BLENDS OF POLY(4-VINYLPYRIDINE) AND DIHYDRIC PHENOLS: THERMAL AND INFRARED SPECTROSCOPIC STUDIES. PART III

NICOLÁS GATICA* AND ORLANDO MONARES

Departamento de Polímeros, Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile.

(Received: May 6, 2010 - Accepted: July 9, 2010)

ABSTRACT

The blending of the functionalized vinyl polymer poly(4-vinylpyridine) (P4VPy) with the low molecular weight compounds 4,4'-biphenol (44BP) and 2,2'-biphenol (22BP) was studied. The binary systems formed by P4VPy and 44BP (blend A) and by P4VPy and 22BP (blend B) were characterized by Differential Scanning Calorimetry (DSC) to study the effect of the blending on characteristic transition, such as the glass transition of P4VPy and the melting of 44BP and 22BP. The results suggest the postulate that the components of both blends are miscible, with a comparatively higher intermolecular interaction level in the case of blend A. Using Fourier Transform Infrared Spectroscopy (FTIR), the formation of hydrogen bonding between the components of the blends A and B was detected. The behaviour observed with the FTIR corroborates the DSC results. Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) were used as additional analytical techniques and the results show a good agreement with the DSC and FTIR results and they complement the characterization of the studied systems.

Keywords: blends, poly(4-vinylpyridine), 4,4'-biphenol, 2,2'-biphenol, hydrogen bond, low molecular weight compounds.

INTRODUCTION

In the early development of the macromolecular chemistry, research centered on the synthesis and characterization of homo and copolymers. Subsequently, a considerable interest arose for the chemical modification, such as graft copolymerization, as a way to improve the properties of the polymer materials. However, due to the high costs and environment pollution involved in the polymer synthesis processes, the study of polymer blends was notably developed in the last few decades¹⁻⁶. These blends, by means of the simple mix of functionalized homo and copolymers, have been a very useful way to obtain new materials with novel properties⁷⁻¹⁰.

When one of the polymer components is substituted by a low molecular weight compound (LMWC), interesting materials are also obtained from both a fundamental and applied point of view¹¹⁻¹⁵. A significant number of works describes the addition of LMWCs as additives to keep, improve or modify the properties of the polymeric product¹⁶⁻¹⁸. However, most of these works focuses attention on the final properties rather than on a molecular characterization.

In the last decade, some works have described the molecular behavior of this kind of systems. Inoue *et al.* studied the blends containing poly(ϵ -caprolactone), poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with dihydic phenols and diamino compounds¹⁹⁻²². Atorngitjawat *et al.* reported the effects of the addition of low molecular weight phenols (containing from one to six hydroxyl groups) on the dynamics of a host polymer: poly(2-vinylpyridine)²³. Other works describe the calorimetric and morphologic characterization of blends formed by functionalized polymers and LMWCs^{1,15,24-26}. The last ones have also been incorporated into polymer blends as compatibilizers of immiscible polymers. In these cases, bifunctional LMWCs have been used²⁷⁻²⁹.

In the case of both polymer + LMWC blends and immiscible polymers + LMWC blends, it is important to characterize the intermolecular interactions responsible for the miscibility between the components. In this context, one of the most useful analytical techniques, used in this work, is infrared spectrophotometry as can be observed in a series of studies^{1,2,5,30-32}.

We have recently reported the results about the miscibilization behaviour of some functionalized vinyl polymers such as poly(2-vinylpyridine) (P2VPy), poly(4-vinylpyridine) (P4VPy) and poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MA)] (as polymer components) with some dihydic phenols such as 4,4'-thiodiphenol (TDP) and 4,4'-methylenediphenol (MDP) (as low molecular weight components)^{33,34}. The present paper studies the compatibility in blends formed by P4VPy as the polymer component and 4,4'-Biphenol (44BP) and 2,2'-Biphenol (22BP) as LMWCs. The study was carried out using the analytical techniques used in the previous works, i. e., Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy

(FTIR) and Thermogravimetric Analysis (TGA) as well as Scanning Electron Microscopy (SEM). The structural formulae of P4VPy, 44BP and 22BP are shown in Figure 1.

