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# Miscibility in Binary Blends of Poly(vinyl phenol) and Poly(*n*-alkylene 2,6-naphthalates)

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**Abstract:** We have performed Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) studies on blends of poly(vinyl phenol) (PVPh) with poly(*n*-alkylene 2,6-naphthalates) containing alkylene units of different lengths. The results indicate that each poly(ethylene 2,6-naphthalate) (PEN) and poly(trimethylene 2,6-naphthalate) (PTN) blend with PVPh is immiscible or partially miscible, but blends of poly(butylene 2,6-naphthalate) (PBN) with PVPh are miscible over the whole range of compositions in the amorphous state. FTIR spectroscopic analysis confirmed that significant degree of intermolecular hydrogen bonding occurs between the PBN ester carbonyl groups and the PVPh hydroxyl groups. The large difference in the degree of mixing in these blend systems is described in terms of the effect that chain mobility has on the accessibility of the ester carbonyl functional groups toward the hydroxyl groups of PVPh, which in turn impacts the miscibility of these blends.

*Keywords*: poly(*n*-alkylene 2,6-naphthalates), poly(vinyl phenol), polymer blends, intermolecular hydrogen bonding, chain mobility, functional group accessibility, miscibility.

## Introduction

Polymer blending is a common and potentially versatile way of developing new materials with a desirable combination of properties of component polymers.[1] There are essentially two classes of polymer blends, miscible and immiscible. Polymers may be miscible and form a single homogeneous phase when blended. Alternatively, they may be immiscible and phase separate then form heterogeneous phases when mixed. The miscibility of two polymers is best described by polymer blend thermodynamics. Because of the unfavorable thermodynamics of polymer-polymer mixing, it is difficult to obtain miscible compositions of two high molecular weight polymers. The fundamental thermodynamic quantity that controls polymer blend miscibility is the Gibbs free energy change of mixing ($\Delta G_m$) which contains enthalpic ($\Delta H_m$) and entropic ($\Delta S_m$) contributions: $\Delta G_m = \Delta H_m - T\Delta S_m$, where $T$ is the absolute temperature.

At equilibrium, for a blend to be a single homogenous phase the requirement that $\Delta G_m < 0$ must be fulfilled. Additionally, the second derivative of $\Delta G_m$ with composition must be greater than zero. In the absence of specific intermolecular interactions, $\Delta G_m$ is usually positive for polymer blends due to a small combinatorial entropy of mixing and positive enthalpy of mixing. Therefore, to exhibit thermodynamic miscibility of the blend in general, there needs to be some degree of intermolecular interactions such as hydrogen bonding between the constituent polymers, resulting in a favorable heat of mixing. Over the past two decades there has been considerable interest in enhancing the miscibility of polymer blends either by adding a third component as a compatibilizing agent or by introducing specific functional groups into the polymers to promote exothermic interactions between them. Many novel and useful polymer blends have been formed in this manner.[1-3]

It is widely accepted that polymer blend systems that are capable of strong intermolecular interactions have an increased possibility of achieving thermodynamic miscibility.[4,5] For examples, there exists a fair amount of work in the literature concerning the miscibility of poly(vinyl phenol) (PVPh) and its copolymers because the phenolic hydroxyl group is capable of hydrogen bonding with a range of partners. Among those hydrogen-bonding acceptor polymers there are a number of polymers containing carbonyl groups have been found to be miscible with PVPh, such as poly (vinyl acetate) and its random copolymers,[6] polyacrylates,[7] poly(*N*-vinyl pyrrolidone),[8] and main-chain aliphatic polyesters.[9] A survey of the miscibility of PVPh with a number of classes of polymers, including polyamides, polyimides,

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polyurethanes, polyesters, and polycarbonates has been conducted.[10] Another survey of the miscibility of PVPh blends with various aromatic polyesters has also been conducted by the Eastman Kodak researchers.[11]

