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Two-dimensional Near-infrared Correlation Spectroscopy Studies of Polymer Blends I: Composition-dependent Spectral Variations of Blends of Atactic Polystyrene and Poly[2,6-dimethyl-1,4-phenylene Ether]

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Abstract: Generalized two-dimensional (2D) near-infrared (NIR) correlation spectroscopy has been applied to study the conformational changes and molecular interactions in blends of atactic polystyrene (PS) and poly[2,6-dimethyl-1,4-phenylene ether] (PPE). NIR diffuse reflectance spectra have been measured for PS, PPE and their blends of different compositions, i.e., PS/PPE=90/10, 70/30, 50/50, 30/70, 10/90. The 2D synchronous correlation analysis of these composition-dependent NIR spectral variations separates the bands of PS from those of PPE. The 2D asynchronous analysis identifies spectral features indicative of the conformational changes or the specific interaction of PS and PPE. It can also detect "blend bands" whose origin is attributed to the formation of the polymer blends. Two "blend bands" of PS are identified at 6887 and 4836 cm^{-1}, and three "blend bands" of PPE are observed at 5752, 5679 and 4647 cm^{-1}. These "blend bands" are due to vibrations of the aromatic rings of PS or PPE and of the CH_3 of PPE. Thus, not only the aromatic rings of PS and PPE but also the CH_3 groups of PPE play important roles in the formation of the blends.

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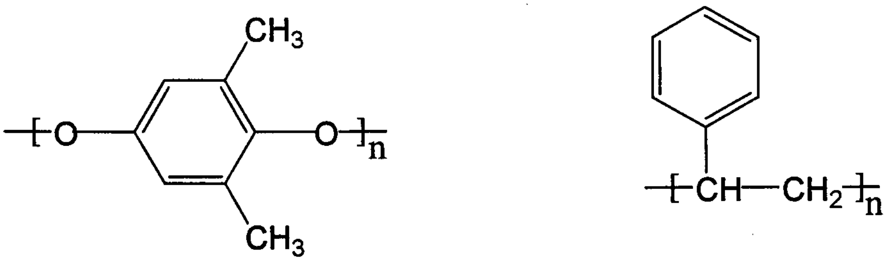
INTRODUCTION

The purpose of this paper is to demonstrate the potential of generalized two-dimensional (2D) near-infrared (NIR) correlation spectroscopy in studies of polymer blends (Refs. 1-3). NIR spectroscopy has been employed extensively for polymer research, from basic studies to industrial applications (Refs. 2-10). It has several advantages for studies of polymers over mid-IR spectroscopy. For example, NIR spectroscopy is particularly useful for the studies of inter- and intramolecular interactions including hydrogen bonds in polymers, because bands involved in the interactions are better separated in the NIR region. NIR spectroscopy can also be unique in permitting nondestructive analysis of polymers. However, spectral analysis in the NIR region is not always straightforward because a number of overtones and combination bands overlap with each other. Generalized 2D correlation spectroscopy, which enhances similarities and differences in the variations of individual spectral intensities, is powerful in analyzing the rather complicated NIR region (Ref. 1-3). The 2D correlation spectroscopy may be able to monitor "new bands" arising from the formation of polymer blends.

Extensive mid-IR and NIR spectroscopic studies on specific interactions in polymer blends have been reported (Ref. 11-14). However, the studies have been restricted mainly to hydrogen bonding interactions between the component polymers, which are believed to enhance the miscibility of the polymer blends (Ref. 11-14). The main reason for this comes from the idea that the interactions involving hydrogen bonds show clear spectral changes which may be studied easily by downward shifts of stretching vibration frequencies and upward shifts of deformation vibration frequencies. In contrast, the spectroscopic studies of the specific interactions in polymer blends without hydrogen bonding have rarely been reported. This may be due to the difficulty in identifying spectral symptoms for the interactions between the component polymers.

In the present study generalized 2D NIR correlation spectroscopy was applied to study the intermolecular interactions without hydrogen bonding in blends of atactic polystyrene (PS) and poly[2, 6-dimethyl-1, 4-phenylene ether] (PPE) (Fig. 1). PS and PPE are well known to be compatible without any miscibility enhancers (Ref. 15-19). Wellinghoff et al. (Ref. 19) claimed that the dispersion interaction between the phenyl ring of PS and the phenylene ring of PPE is responsible for the blend compatibility. They pointed out a change in the shape of an IR band of PPE at 856 cm^{-1} due to the aryl CH symmetric wag vibration as an evidence of this interaction. However, based upon NMR measurements of the blends, Djordjevic and Porter (Ref. 20) suggested that the interaction between the methyl groups of PPE and the phenyl ring of PS is responsible for the compatibility between PS and PPE. Therefore, there is a controversy about the origin of the compatibility.