Figure 1. Structural formulas of poly(4-vinyl pyridine) (P4VPy), 4,4'-biphenol (44BP) and 2,2'-biphenol (22BP).

EXPERIMENTAL

Blend components

Aldrich's P4VPy, 44BP and 22BP were used. The weight average molecular weight (Mw) and the glass transition temperature (Tg) of P4VPy are 60,000 g/mol and 151.2 °C respectively. Melting points (Tm) of 44BP and 22BP are 281.8 and 108.7 °C respectively.

Preparation of blends

Blends of different compositions were obtained by solution casting using methanol as solvent. From mother dissolutions of the pure components, the blends were prepared on Petri dishes with stirring during approximately 5 h. Subsequently, the solvent was evaporated at room temperature and then the samples were vacuum dried at room temperature for 2-3 weeks until constant weight. The blend concentration was about 2 weight %.

Table 1 shows the compositions and the denomination of the blends included in this work.

DSC measurements

The glass transition temperature (Tg) of P4VPy and blends and the melting temperatures (Tm) of 44BP, 22BP and blends were obtained by Differential Scanning Calorimetry (DSC) from the thermograms obtained with a Differential Scanning Calorimeter TA Instruments Q200. Samples (3-5 mg) were placed inside aluminum pans and heated under flowing nitrogen (50 mL/min), ranging from 0 to 300 °C for blend A and from 0 to 200 °C for blend B, with the temperature increased at 10 (°C/min).

To minimize differences in the samples' thermal history, the corresponding thermograms were obtained according to the following temperature program: heating until T_i temperature (dynamic stage), isothermal stage at T_i (static), cooling down to the initial temperature (dynamic, quenching step), isothermal step at the initial temperature (static) and heating until the final temperature (dynamic) [T_i = 200 °C and

80 °C for blends A and B respectively; final temperature = 300 °C and 200 °C for blends A and B respectively]. In all cases, T_g, T_m and the heat of fusion (DH_{fus}) were evaluated from the last stage.

Samples were dried under reduced pressure in a vacuum oven prior to measurements.

FTIR spectra

Infrared spectra of P4VPy, LMWCs and their blends were recorded on a Nicolet Magna IR 550 Fourier transform infrared spectrophotometer. Spectra were recorded with a resolution of 1 cm⁻¹. Samples were prepared directly in KBr pellets.

TGA measurements

Thermogravimetric measurements were performed using a Thermal Analyzer TA Instruments Q50. Samples (about 3 mg) were placed inside aluminum pans and heated under flowing nitrogen (60 mL/min) ranging from 25 to 600 °C at 10 °C/min, obtaining the corresponding thermal decomposition profiles.

Samples were dried under reduced pressure in a vacuum oven prior to measurements.

SEM micrographs

Blends were prepared according to the procedure described in Preparation of blends section. However, in this case a glass slide was deposited into the Petri dish, which was then removed and kept at room temperature for total solvent evaporation. The dry samples were metallized by fixing of a carbon conducting band and gold ions were deposited to obtain conducting samples. Finally, the required magnifications were programmed with the microscope software and the images were obtained.

Table 1. Composition and denomination of the studied blends.

Blend	Composition (weight % in LMWC)	Correlative denomination
P4VPy + 44BP (A)	0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100	1A, 2A, 3A, 4A, 5A, 6A, 7A, 8A, 9A, 10A, 11A
P4VPy + 22BP (B)	0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100	1B, 2B, 3B, 4B, 5B, 6B, 7B, 8B, 9B, 10B, 11B

RESULTS AND DISCUSSION

Figure 2 shows the thermograms obtained for the 1A-11A and 1B-11B samples. From the individual thermograms, the glass transition of P4VPy and the melting of 44BP and 22BP were studied. As can be observed in this Figure, the size of the melting peaks does not allow the observation of the corresponding glass transition temperature (T_g) signals. Figure 3-a presents the thermogram, with heat flow scale modified, obtained for the 3A sample to illustrate the kind of sign obtained to evaluate the T_g. At this temperature, the heat capacity increases; more energy is required to keep the sample temperature equal to the reference temperature. The heat flow to the sample originates a drop in the DSC curve as shown in Figure 3-a. From this kind of plots, T_g values of the different blend compositions were determined and listed in Table 2.