Most of the aromatic polyester blends reported in the literature have focused on the transesterification reactions between different aromatic or aliphatic polyesters[12] in which block and random copolymers are formed in situ then these act as a compatibilizer which would be located at the interface of the component polymers.[13] However, literature concerning about the miscibility of the blend systems of aromatic polyesters with other polymers of dissimilar chemical structure is relatively rare.[14]

In a recent publication we reported the results obtained from thermal analysis and infrared spectroscopic studies of the miscible PBN/PVPh blends in the solid state.[15] Evidence supporting the existence of specific intermolecular hydrogen-bonding interactions between the naphthaloyl carbonyls and phenolic hydroxyl groups in the blend was presented and it was inferred that these intermolecular interactions could play a significant role in the thermodynamic miscibility of this blend system.

The present work focuses on the phase behavior of the PVPh blends with a series of poly(*n*-alkylene 2,6-naphthalates) containing various alkylene glycol units: poly(ethylene 2,6-naphthalate) (PEN, $n=2$), poly(trimethylene 2,6-naphthalate) (PTN, $n=3$), and poly(butylenes 2,6-naphthalate) (PBN, $n=4$), where $n$ is the number of methylene units. More specifically, the aim of this study is to explore the interplay between the effect of the chain mobility of poly(*n*-alkylene 2,6-naphthalates) and their ester carbonyl functional group accessibility to form intermolecular hydrogen bonds to phenolic hydroxyl groups of PVPh, which in turn impacts on the phase behavior of these blend systems. This will be accomplished by utilizing infrared spectroscopy and thermal analysis to determine the amount of intermolecular hydrogen bonding and the miscibility of these binary polymer blends.

## Experimental

**Materials and Sample Preparation.** Poly(vinyl phenol) (PVPh) was purchased from Polysciences Inc. Reported molecular weight was $M_w=22{,}000$ g/mol. Poly(ethylene 2,6-naphthalate) (PEN), poly(trimethylene 2,6-naphthalate) (PTN), and poly(butylene 2,6-naphthalate) (PBN) were synthesized by two step melt polycondensation reactions. Dimethyl 2,6-naphthalate (DMN) was obtained from Samyang Inc. Reagent grade ethylene glycol (Mallinckrodt Co.), 1,3-propanediol (Acros Co.), and 1,4-butanediol (Junsei Chemical Co.) were purchased and used in the transesterification reactions without any further purification.

The blending was performed by dissolving component polymers in a mixture of phenol/tetrachloroethane (60/40,v/v). Blend samples for thermal analysis were prepared by co-precipitating the blend into excess amount of *n*-hexane from a solution of common solvent. Thin films of the blend samples for infrared spectroscopic studies were cast onto KBr windows from 1% (w/v) solutions and dried under vacuum at 120 °C for at least three days .

**Measurements.** Thermal analysis of the blends was performed using a Perkin-Elmer DSC-4 using heating rate of 20 °C/min. The glass transition temperature ($T_g$) was defined as the midpoint of the change in the specific heat and the crystalline melting temperature ($T_m$) was taken as the maximum of the melting endotherm.

Infrared spectra were obtained on Bruker 66v Fourier transform infrared (FTIR) spectrometer. A minimum of 64 scans of resolution of 2 $cm^{-1}$ were signal averaged and stored on a magnetic disk system. A Spectra Tech high temperature cell mounted in the spectrometer was used to obtain elevated temperature spectra.

## Results and Discussion

**PBN/PVPh Blends.** In our previous paper, we have reported that the binary blends composed of semi-crystalline PBN and amorphous PVPh are thermodynamically miscible based on the results of thermal analysis.[15] Since the $T_g$s of the component polymers were 81 °C apart (PBN. $T_m=$ 240 °C, $T_g=$ 70 °C and PVPh. $T_g=$ 151 °C), the criterion of a single composition dependent $T_g$ could be used to assess miscibility of the blend. For all blend compositions, the PBN/PVPh blends exhibited only a single $T_g$ intermediate between those of the pure constituents. The composition dependence of the $T_g$ of the blends indicates that the amorphous phases of the two polymers are miscible.