PPE **PS**

Fig. 1 Structure of PS and PPE

In this paper we use 2D correlation spectroscopy to pick out "new bands" indicative of interactions in the blends from the highly overlapped NIR spectra. It was found that the interactions between PS and PPE not only change band shapes of some bands but also yield new bands. Generalized 2D correlation spectroscopy requires a series of perturbation-dependent spectra. In the present case these have been generated by varying the composition of the blends of PS and PPE. NIR diffuse reflectance spectra were measured for PS, PPE and their blends of five different compositions, i.e., PS/PPE=90/10, 70/30, 50/50, 30/70 and 10/90. The PS/PPE blends of different compositions have different mechanical behavior, implying different molecular environments and intermolecular interactions (Refs. 15-18).

EXPERIMENTAL SECTION

A high molecular weight atactic PS (M_w=240.000, M_n=528,000; Idemitsu Petrochemical Co., Ltd.) was mixed with additive-free PPE (Asahi Chemical Industry Co., Ltd.) at 280°C. PS was shown to be atactic by FT-IR and FT-Raman spectroscopy.

The NIR diffuse reflectance spectra were measured at a 2 nm resolution with a Bran+Luebbe Infralyser 500 spectrometer. PPE was obtained as powder, while PS and its blends with PPE were provided as pellets. In general, the baselines of diffuse reflectance NIR spectra depends strongly on the conditions and forms of the samples. In the present case the baseline of the NIR spectrum of PPE in the powder state is somewhat different from that of the spectra of the rest in the pellet form, so that the spectrum of PPE was excluded from the 2D correlation analysis. The reference spectrum used was that of PS. All the spectra employed in the 2D correlation analysis were normalized, and arranged in the following order: PS, SE91(90%PS plus 10%PPE), SE73(70%PS plus 30%PPE), SE55(50%PS plus 50%PPE), SE37(30%PS plus 70%PPE), SE19(10%PS plus 90%PPE). The program for the 2D correlation analysis named "2D Pocha" was composed by D. Adachi of our group (Kwansei Gakuin University). The one-dimensional reference spectra shown at the side and top of the 2D correlation maps are the average over the above spectra. In the 2D correlation maps unshaded regions always indicate positive correlation intensities, while shaded regions always indicate negative correlation intensities.

RESULTS AND DISCUSSION

Fig. 2 shows NIR diffuse reflectance spectra of PPE, SE19, SE37, SE55, SE73, SE91 and PS. It can be clearly seen that the spectrum of PPE is very different from the other six spectra. This is because PPE was provided as a powder, while the others were obtained as pellets. Most of bands in the 9000-8000 and 6100-5700 cm^{-1} regions are due to the second and first overtones of CH (aromatic and aliphatic) stretching modes. Bands in the 7600-6600 and 5600-4000 cm^{-1} regions are assigned to combination modes. More detailed band assignments will be discussed later (see Table I and II).

