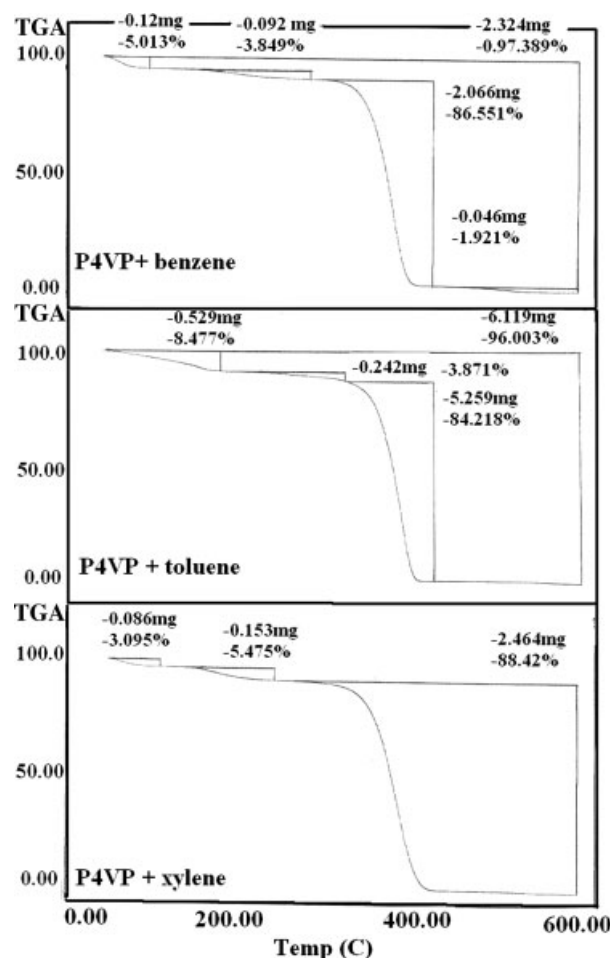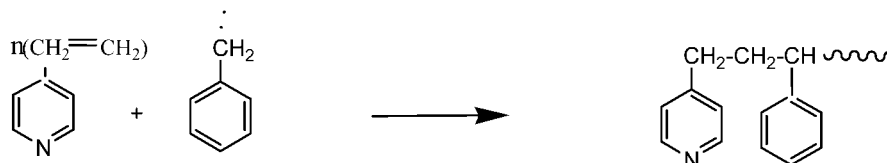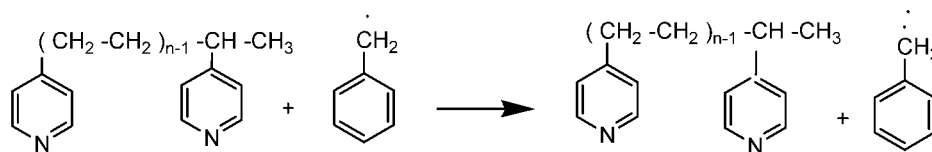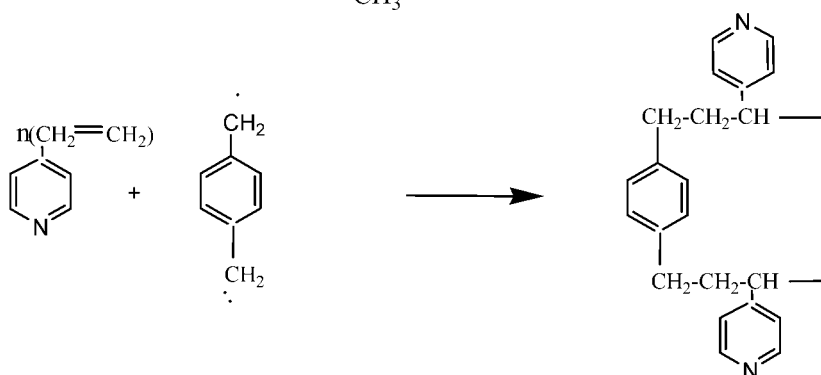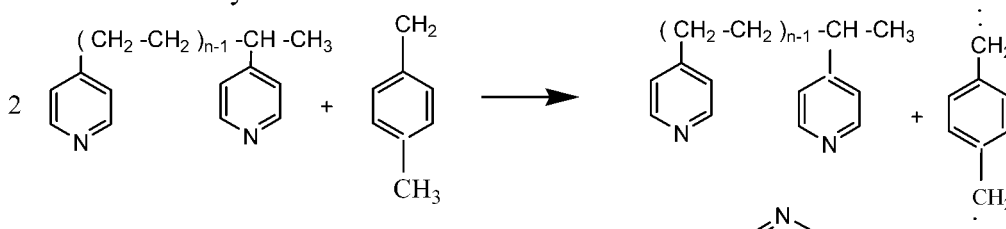