The crystalline melting behavior of a miscible blend with strong interactions is influenced by the miscible amorphous phase.[3] A significant crystalline melting point depression was observed for the PBN/PVPh blends. Crystallization of the PBN in the blends was also influenced by the presence of the amorphous PVPh. No crystallinity was detected by DSC for the blends containing more than 60 wt % of PVPh. Both results of the single $T_g$ and the depression of $T_m$ for PBN/PVPh blends indicate that the blends are thermodynamically miscible at the molecular level. Figure 1 shows the $T_g$ and $T_m$ as determined by DSC versus blend composition for PBN/PVPh blends. The thermodynamic melting temperatures for PBN and PBN/PVPh blends, were obtained by using Hoffman-Weeks plots,[16] ranging from 276 °C for PBN homopolymer to 255 °C for PBN/PVPh blend containing 60 wt% PBN, indicating a total 21 °C melting temperature depression. Using the Nish-Wang equation,[17] we derived the Flory interaction parameter, $\chi$, between PBN and PVPh. The depression of the thermodynamic melting temperature and the conclusion of negative $\chi$ values for PBN/PVPh blends were in agreement with the observed miscibility of this blend system.

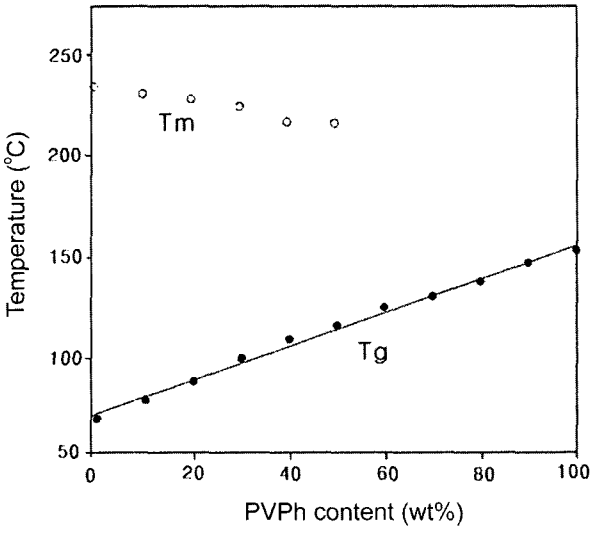


**Figure 1.** Thermal transition behavior of the PBN/PVPh blends: ( ● ) $T_g$ versus overall blend composition; ( ○ ) variation of crystalline melting temperature.