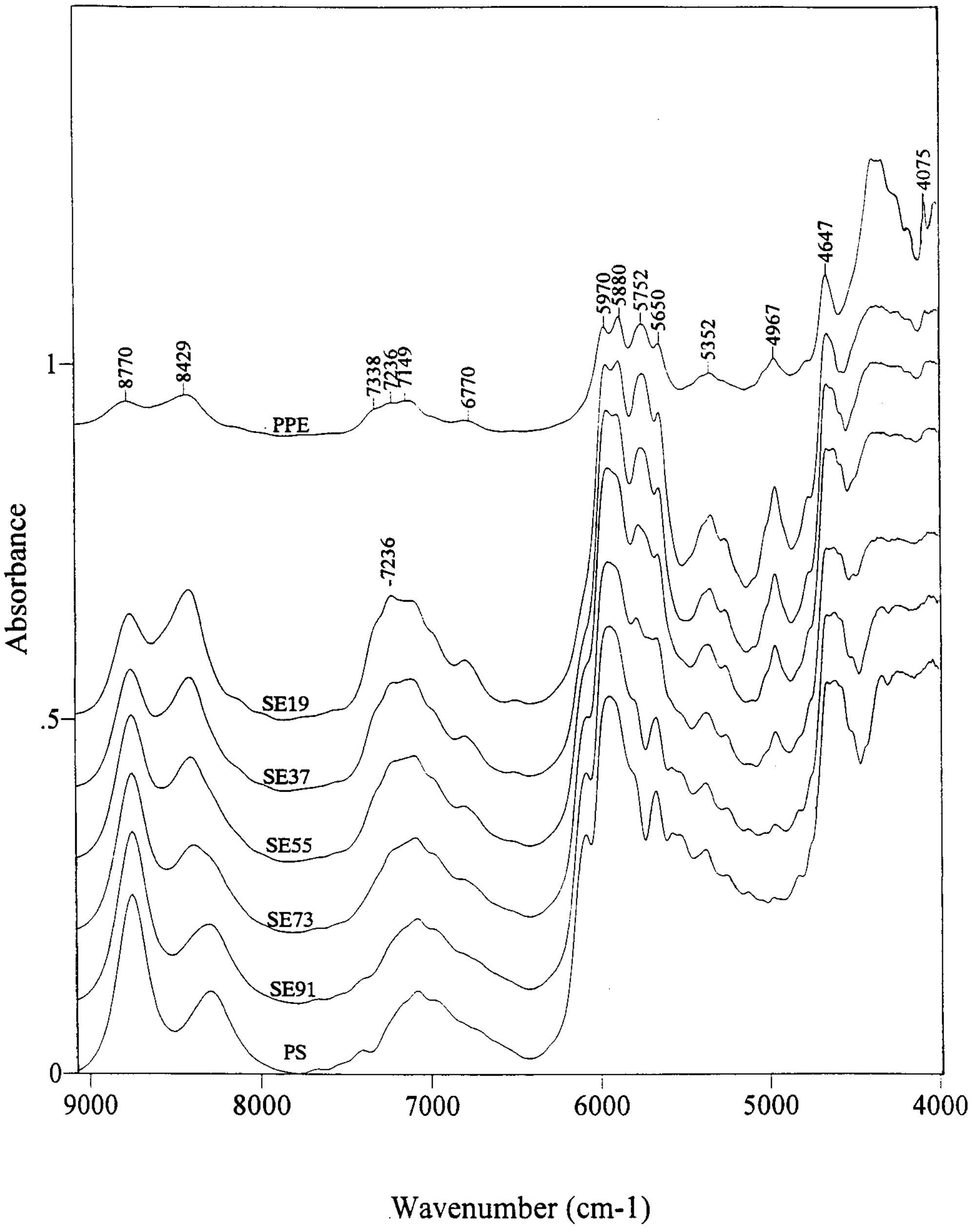


Fig. 2 Near-infrared diffuse reflectance spectra of PS, PPE and their blends of different compositions (PS/PPE=90/10, 70/30, 50/50, 30/70, 10/90)

Table I Bands assignable to PS in the diffuse reflectance NIR spectra of PS/PPE blends

Frequency (cm^{-1})	Assignments
8734	second overtone of aromatic C-H str.
8225	second overtone of CH_2 str.
7192	first overtone of CH_2 str.+CH_2 def.
7090	2×C-H str.+C-H in-plane bending (aromatic)
6887	2×C-H str.+C-H in-phase out-of-plane wag at 760 cm^{-1} (aromatic)
6625	first overtone of CH str.+C-H in-plane bending (aromatic)
6116	2×C-H str. (aromatic)
5519	C-H str.+first overtone of C-H in-plane bending (aromatic)
5127	C-H str.+first overtone of C-H in-plane bending (aromatic)
4836	aromatic C-H str.+ the summation band around 1800 cm^{-1}
4574	aromatic C-H str.+ aromatic ring str.
4254	C-H str.+C-H in-plane bending (aromatic)

Bands with an underline are assigned to "blend bands"
str = stretch

The bands observed in Fig. 2 can be classified into two categories; "normal bands" and "blend bands". "Normal bands" are those which are not directly involved in polymer-polymer interactions in the polymer blends, while "blend bands" are those which are directly involved in interactions within the polymer blends. The 2D NIR study of the blends of PS and PPE has a dual purpose. One is to separate the bands of PS from those of PPE in the spectra of the blends. Another is to detect "blend bands" symptomatic of the intermolecular interactions between PS and PPE in the blends in order to investigate the mechanism of blend formation.