Table 2. Glass transition temperature (T_g), melting temperature (T_m) and heat of fusion (DH_{fus}) for the indicated compositions.

Composition (blend A)	T _g (°C)	T _m (°C)	DH _{fus} (kJ/ mol)	Composition (blend B)	T _g (°C)	T _m (°C)	DH _{fus} (kJ/ mol)
1A	151.2	-	-	1B	151.2	-	-
2A	145.1	-	-	2B	132.1	-	-
3A	140.9	-	-	3B	112.9	-	-
4A	137.9	-	-	4B	106.2	-	-
5A	135.1	-	-	5B	92.8	-	-
6A	132.0	-	-	6B	86.9	-	-
7A	134.4	-	-	7B	-	-	-
8A	129.6	274.3	21.3	8B	-	-	-
9A	-	275.5	18.2	9B	-	108.4	18.1
10A	-	280.1	30.4	10B	-	108.2	15.0
11A	-	281.8	90.4	11B	-	108.7	19.8

In both blends a shifting of the polymer T_g to lower values is observed

as the LMWC content increases (Figure 3-b). This behaviour, known as the *plasticizing effect*, has been described for different commercial products³⁵ and by us in a previous work that studied the blends of poly(4-vinylpyridine) and poly(2-vinylpyridine) with 4,4'-thiodiphenol and 4,4'-methylenediphenol³⁴. When the material reaches the T_g, it is softer and more flexible; the polymer is then more malleable for used. The LMWC, acting as a plasticizing compound originates an increase in the free volume between the polymer chains. As a result, a lower energy amount is required for the motion of the chain segments.

Figure 2. Thermograms of the 1A-11A (a) and 1B-11B (b) series.

Figure 3. a) Thermogram for the 3A sample (80 weight % P4VPy / 20 weight % 44BP). b) Glass transition temperature (T_g) variation with the composition, for the blends A (■) and B (●).

The thermograms presented in Figure 2 were used to study the change originated in the melting point of the LMWCs as a consequence of the blending processes. 44BP (11A) shows a melting temperature (T_m) of 281.8 °C, which shifts to lower values as the P4VPy content increases (280.1, 275.5 and 274.3 °C for 10A, 9A and 8A respectively). T_m disappears when the blend composition is 40 % in P4VPy (7A). From the corresponding melting peaks, heats of fusion (ΔH_{fus}) were determined. A trend of decreasing was observed as the polymer content increased (90.4, 30.4, 18.2 and 21.3 kJ/mol for 11A, 10A, 9A and 8A respectively). A lower amount of energy is required to melt 44BP as the blend is richer in P4VPy. This result suggests that the LMWC crystallinity lowers with the polymer content until 44BP exists in an amorphous state and its crystallization is hindered in the blends 7A-2A. The T_m and ΔH_{fus} values determined for this blend are presented in Table 2.

In the mixture, the 44BP molecules are distributed between the polymer chains, resulting in a diminishment in the molecular order of this LMWC. As a result, the crystallinity should lower. We have reported the same behaviour for blends formed by P4VPy, poly(2-vinylpyridine) (P2VPy) and poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MA)] as polymer components and 4,4'-thiodiphenol (TDP) and 4,4'-methylenediphenol (MDP) as low molecular weight components³³⁻³⁴. In all the cases, the observed behaviour suggests some kind of intermolecular interaction between the polymer and the LMWC.

The T_m and ΔH_{fus} values obtained for the blend B are also presented in Table 2. In this case, only a moderate fall of ΔH_{fus} is observed from 11B (pure 22BP) to 10B (10 % P4VPy). Heat of fusion and melting temperature are maintained relatively constant with the composition (for the samples 11B, 10B and 9B). These results would reflect both the 22BP's lower degree of crystallinity ($T_m = 108.7$ °C) and a comparatively lower level of intermolecular affinity between the components forming the blend B.