Figure 1 Thermogravimetric diagrams of modified P4VP: (A) benzene, (B) toluene, and (C) xylene.

1- In the case of toluene :

2- In the case of xylene:

Xylene radical (as a solvent) starts the propagation of two chains of 4-VP

Scheme 4

et al.[27] proposed a semiempirical equation that can be used to evaluate this parameter:

$$f = AI_3V_f \tag{3}$$

where I_3 is the relative intensity of the o-Ps lifetime component, $V_f = \frac{4}{3}\pi R^3$ is the free volume of the single hole (nm^3), and the R value is taken from eq. (1). A is the normalization constant.

Doppler broadening of annihilation radiation measurements

The positrons were annihilated with the sample electrons emitting 511-keV radiation. The annihilation peak was recorded with a high-energy-resolution hyperpure germanium detector to evaluate the Doppler broadening for the peak. The energy resolution of the detector was 1.2 keV at the 662-keV peak of Cs-137. The data were analyzed in terms of S and W. The S parameter is a measure of the relative contribution of low-momentum electrons in the annihilation peak.[28] It was obtained by the division of the counts in the central area of the 511-keV peak into the total counts in the peak after the subtraction of the background. The W parameter represents the relative contribution of high-momentum electrons, which is given as the area of the tail region (high-momentum) far from the center in a fixed interval by the total area.

RESULTS AND DISCUSSION

TGA

TGA is considered the most important method for studying the thermal stability of polymers. It monitors changes in a sample's weight as a function of temperature. Figure 1 shows the effect of tempera-
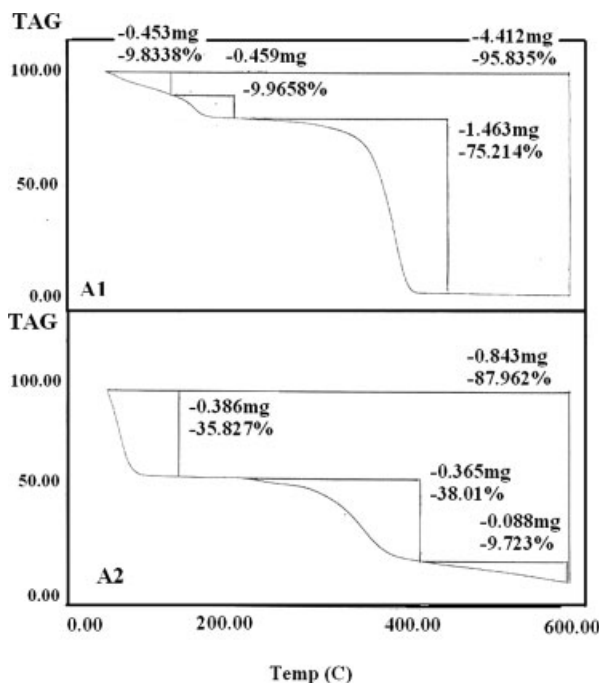
Figure 2 Thermogravimetric diagram of P4VP–benzene: (A1) KCl and (A2) CuCl$_2$·2H$_2$O.

ture on modified P4VP samples with different solvents. By comparing the polymers prepared in the presence of different solvents, we found that all the polymers were stable with no weight loss up to 150°C, and the thermal degradation of P4VP started beyond 150°C. On the other hand, the values of the weight loss caused by thermal degradation were 97.389, 98.003, and 88.428% at 387.82, 385.25, and 384.91°C for P4VP samples with benzene, toluene, and xylene, respectively. That the lowest values of weight loss occurred with xylene as the solvent means that the polymer was more stable with xylene than toluene and benzene because of the reaction between the solvent and the polymer as a result of proton transfer to the solvent.[29]

Furthermore, because of the presence of two groups of —CH$_3$ in xylene, which has an inductive effect (+I), the electronic density or electron negativity on the benzene ring in xylene is higher in comparison with toluene and benzene, whereas the para position of the two groups of —CH$_3$ increases the resonance in the benzene ring. The chain transfer of the solvent is expected, as shown in Scheme 4. The xylene molecule is changed to the xylene radical.