Table II Bands assignable to PPE in the diffuse reflectance NIR spectra of PS/PPE blends

Frequency (cm^{-1})	Assignments
8792	second overtone of aromatic C-H str.
8429	second overtone of CH_3 str.
7338	first overtone of CH_3 str.+ CH_3 def.
7236	2×C-H str.+C-H in-plane bending (aromatic)
7149	2×C-H str.+C-H in-plane bending (aromatic)
6770	2×C-H str.+C-H in-plane bending (aromatic)
5970	first overtone of aromatic C-H str.
5869	first overtone of CH_3 str.
5752	first overtone of CH_3 str.
5679	first overtone of CH_3 str.
4967	C-H str.+first overtone of C-H in-plane bending (aromatic)
4647	aromatic C-H str.+the summation band at 1700 cm^{-1}
4443	aromatic C-H str.+C-H in-plane bending
4414	methyl C-H str.+aromatic C-H in-plane bending
4312	methyl C-H str.+methyl C-H bending

Bands with an underline are assigned to “blend bands”

Within the scope of the present study, synchronous 2D correlation spectra always have less features, and are easy to analyze. The intensities of the “normal bands” of PS are decreasing while those of PPE are increasing in the series of spectra of the blends. If we use Φ and Ψ to designate synchronous and asynchronous 2D correlation intensities between two wavenumbers, respectively, for “normal bands” we have the following relations

$\Phi[\upsilon(PS),\upsilon(PS)]>0$, $\Phi[\upsilon(PPE),\upsilon(PPE)]>0$, $\Phi[\upsilon(PS),\upsilon(PPE)]<0$, $\Phi[\upsilon(PPE),\upsilon(PS)]<0$.

Using these relations, we are able to ascribe bands in the highly overlapped spectra of the blends to PS or PPE.

The asynchronous correlation analysis can pick out bands that are indicative of the specific interaction between and the conformational change of PS and PPE in their blends. An asynchronous correlation peak $\Psi[\upsilon_1, \upsilon_2]$ appears only if the intensity change of two bands at υ_1 and υ_2 have essentially a dissimilar trend. In other words, the bands at υ_1 and υ_2 vary out-of-phase. In this paper the appearance of any asynchronous peak can only be ascribed to structural changes in the blends of PS/PPE. The composition change in the blends causes band intensity changes that are proportional to the mole fraction of the component polymer. Simple composition change alone can not give rise to asynchronous peaks between a PS band and a PPE band, between two PS bands, or between two PPE bands.

The sign of an asynchronous correlation peak $\Psi[\upsilon_1, \upsilon_2]$ gives information about the sequential order of intensity change between two bands at υ_1 and υ_2. According to Noda,[1] $\Phi[\upsilon_1, \upsilon_2]<0$ and $\Psi[\upsilon_1, \upsilon_2]>0$ imply that the intensity change at υ_1 occurs at higher PPE content compared to that at υ_2. $\Phi[\upsilon_1, \upsilon_2]>0$ and $\Psi[\upsilon_1, \upsilon_2]<0$. $\Phi[\upsilon_1, \upsilon_2]<0$ and $\Psi[\upsilon_1, \upsilon_2]<0$ imply that the intensity change at υ_1 takes place at lower PPE content than that at υ_2, as do $\Phi[\upsilon_1, \upsilon_2]>0$ and $\Psi[\upsilon_1, \upsilon_2]>0$. We shall use these relationships to determine the sequential order of intensity change between two bands.

The C-O-C asymmetric stretching band of PPE at 1188 cm^{-1} is very sensitive to the conformational change of PPE when blended with PS (Ref. 19), since the ether bond is along the main chain. Consequently, the NIR bands containing contributions from this band are expected to give rise to asynchronous peaks, and these asynchronous peaks will be ascribed to conformational changes of PPE. Similarly, the NIR bands containing contributions from methylene vibrations along the main chain of PS are expected to produce asynchronous peaks, which will be ascribed to conformational changes of PS.