The blends studied in this work were also analysed with infrared spectroscopy in order to detect and identify the kind of intermolecular interaction. The shifting of the infrared absorption band corresponding to a determined functional group is interpreted as a direct consequence of specific intermolecular interactions due to the changes in the electronic density of the involved chemical bonds³⁴ and references therein. From the structural formulae of P4VPy, 44BP and 22BP presented in Figure 1, the hydrogen bonding formation is proposed to be due to the presence of the pyridine group in P4VPy and the hydroxyl groups in 44BP and 22BP.

Spectroscopic procedures are the techniques most used to characterize and study hydrogen bonding in polymers³⁰. Fluorescence or nuclear magnetic resonance studies have been performed, although the spectral technique commonly used to study hydrogen bonding and especially in polymer blends, is the infrared spectroscopy³⁰.

Different spectral modes corresponding to protons donors or acceptor groups are notably affected both in intensity and in position when they are part of a hydrogen bond. Frequently, the functional groups involved in these bonds are different in each polymer and they do not overlap, simplifying the spectral analysis³⁰. For example, pyridine rings of polyvinylpyridines, typical proton acceptor polymers, suffer evident modifications. The mode

corresponding to the deformation of the ring, centred in 993 cm^{-1} for non-bonded groups, experiments a shift towards higher wave numbers when it forms part of a hydrogen bond, which is attributed to an increase in the stiffness of the associated ring^{30,34}. Figure 4 shows the FTIR spectra of the blend A for selected compositions as representative examples. The monomer units of P4VPy contain pyridine groups, whose absorption band associated to the ring deformation appears at about 995-996 cm^{-1} . On the other hand, 44BP and 22BP do not have pyridine groups, and thus, do not present this characteristic band. Then, any modification in this spectral region can be related with some electronic variation in the environment of the ring.

Figure 4. FTIR spectra for blend A (compositions 1A, 2A, 4A, 6A, 8A and 10A) at the 700-1300 cm^{-1} zone.

The position of the band corresponding to ring deformation was analyzed as a function of the LMWC content. The obtained results can be observed in Figure 5, which shows the shifting to higher wave numbers as the 44BP and 22BP percentage increases. This behaviour reveals the increase in ring stiffness due to the formation of hydrogen bonding between the pyridine nitrogen of P4VPy and the hydroxyl group of the LMWCs. In effect, when the pyridinic nitrogen is associated by hydrogen bonds with 44BP and 22BP, the stiffness of P4VPy's aromatic ring increases. As a result, more energy is required to produce a deformation vibration and consequently the corresponding wave number is higher.

Figure 5. Wave number corresponding to the deformation absorption of the pyridine groups in the blends A (■) and B (●).

Another interesting fact is implied by the results shown in Figure 5. A higher variation for the wave number of the band associated to the pyridinic ring deformation with the composition is observed for the blend A, i. e., when P4VPy is blended with 44BP. According to the prior analysis, more energy is necessary to produce the vibration by deformation, which reflects a higher degree of molecular affinity between these components. Hydrogen bond formation requires not only the presence of a hydrogen atom bonded

to another electronegative atom, but also an appropriate spatial disposition. 44BP and 22BP are position isomers and therefore with similar features such as molecular size and the kind of functional group. However, in the case of 44BP each hydroxyl group is in position 4 with respect to the other ring, which implies a better spatial disposition for the intermolecular interaction. In 22BP the hydroxyl group is less accessible for the interaction. Even if the aryl-aryl simple bond of 22BP can rotate, each -OH group is always in position 2 with respect to the other ring, i. e., closer to the di-substitution position and thus more sterically hindered. This behaviour shows a good agreement with the first results obtained by DSC with respect to the components forming the blend A, which presents a comparatively higher level of molecular affinity.

The analytical techniques of Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM) were also used, as complementary tools, to characterize the studied blends. Figure 6 shows the thermal decomposition profiles obtained by TGA for the blends A and B. In all the cases, intermediate decomposition curves with respect to the pure components were obtained. An evident trend to the diminishing of the P4VPy's thermal stability with LMWC content is observed. The TGA profiles were also used as prior evidence when setting the temperature ranges for the DSC since the obtaining of information from the corresponding thermograms requires the samples' thermal stability.