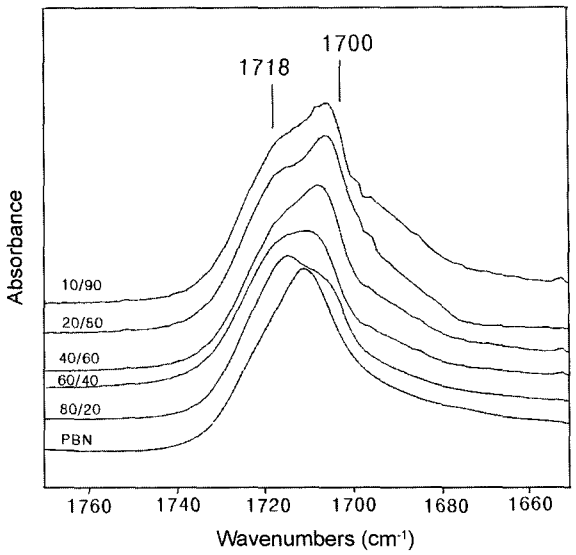


**Figure 3.** FTIR spectra in the C=O stretching vibration absorption region of the PBN/PVPh blends.

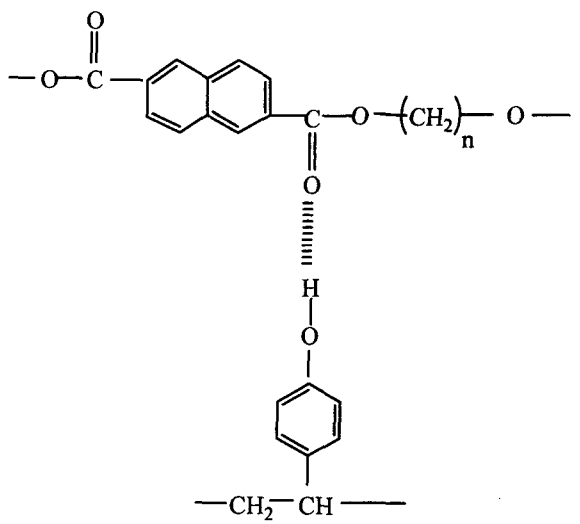

**Figure 2.** Proposed hydrogen bonding interaction occurred in poly(*n*-alkylene 2,6-naphthalate)/PVPh blends.

FTIR spectroscopy has been used to identify the specific intermolecular interactions occurred in PBN/PVPh blends. FTIR spectroscopic analysis confirmed that strong intermolecular hydrogen bonding interactions between the ester carbonyl groups of the PBN and the hydroxyl groups of the PVPh are occurred. Schematic representation of the potential favorable intermolecular hydrogen bonding interaction occurred in poly(*n*-alkylene 2,6-naphthalate)/PVPh blends is shown in Figure 2.

Figure 3 shows the FTIR spectra in the C=O stretching region (1770-1650 $cm^{-1}$) for PBN and PBN/PVPh blends with various blend composition recorded at room temperature. Only a few infrared spectroscopic studies of the semi-crystalline PBN have been reported.[18] It is well known that there exist two different crystal forms ($\alpha$- and $\beta$-forms) in a semi-crystalline PBN depending on the crystallization conditions.[18,19] In the present study, we focused only on the carbonyl absorption bands. The spectrum of the pure semi-crystalline PBN shows a dominant contribution from the crystalline (preferred conformation) band at 1710 $cm^{-1}$ which is attributable to the C=O groups in the $\beta$-form crystals and a relatively weak contribution from the C=O groups in both amorphous region and the $\alpha$-form crystals at 1718 $cm^{-1}$.[18] The amorphous band is characteristically broader than the crystalline band reflecting an increase in conformational freedom of the polymer chain in the amorphous phase. Further complexity may be introduced when a semi-crystalline polymer is blended with other polymers that are miscible with the semi-crystalline polymers. Indeed, significant spectral changes can be observed in the PBN/PVPh blends as the amorphous PVPh content in the blend increases. The IR spectra for the PBN/PVPh blends in the C=O stretching region show essentially more than three peaks that are mainly attributable to the free (non-hydrogen-bonded) C=O groups at 1718 $cm^{-1}$, the intermolecularly hydrogen-bonded C=O groups (to O-H groups) at 1700 $cm^{-1}$, and the PBN crystalline band at 1710 $cm^{-1}$. This figure qualitatively demonstrates that the amount of intermolecularly hydrogen bonded C=O groups of the PBN are increased as the PVPh composition of the PBN/PVPh blend increases.

Figure 4 shows scale expanded FTIR spectra of the 50/50 PBN/PVPh blend recorded at various temperatures over the