An asynchronous peak $\Psi[\upsilon_1, \upsilon_2]$ will be considered as due to the specific interaction between PS and PPE in the following cases. Firstly, υ_1 and υ_2 represent bands from different components and vibrations of the aromatic rings of PS and PPE, since Wellinghoff et al. (Ref. 19) emphasized the interaction between the phenyl ring of PS and the phenylene ring of PPE. Secondly, υ_1 and υ_2 represent bands from different components and vibrations of the phenyl ring of PS and the methyl groups of PPE, since Djordjevic and Porter (Ref. 20) proposed the interaction between the methyl groups of PPE and the phenyl ring of PS.

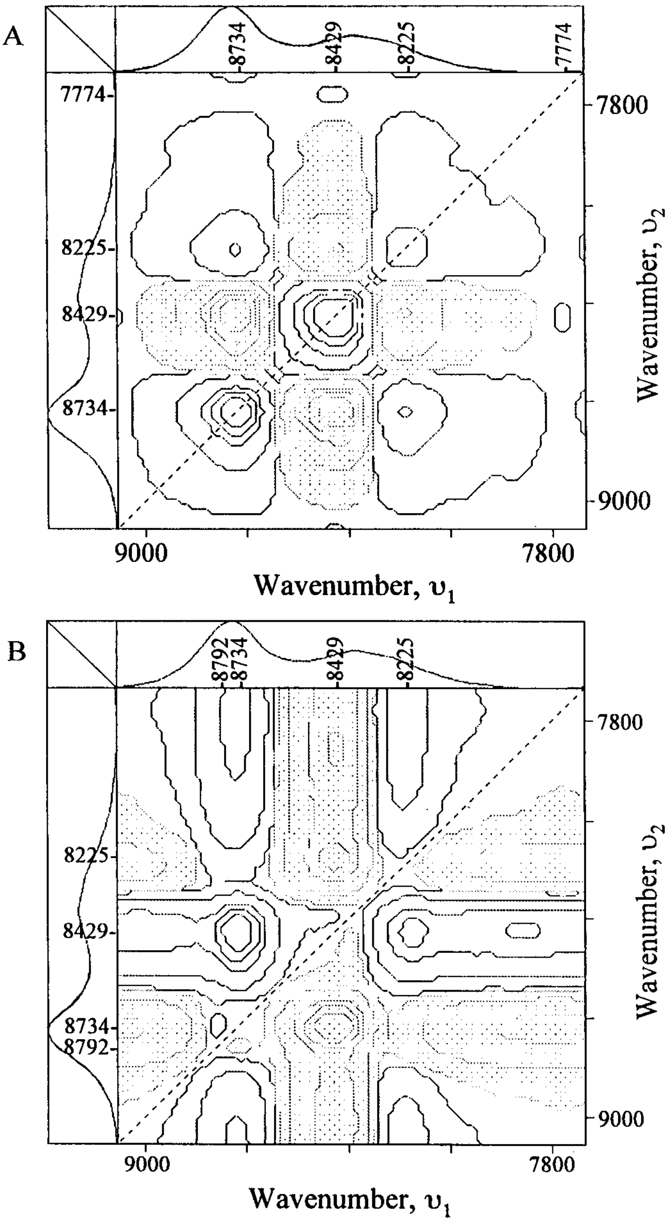


Fig. 3 Synchronous (A, top) and asynchronous (B, bottom) 2D NIR correlation spectra in the range of 9000-7700 cm^{-1}, constructed from composition-dependent spectral changes of five PS/PPE blends and PS

Fig. 3A shows the synchronous 2D NIR correlation spectrum in the region of 9000-7700 cm^{-1}, where the second overtones of CH (aromatic and aliphatic) stretching modes are expected to appear. The synchronous spectrum depicts three autopeaks and six major cross peaks. Judging from its frequency (Fig. 2), the peak at 8429 cm^{-1} probably corresponds to the second overtone of a methyl stretching mode of PPE (Refs. 4, 5, 7, 8). Therefore, the negative cross peaks at (8429, 8734) and (8429, 8225) indicate that bands at 8734 and 8225 cm^{-1} are due to PS.

The corresponding asynchronous spectrum shown in Fig. 3B develops three pairs of cross peaks, namely, (8429, 8225), (8429, 8734) and (8734, 8792). The asynchronous correlation peak at (8429, 8225) is indicative of the conformation change of PS, since the band at 8225 cm^{-1} arises from the methylene group along the main chain, as listed in Table I. According to the rule described above, the peaks at (8429, 8734) and (8734, 8792) are indicative of the specific interaction between PS and PPE, that is, both the aromatic rings of PS and PPE and the methyl groups of PPE are involved in the blend formation. The properties of these asynchronous peaks are listed in Table III.