Figures 2–4 show the effect of temperature on the P4VP–KCl and P4VP–CuCl$_2$ complexes (in the presence of different solvents). Also, the metal complexes of P4VP were stable with no weight loss up to 150°C. From these figures, we can observe that 95.835 and 73.96% of the weight was lost in P4VP–CuCl$_2$ and P4VP–KCl complexes at 384.07 and 348.75°C with benzene as the solvent (Fig. 2); 94.673
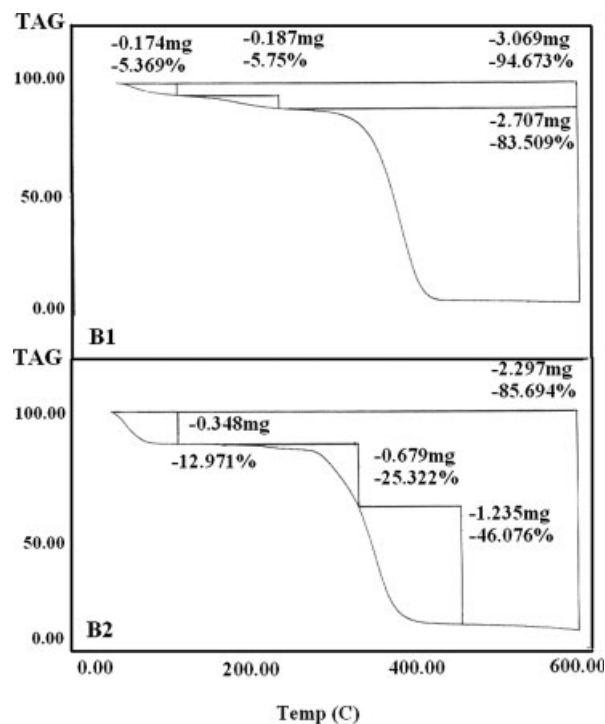
and 85.694% of the weight was lost in P4VP–CuCl$_2$ and P4VP–KCl complexes at 382.26 and 350.84°C with toluene (Fig. 3); and 85.440 and 81.808% of the weight was lost in P4VP–CuCl$_2$ and P4VP–KCl complexes at 380.62 and 331.79°C with xylene (Fig. 4). It
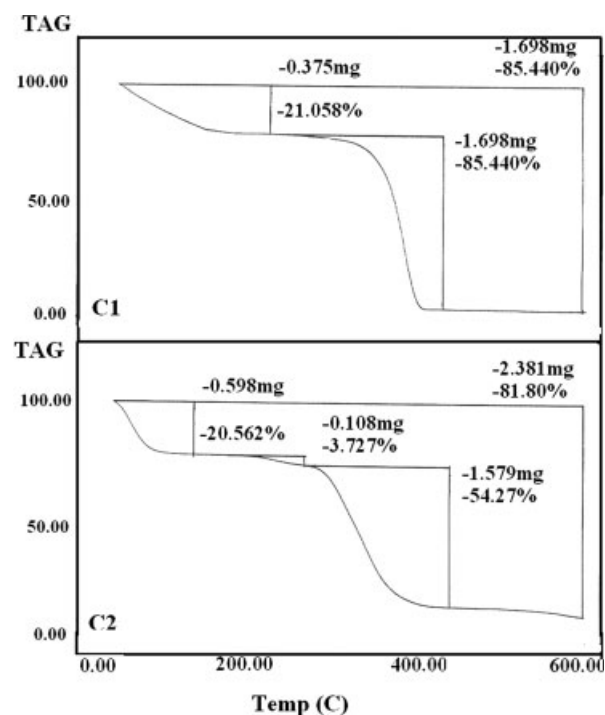