Figure 6. Thermal decomposition profiles of a) blend A and b) blend B.

Different temperature values are used to represent the extent of the thermal decomposition in a polymer sample, e. g., T_{50} , the temperature at which the weight reduction reaches 50 weight %. From the decomposition profiles shown in Figure 6, T_{50} was determined and plotted against the 44BP and 22BP content. The obtained results are presented in Figure 7, in which a decrease in P4VPy's thermal stability as the LMWC content increases is observed.

Figure 7. Variation of T_{50} with the composition for the blends A (■) and B (●).

Scanning electron microscopy (SEM) was used for the morphological characterization of the studied binary systems. Figure 8 shows the SEM micrographs of the blend A and B for selected compositions as representative examples. According to these images, P4VPy's surface is observed to have a continuous and uniform aspect, which is altered as a consequence of the blending process as the LMWC content increases. A change in the blend morphology is revealed and the formation of structures such as granules and orifices associated to the incorporation of the crystalline compounds 44BP and 22BP, is observed. When P4VPy is blended with 22BP (blend B), the characteristic structures associated to 22BP becomes evident only from sample 9B, corresponding to 80 % in the LMWC. Nevertheless, when the polymer is blended with 44BP (blend A) an evident formation of these structures can be noted for samples 5A-10A, i. e., from 40 % in the LMWC. The presence of the LMWC is observed at a lower content in the case of the blend A, a result that complements the behaviour obtained by DSC and FTIR with respect to the comparatively higher molecular affinity level between the components P4VPy and 44BP.

Figure 8. SEM micrographs for blend A (compositions 1A, 3A, 6A, 9A and 11A) and blend B (compositions 1B, 3B, 6B, 9B and 11B).

CONCLUSIONS

The addition of 44BP and 22BP originates a plasticizing effect on P4VPy, i. e., the diminishing of the glass transition temperature, which reflects the disposition of the LMWC molecules between the polymer chains.

The addition of P4VPy produces the decrease in the melting temperature and the heat of fusion for 44BP and 22BP, which can be interpreted in terms of the decrease in the molecular order of the LMWCs due to their interaction with P4VPy.

A shifting of the infrared absorption band, associated to the pyridine ring deformation, towards higher wave numbers is detected as the blend is richer in LMWC. This variation represents the increased stiffness of the aromatic ring of P4VPy due to the formation of hydrogen bonding.

P4VPy's thermal stability decreases as the content of 44BP and 22BP increases.

The molecular affinity detected for the studied system produces morphologic changes that were observed by scanning electron microscopy.

Miscible blends formed by a functionalized vinyl polymer and by bifunctional low molecular weight compounds were prepared, revealing the importance of specific interactions, such as hydrogen bonding, in blends containing polymers.

ACKNOWLEDGEMENTS

The authors thank the Dirección de Investigación Universidad de Concepción, Grant 207.024.036-1.0 for financial support.