Fig. 4A shows the synchronous 2D NIR correlation spectrum in the region of 7700-6400 cm^{-1}. Four auto peaks are clearly seen in the spectrum. The bands at 7338 and 7236 cm^{-1} in the average spectrum are mainly due to PPE (see Fig. 2A). Based on the signs of cross peaks, it can be concluded that bands at 6887 and 6625 cm^{-1} are due to PS, while a band at 6770 cm^{-1} is ascribed to PPE.

Six pairs of cross peaks, namely, (7192, 7149), (7090, 7149), (6625, 7338), (6887, 7236), (6887, 6770) and (6625, 6770) are observed in the asynchronous spectrum shown in Fig. 4B. The asynchronous peak at (7192, 7149) must come from the conformational change of PS, since the band at 7192 cm^{-1} is due to a combination of the first overtone of the methylene stretching mode with its deformation mode. The other cross peaks are indicative of the specific interaction.

Table III The signs of cross peaks in the synchronous and asynchronous 2D correlation maps, the property of the asynchronous peak.

Row	Φ (syn. int.)	Ψ (asyn. int.)	assignments	property[1]	order[2]
1	$\Phi(8429, 8225)<0$	$\Psi(8429, 8225)<0$	(PPE, PS)	C	before
2	$\Phi(8429, 8734)<0$	$\Psi(8429, 8734)<0$	(PPE, PS)	S	before
3	$\Phi(8792, 8734)>0$	$\Psi(8792, 8734)>0$	(PPE, PS)	S	before
4	$\Phi(7149, 7192)>0$	$\Psi(7149, 7192)>0$	(PPE. PS)	C	before
5	$\Phi(7149, 7090)>0$	$\Psi(7149, 7090)>0$	(PPE, PS)	S	before
6	$\Phi(7338, 6625)<0$	$\Psi(7338, 6625)<0$	(PPE, PS)	S	before
7	$\Phi(7236, 6625)<0$	$\Psi(7236, 6625)<0$	(PPE, PS)	S	before
8	$\Phi(6770, 6625)<0$	$\Psi(6770, 6625)<0$	(PPE, PS)	S	before
9	$\Phi(7236, 6887)<0$	$\Psi(7236, 6887)<0$	(PPE, PS)	S	before
10	$\Phi(6770, 6887)>0$	$\Psi(6770, 6887)<0$	(PPE, PS)	S	after
11	$\Phi(5752, 5127)<0$	$\Psi(5752, 5127)<0$	(PPE, PS)	S	before
12	$\Phi(5679, 5127)<0$	$\Psi(5679, 5127)>0$	(PPE, PS)	S	after
13	$\Phi(5752, 5519)<0$	$\Psi(5752, 5519)<0$	(PPE, PS)	S	before
14	$\Phi(5679, 5519)<0$	$\Psi(5679, 5519)>0$	(PPE, PS)	S	after
15	$\Phi(5752, 5970)<0$	$\Psi(5752, 5970)>0$	(PPE, PPE)	C	after
16	$\Phi(4967, 4414)>0$	$\Psi(4967, 4414)<0$	(PPE, PPE)	C	after
17	$\Phi(4967, 4647)<0$	$\Psi(4967, 4647)>0$	(PPE, PPE)	S	after
18	$\Phi(4967, 4254)>0$	$\Psi(4967, 4254)>0$	(PPE, PS)	S	before
19	$\Phi(4836, 4254)<0$	$\Psi(4836, 4254)<0$	(PS, PS)	S	before
20	$\Phi(4312, 4254)>0$	$\Psi(4312, 4254)>0$	(PPE, PS)	S	before

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[1] C: conformational change; S: specific interaction.

[2] After (before) means for the asynchronous peak at $\Psi(\upsilon_1, \upsilon_2)$ the intensity change of the band at υ_1 occurs at higher (lower) PPE contents than that at υ_2.