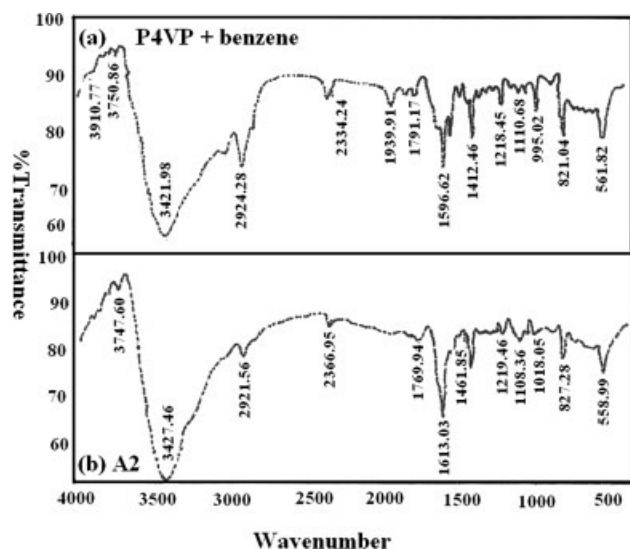**Figure 3** Thermogravimetric diagram of P4VP–toluene: (B1) KCl and (B2) CuCl$_2$·2H$_2$O.

Figure 4 Thermogravimetric diagram of P4VP–xylene: (C1) KCl and (C2) CuCl$_2$·2H$_2$O.

Figure 5 FTIR spectra of P4VP: (a) A and (b) A2.

Figure 7 FTIR spectra of P4VPL: (a) C, (b) C1, and (c) C2.

can be concluded that the degradation of P4VP–KCl complexes is less than that of P4VP–CuCl$_2$ and modified P4VP. This is due to the small K atom and the molecule of KCl, which are completely ionized in the saturated solution, leading to less stability. It has been suggested that the degradation takes place at different stages with various complexes. This
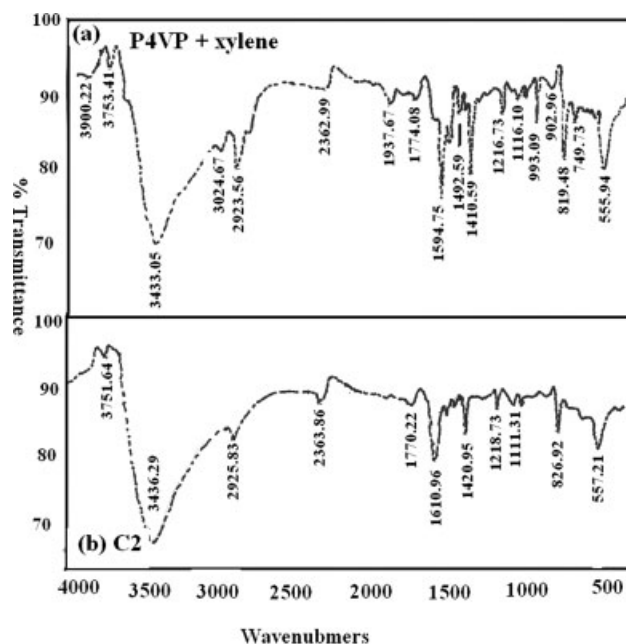
means that the P4VP–CuCl$_2$ complex is more stable than the P4VP–KCl complex and the pure polymer itself. This is due to the resonance effect of nitrogen
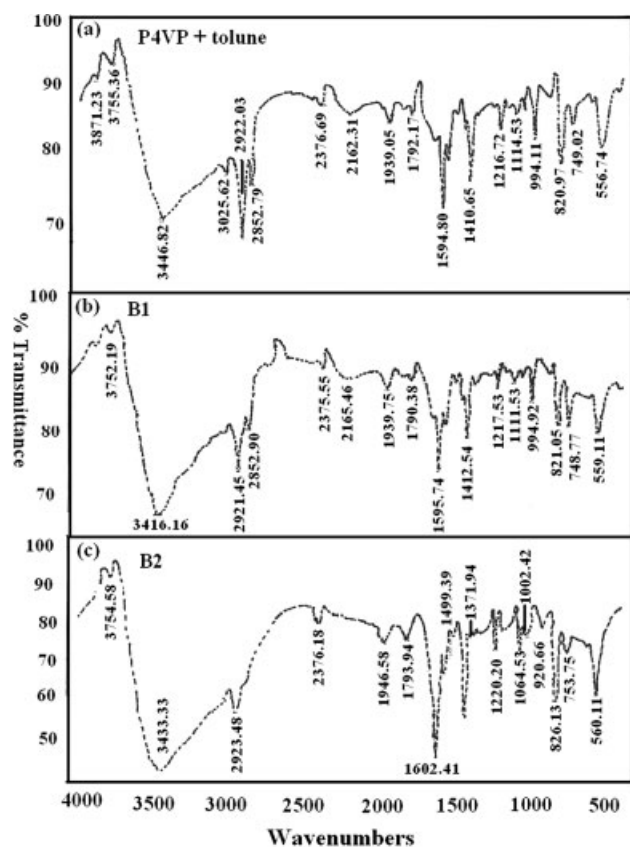