REFERENCES

1. M. Coleman, D. Skrovanek, J. Hu, P. Painter, *Macromolecules* **21**, 59, (1988).
2. J. Moore, S. Kaur, *Macromolecules* **31**, 328, (1998).
3. Y. Park, B. Veytsman, M. Coleman, P. Painter, *Macromolecules* **38**, 3703, (2005).
4. M. L. Xue, Y. L. Yu, H. H. Chuah, J. M. Rhee, N. H. Kim, J. H. Lee, *Eur. Polym. J.* **43**, 3826, (2007).
5. E. Zuza, A. Lejardi, J. Ugartemendia, N. Monasterio, E. Meaurio, J. R. Sarasua, *Macromol. Chem. Phys.* **209**, 2423, (2008).
6. I. Kalogeras, W. Brostow, *J. Polym. Sci.-Polym. Phys.* **47**, 80, (2009).
7. K. Okamoto, T. Ichikawa, T. Yokohara, M. Yamaguchi, *Eur. Polym. J.* **45**, 2304, (2009).
8. M. Faker, M. K. Razavi Aghjeh, M. Ghaffari, S. A. Seyyedi, *Eur. Polym. J.* **44**, 1834, (2008).
9. R. Brandalise, M. Zeni, J. Martins, M. Forte, *Polym. Bull.* **62**, 33, (2009).
10. M. Lukasiewicz, A. Ptaszek, L. Koziel, B. Achremowicz, M. Grzesik, *Polym. Bull.* **58**, 281, (2007).
11. K. Pielichowska, S. Glowinkowski, J. Lekki, D. Binias, K. Pielichowski, J. Jenczyk, *Eur. Polym. J.* **44**, 3344, (2008).
12. I. Krupa, G. Miková, A. S. Luyt, *Eur. Polym. J.* **43**, 4695, (2007).
13. J. Liu, N. Hameed, Q. Guo, *J. Polym. Sci.-Polym. Phys.* **47**, 1015, (2009).
14. J. M. Huang, S. W. Kuo, Y. J. Lee, F. C. Chang, *J. Polym. Sci.-Polym. Phys.* **45**, 644, (2007).
15. J. Zhang, S. Li, Xiaodong Li, Xiaohui Li, K. Zhu, *Polymer* **50**, 1778, (2009).
16. Y. He, N. Asakawa, Y. Inoue, *J. Polym. Sci. Polym. Phys.* **38**, 1848, (2000).
17. R. Kirk, D. Othmer, "Encyclopedia of Chemical Technology", John Wiley & Sons, 4th Ed., New York, USA, 1992; vol. 3, 435.
18. R. Kirk, D. Othmer, "Encyclopedia of Chemical Technology", John Wiley & Sons, 4th Ed., New York, USA, 1992; vol. 2, 18.
19. Y. He, N. Asakawa, Y. Inoue, *J. Polym. Sci. Polym. Phys.* **38**, 2891, (2000).
20. Y. He, N. Asakawa, Y. Inoue, *Macromol. Chem. Phys.* **202**, 1035, (2001).
21. T. Watanabe, Y. He, N. Asakawa, N. Yoshie, Y. Inoue, *Polym. Int.* **50**, 463, (2001).
22. B. Zhu, Y. He, N. Yoshie, N. Asakawa, Y. Inoue, *Macromolecules* **37**, 3257, (2004).
23. P. Atorngitjawat, R. Klein, A. McDermott, K. Masser, P. Painter, J. Runt, *Polymer* **50**, 2424, (2009).
24. M. Sugimoto, K. Sakai, Y. Aoki, T. Taniguchi, K. Koyama, T. Ueda, *J. Polym. Sci. Polym. Phys.* **47**, 955, (2009).
25. E. Kiran, K. Liu, K. Ramsdell, *Polymer* **49**, 1853, (2008).
26. C. H. Kim, D. W. Kim, K. Y. Cho, *Polym. Bull.* **63**, 91, (2009).
27. X. D. Li, S. H. Goh, *J. Polym. Sci. Polym. Phys.* **39**, 1815, (2001).
28. S. W. Kuo, S. C. Chan, F. C. Chang, *Polymer* **43**, 3653, (2002).
29. S. Park, S. Choe, *Macromol. Res.* **13**, 297, (2005).
30. L. Cesteros, *Revista Iberoamericana de Polimeros* **5**, 111, (2004).
31. J. Zhang, A. Beshra, A. Domb, Y. Ozaqui, *Eur. Polym. J.* **43**, 3016, (2007).
32. N. Salim, N. Hameed, Q. Guo, *J. Polym. Sci. Polym. Phys.* **47**, 1894, (2009).
33. N. Gatica, N. Alvarado, D. Sepúlveda, *J. Chil. Chem. Soc.* **51**, 945, (2006).
34. N. Gatica, N. Alvarado, *J. Chil. Chem. Soc.* **54**, 945, (2009).
35. A. Kumar, R. Gupta, *Fundamentals of Polymer Engineering*, Marcel Dekker, 2nd Ed., New York, USA, 2003; p. 449.