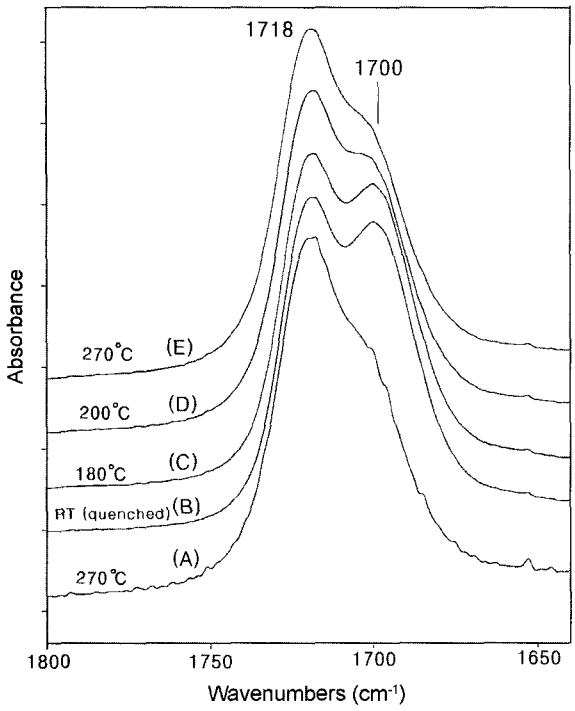


**Figure 4.** In-situ FTIR spectra in the 1600 ~ 1800 $cm^{-1}$ region for 50/50 wt% PBN/PVPh blend recorded as a function of temperature: (A) 270 °C; (B) room temperature quenched from 270 °C; (C) 180 °C; (D) 200 °C; (E) 270 °C.

range of 1640 to 1800 $cm^{-1}$. The first spectrum (Figure 4(A)) was recorded as the sample was first heated up to 270 °C (above the PBN crystalline melting temperature, if any), and then cooled to room temperature (Figure 4(B)). The rest of the spectra (Figure 4(C)-(E)) were recorded as a function of temperature as the sample was re-heated to 270 °C. As one might expect, the characteristic infrared band indicative of intermolecular hydrogen bonding between the ester carbonyl and phenolic hydroxyl groups are immediately apparent at 1700 $cm^{-1}$. This indicates that intermolecular interactions are occurring between the two polymers in this blend, which in turn suggests a significant degree of mixing has taken place. The effect of temperature up to 180 °C is not so dramatic. However, a measurable decrease in the intensity of the 1700 $cm^{-1}$ band is observed above 200 °C, which recovers when cooled to room temperature. This indicates that the intermolecular hydrogen bonds involved in PBN/PVPh blend system are thermally stable enough to retain a homogeneous phase in the limited temperature range covered.

**PEN/PVPh and PPN/PVPh Blends.** The same criterion of a single composition dependent $T_g$ used to assess the miscibility of PBN/PVPh blend was applied to both PEN/PVPh and PTN/PVPh blends. Both PEN and PTN are semi-crystalline polymers; PEN. $T_g$ = 127 °C, $T_m$ = 274 °C and PTN. $T_g$ = 78 °C, $T_m$ = 260 °C. Figure 5 shows the experimental DSC thermograms of a series of both PEN/PVPh and PTN/