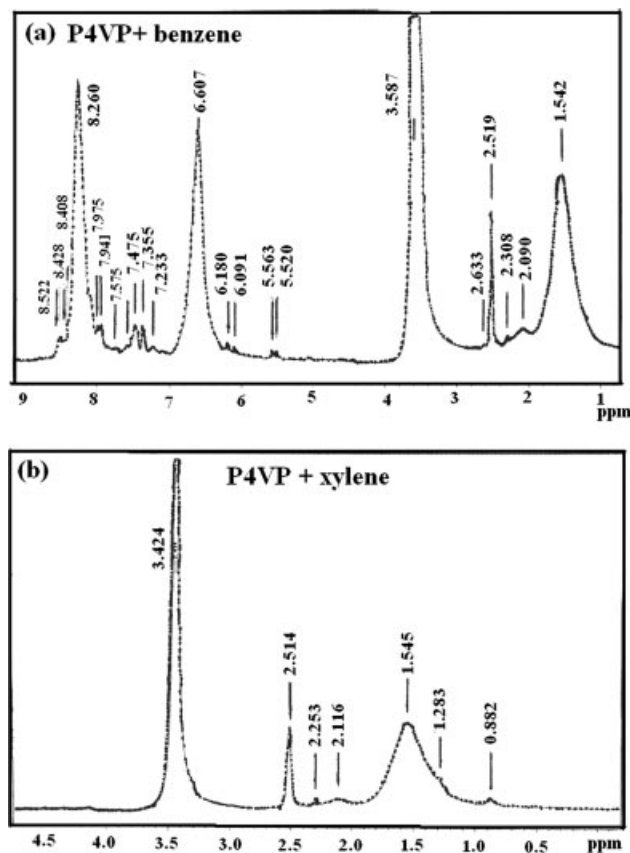**Figure 6** FTIR spectra of P4VP: (a) B, (b) B1, and (c) B2.

Figure 8 NMR spectra of modified P4VP: (a) benzene and (b) xylene.

Sample	τ_3 (ns)	I_3 (%)	V_f (Å^3)	f (%)	S
P4VP–benzene (A)	1.759 ± 0.012	10.97 ± 0.28	74.877 ± 0.921	1.478 ± 0.005	0.3427 ± 0.0005
P4VP–toluene (B)	1.613 ± 0.025	13.50 ± 0.26	62.579 ± 0.862	1.521 ± 0.005	0.3465 ± 0.0005
P4VP–xylene (C)	1.754 ± 0.012	12.82 ± 0.24	74.55 ± 0.941	1.720 ± 0.005	0.3519 ± 0.0005

in the pyridine ring, which in turn acts on a carbonium ion on the polymer chain.[30] Also, with benzene as the solvent, the stability of P4VP–CuCl$_2$ is higher than with toluene and xylene as solvents in the polymerization.

FTIR spectra

The FTIR spectra of P4VP samples were evaluated and are presented in Figures 5–7. The bands at 995 and at 1412 cm^{-1} are due to the vibration of the vinyl group, and the vibration near 3500 cm^{-1} is due to imines [Fig. 5(a)]. In Figure 5(b), the bands between 827 and 558 cm^{-1} are due to C—Cl vibrations, and the band at 1613 cm^{-1} is due to vibrations of amine salt due to an electron bond between nitrogen and chlorine. The bands at 1410 and 994 cm^{-1} may be due to the presence of the methyl group in toluene, and the vibrations of the cyclic six-membered ring are located at about 1650–1450 cm^{-1} [Fig. 6(a)]. The presence of the bands at 2921 and 2852 cm^{-1} may be due to toluene, as mentioned before, and the small band at 2375 cm^{-1} may be due to ammonium salt [Fig. 6(b)]. Figure 6(c) is characterized by the disappearance of the band at 2852 cm^{-1}. In Figure 7(a), there are small bands at 1774 cm^{-1} that may be due to cyclic lactom fused to another ring; the band at 2852 cm^{-1} disappeared. There is a band at 1610.9 cm^{-1} that may be due to amine salt, as shown in Figure 7(b).

NMR spectra

Figure 8 shows the NMR spectra of P4VP–benzene and P4VP–toluene, respectively. There is a band near 1.5 ppm, which is due to CH$_3$ groups.

The CH groups of the pyridine ring and CH of the benzene ring, as well as CH and CH$_2$ of the vinyl group, appeared near 2.5, 3.5, 6.6, and 8.2 ppm, respectively.

Positron annihilation results

Effects of different solvents on the free-volume parameter of P4VP

In our results, we consider P4VP modified with benzene as a reference because toluene and xylene contain a benzene ring in addition to CH$_3$ groups. The values of the o-Ps lifetime components (τ_3 and I_3),

which are related to V_f and f as well as the S parameter (which is a measure of the amount of Ps formation in the free-volume holes), are listed in Table II.

The τ_3 and I_3 values are strongly influenced by the polymer structure; different solvents lead to changes in V_f and f. The table shows that (1) using toluene as a solvent in P4VP decreases V_f by 17.8% and increases f by 2.8% from the corresponding values of benzene and (2) using xylene as a solvent in P4VP increases f by 15% from the corresponding value of benzene. This means that using toluene as a solvent in P4VP decreases V_f and increases f, whereas xylene increases f or the probability of o-Ps formation, which appears as a higher value of S. In such a case, the presence of two groups of CH$_3$ in xylene has two important effects, namely, making P4VP less disordered and leading to less variation in V_f and an increase in both f and S.

Figure 9 shows the effects of the aforementioned solvents on the V_f distributions of P4VP, which confirmed the aforementioned results. This figure shows $g(V_f)$, which gives the volume fraction of the free-volume holes with volumes between V_f and $V_f + dV_f$ (the change in V_f). The distribution has maximum values at 75, 62, and 74 Å^3 and widths of 71, 69, and 57 Å$_3$ for P4VP–benzene, P4VP–toluene, and P4VP–xylene, respectively.

Effect of KCl and CuCl$_2$·2H$_2$O on the free-volume parameters of modified P4VP

The variations of the o-Ps lifetime components (τ_3 and I_3) and S and W parameters versus the type of
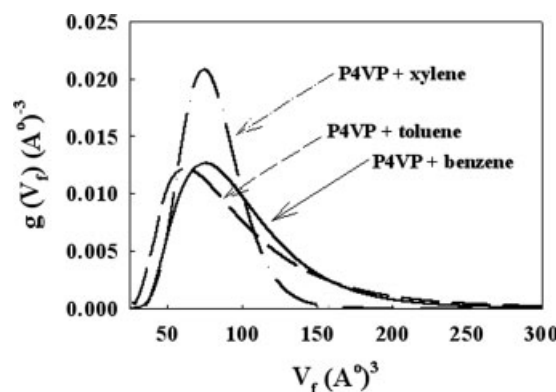