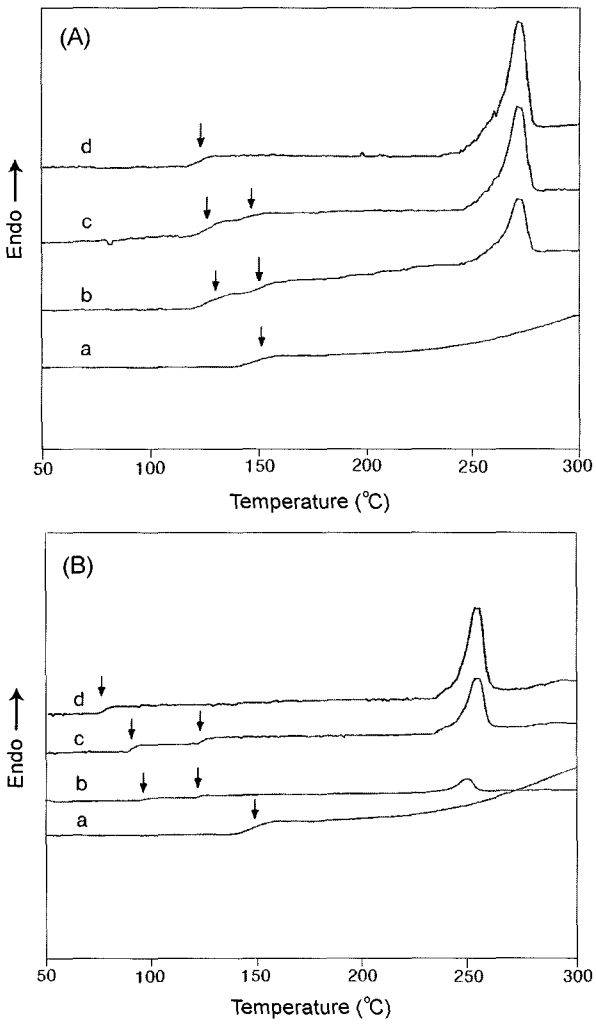


**Figure 5.** DSC thermograms of (A) PEN/PVPh and (B) PTN/PVPh blends: (a) PVPh; (b) 20/80; (c) 50/50; (d) 100/0 wt% blends.

PVPh blends (80/20, 50/50, and 20/80 wt%). In contrast to the results for the PBN/PVPh blends (Figure 1), each blend sample exhibits two distinctive $T_g$s corresponding to those of pure constituent polymers of the blend. These thermal analysis results indicate that both PEN/PVPh and PTN/PVPh blends are immiscible or partially miscible, which is in line with the infrared spectroscopic results for these blends described below.

Figure 6 shows the infrared spectra of a series of both PEN/PVPh and PTN/PVPh blends (80/20, 50/50, and 20/80 wt%) in the C=O region recorded at room temperature. In comparison with the spectra of the PBN/PVPh blends (Figure 3), it is immediately apparent that there are no analogous frequency shifts or broadening of the ester C=O bands for both PEN and PTN as the PVPh concentration in the blends increases. Both pure PEN and PTN spectra show a single, relatively broad symmetric C=O absorption band at

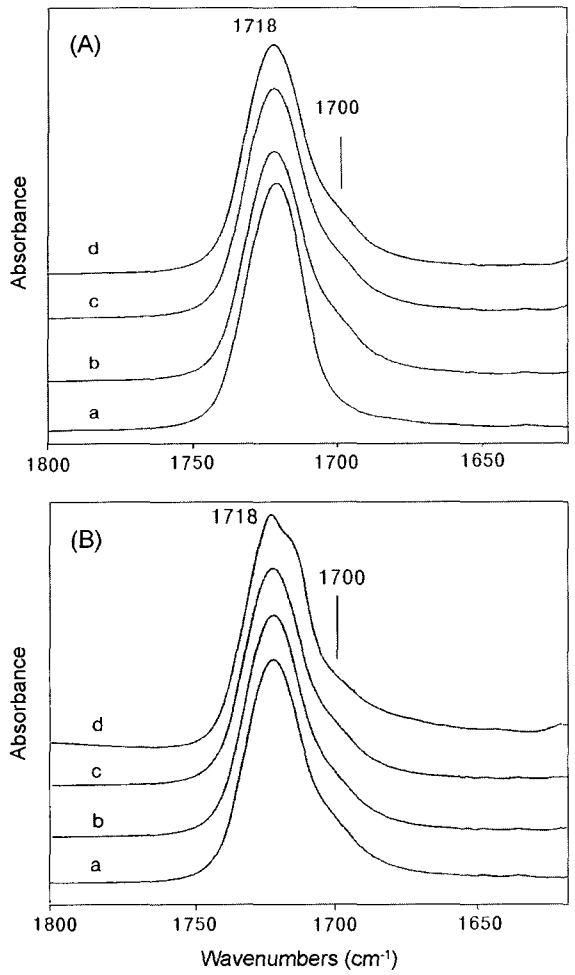


**Figure 6.** FTIR spectra in the 1600~1800 $cm^{-1}$ region for (A) PEN/PVPh and (B) PTN/PVPh blends: (a) 100/0; (b) 80/20; (c) 50/50; (d) 20/80 wt% blends.