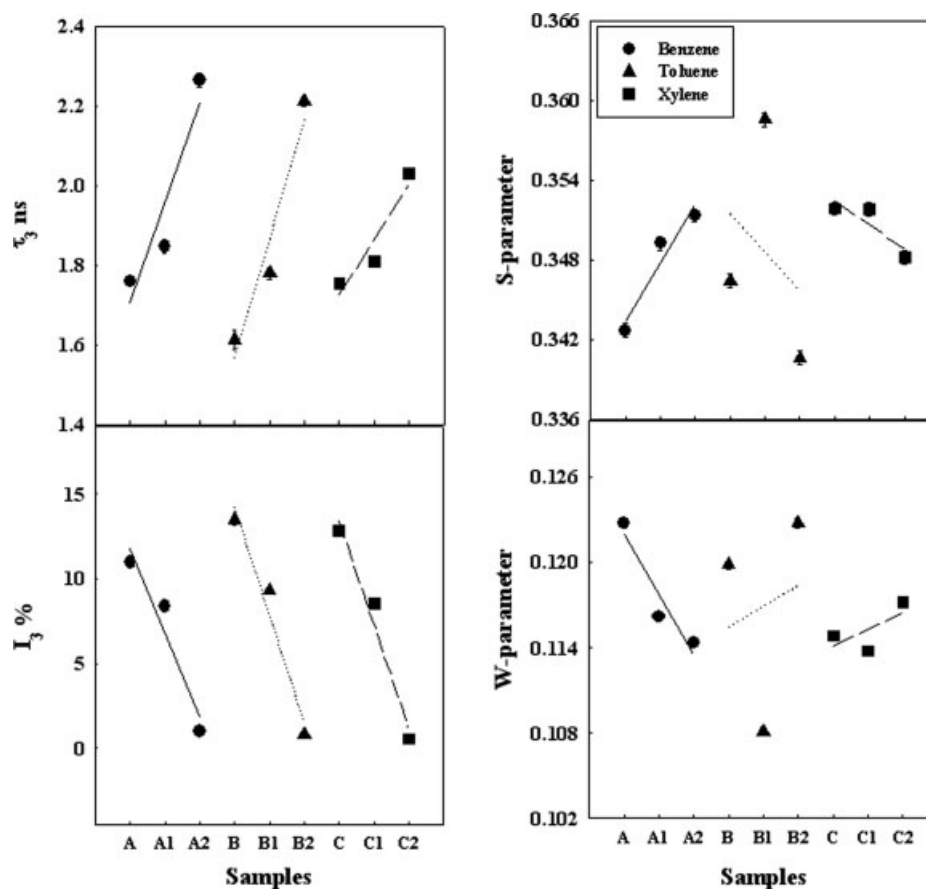**Figure 9** Free-volume distributions of modified P4VP samples.

Figure 10 Plots of τ_3, I_3, S, and W for modified P4VP and its complexes. The lines were drawn to guide the eye.

polymer are plotted in Figure 10. The modified P4VP shows sharp increases in τ_3 and a sharp decrease in I_3 with the addition of KCl and CuCl$_2\cdot$2H$_2$O. This increase in τ_3 is due to the reaction of the molecules of metals with the chains of modified P4VP, and they make the free volume larger. This causes the creation of free space regions in which the electron density is low. In those regions, Ps atoms might be formed, and they may live there longer than in the plain polymer. However, the values of I_3, which is a measure of the fraction of free-volume holes, decrease with the addition of KCl and CuCl$_2\cdot$2H$_2$O to the three types of modified polymers. This decrease might be caused by a lack of free space or a combination of free space to form the o-Ps atoms by the addition of KCl and CuCl$_2\cdot$2H$_2$O to modified P4VP. That could be interpreted in terms of the molecular structure, the molecular packing in the polymer, and the substitution effect.

On the other hand, the S parameter, which reflects the probability of positron annihilation with low-momentum electrons, increases with the addition of KCl and CuCl$_2\cdot$2H$_2$O to P4VP–benzene, whereas it decreases with their addition to P4VP–toluene and P4VP–xylene. The W parameter, which is the probability of positron annihilation with core electrons by
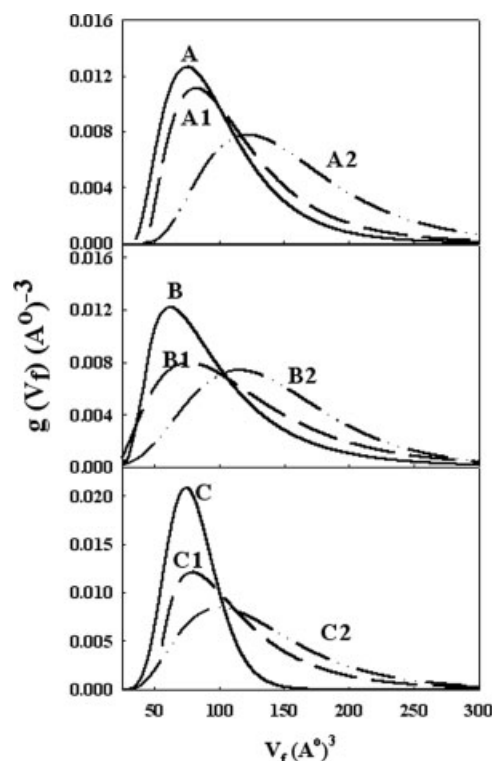

Figure 11 Free-volume distributions of modified P4VP and its complexes.
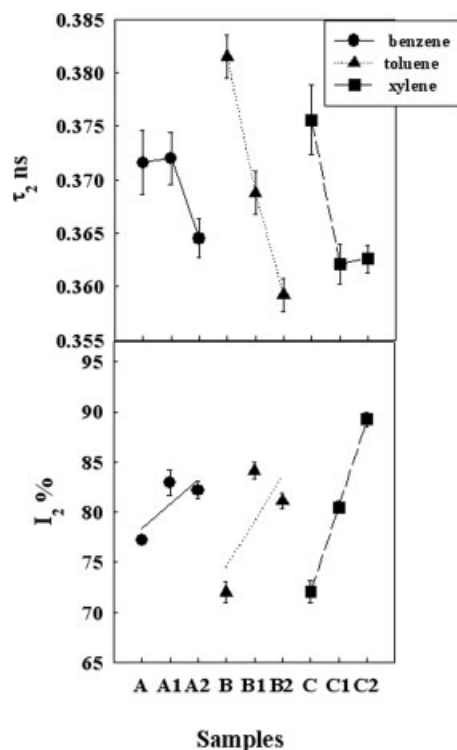
Figure 12 Plots of τ_2 and I_2 for modified P4VP and its complexes. The lines were drawn to guide the eye.

the addition of KCl and $CuCl_2 \cdot 2H_2O$ to modified P4VP, shows the opposite trend.

The opposite trends of the S and W parameters for P4VP–toluene and P4VP–xylene are due to the presence of the CH_3 group in toluene and xylene, which leads to an equilibrium state for the negative charge region because of a ^+I inductive effect. In addition, the presence of the high electron negativity of the benzene ring increases the secondary bond density between the polymer chains, leading to a change in the amount of positron annihilation with valence and core electrons.

Therefore, different representations of the effects of KCl and $CuCl_2 \cdot 2H_2O$ on modified P4VP are shown in Figure 11. The distribution has maximum values at 82 and 122 Å^3 and widths of 69 and 116 Å^3 that increase with the addition of KCl and $CuCl_2$ to P4VP–benzene. Similar behavior was observed for P4VP–toluene and P4VP–xylene. The distributions have maximum values at 76 (B1), 115 (B2), 80 (C1), and 100Å^3 (C2) and widths of 109 (B1), 124 (B2), 71 (C1), and 107 Å^3 (C2).

Figure 12 presents the variation of τ_2 and I_2 as a function of the type of polymer, providing information on the open volume changes in crystalline regions and amorphous–crystalline interfaces of the polymer complexes. The small τ_2 values indicate small open volumes in this region, which are affected by the addition of KCl and $CuCl_2 \cdot 2H_2O$ to

modified P4VP. In addition, the probability of free positron annihilation of positrons (I_2) is significantly larger than the formation probability of o-Ps. This result indicates that there are variations in the electron densities at the polymer matrix and interfaces for P4VP–$CuCl_2$ and P4VP–KCl in the presence of different solvents. On the other hand, these results confirm the creation of free volumes with large sizes and low fractions in the amorphous region of the polymer matrix, as shown in Figure 10.

CONCLUSIONS

This work indicates that the polymer structure differs in the presence of different solvents. Instead of getting rid of the solvents, we have found that the presence of the solvents leads to the formation of a polymer with new properties. These new properties are useful in industry. This change in the polymer structure is affected by the proton transfer of the polymer to the solvent. This change in the structure of the polymer leads to different results in TGA, FTIR spectra, and NMR spectra as well as position annihilation. Also, the introduction of salts such as KCl and $CuCl_2 \cdot 2H_2O$ leads to the reaction of these salts with the polymer via the nitrogen atom in P4VP. The new structure of the complexes formed by the reaction of KCl or $CuCl_2 \cdot 2H_2O$ with the polymer also leads to the variation of the free-volume properties.

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