1718 $cm^{-1}$ which is consistent with an amorphous material. In the blends with PVPh, a second band at 1700 $cm^{-1}$ is apparent that is attributable to the hydrogen bonded C=O band. Their relative intensities are weak for both PEN/PVPh and PTN/PVPh blends as compared to those for PBN/PVPh blends. However, this could imply some molecular mixing in these blends, but necessarily a single phase. More specifically, it can be said that the extent of intermolecular hydrogen bonding occurred in both PEN/PVPh and PTN/PVPh blends is not enough to drive these blends miscible at the molecular level. Also, it is well known that blend samples that are prepared by solvent casting often do not represent equilibrium structure due to varying solvent-polymer interactions among the blend constituents. Therefore, we may have caused phase separation as the solvents (a mixture of phenol/tetrachloroethane) evaporated (so-called $\Delta\chi$ effect)[20] and the blend samples may be in a non-equilibrium state frozen below the $T_g$s of the phases.

These preliminary DSC and FTIR results suggest that both PEN/PVPh and PTN/PVPh blends are immiscible or partially miscible, but PBN/PVPh blends are miscible over the entire blend composition. This of course raises the question of what makes such a difference in the degree of mixing in these blend systems. To address this question we considered the effect of the chain mobility of poly(*n*-alkylene 2,6-naphthalates) on their ester C=O functional group accessibility to form intermolecular hydrogen bonds to the PVPh hydroxyl groups.

It is widely accepted that the naphthyl rings in the analogous polyesters are coplanar with their attached ester C=O groups,[18,21] therefore the rigid naphthaloyl residues in a polymer chain are highly restricted in motion depending on the number *n* of methylene units in polyester chain structure. Horii *et al.*[21] and Mori *et al.*[22] have investigated on the segmental motions of aromatic polyesters containing terephthahloyl and naphthaloyl residues, respectively, using $^{13}C$ nuclear magnetic resonance spectroscopy. According to their results, butylene unit is more flexible than the ethylene unit in these aromatic polyesters so that the high chain mobility of PBN may give a faster crystallization rate,[22] and the butylene sequence may be the smallest unit of independent inner motions of the $CH_2$ sequence in these analogous aromatic polyesters.[21] This chemical structure difference should also give rise to the differences in the amount of intermolecular hydrogen bonding interactions when these aromatic polyesters are blended with PVPh. The ester C=O groups of both PEN and PTN can be thought of as dynamically restricted due to the limited mobility for the ethylene and trimethylene units that will not allow the facile orientation of the C=O groups to the PVPh hydroxyl groups. This limitation, in turn, may result in a blend that can not attain sufficient intermolecular interactions to create a miscible blend. However, the PBN ester C=O groups have more mobility due to the neighboring flexible butylene units, thus allowing them to reorient themselves in such a way that they are readily available for hydrogen bonding to the PVPh hydroxyl groups. Thus, it makes the differences in the degree of mixing in these blend systems. The chain mobility has a significant role in the formation of intermolecular hydrogen bonds in these polymer blends containing poly(*n*-alkylene 2,6-naphthalates), but there are many other factors that need to be considered.[23]

## Conclusions

FTIR and DSC studies of the PVPh blends with three poly(*n*-alkylene 2,6-naphthalates) have been described. PBN/PVPh blends were observed to be miscible over the entire range of blend compositions. FTIR spectroscopic analysis has confirmed that strong intermolecular hydrogen bonding interactions between the ester carbonyl groups of the PBN and the hydroxyl groups of the PVPh are occurred.

This is in marked contrast to the results for both PEN/PVPh and PTN/PVPh blend systems which were shown to be immiscible or partially miscible. Such a difference in degree of mixing in these blend systems has been described in terms of the interplay between the effect of the chain mobility of the poly(*n*-alkylene 2,6-naphthalates) and their ester carbonyl functional group accessibility to form intermolecular hydrogen bonds to phenolic hydroxyl groups, which in turn impacts on the phase behavior of these blend systems.

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