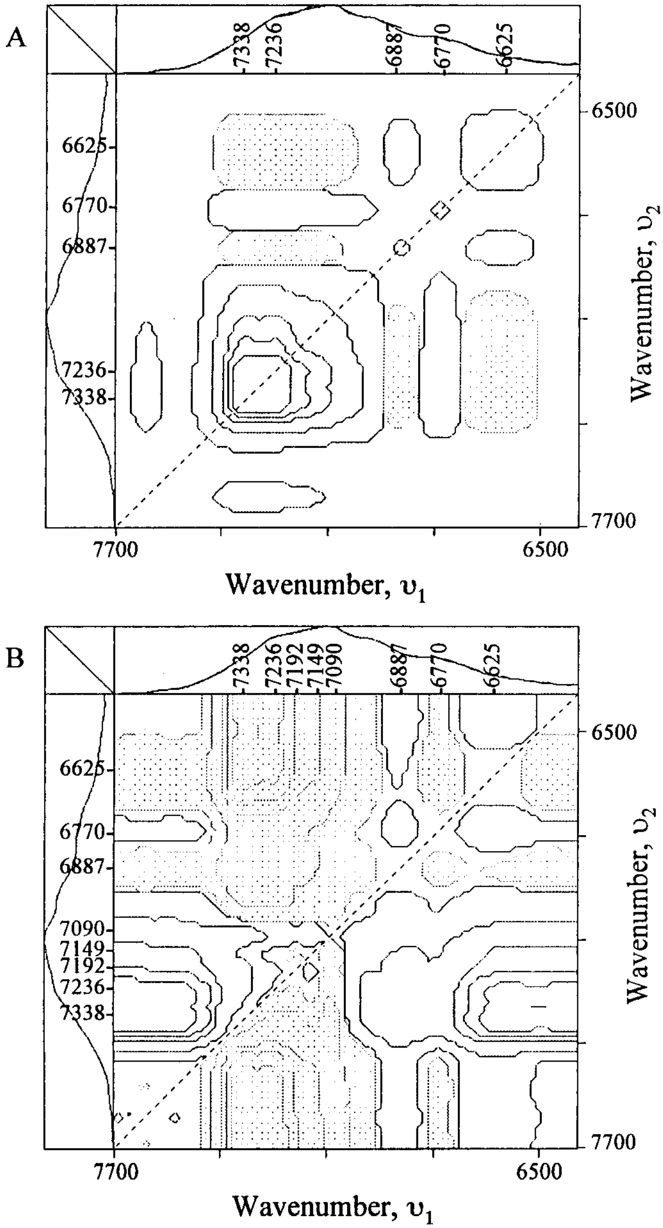

Fig. 4 Synchronous (A, top) and asynchronous (B, bottom) 2D NIR correlation spectra in the range of 7700-6400 cm^{-1}, constructed from composition-dependent spectral changes of five PS/PPE blends and PS

The 9th row of Table III shows that the event at 7236 cm^{-1} occurs before that at 6887 cm^{-1}, and the 10th row of Table III shows that the event at 6770 cm^{-1} occurs after that at 6887 cm^{-1}. From the 9th and 10th rows we would conclude that the event at 6770 cm^{-1} of PPE takes place after that at 7236 cm^{-1} of PPE. This feature is strange, since the bands at 6770 and 7236 cm^{-1} arise from similar modes of the PPE ring and can not vary asynchronously. The above reasoning has used the band at 6887 cm^{-1} as a mediator. Most probably, the band at 6887 cm^{-1} is a "blend band", whose origin is attributable to the blend formation. It is assigned to the combination of the first overtone of a band at 3061 cm^{-1} (aromatic C-H stretching) and a band at 760 cm^{-1} (Table I). The band at 760 cm^{-1} is known as being due to the aryl CH in-phase out-of-plane wag mode, where the five hydrogen atoms all move in the same direction and perpendicular to the ring plane. This mode is obviously sensitive to the face-to-face packing between the phenyl ring of PS and the phenylene ring of PPE.

The synchronous 2D NIR correlation spectrum in the 6400-5000 cm^{-1} region is presented in Fig. 5A. A band at 5752 cm^{-1} in the average spectrum is due to the first overtone of a methyl stretching mode of PPE. Based on the signs of cross peaks, it can be determined that bands at 6116, 5519, and 5127 cm^{-1} are assigned to PS while those at 5869 and 5636 cm^{-1} are due to PPE. Fig. 5B shows many pairs of cross peaks. The cross peaks at (5752, 5127), (5679, 5127), (5752, 5519) and (5679, 5519) are indicative of the specific interaction. Combining the 11th and 12th rows of Table III, we would conclude that the event at 5752 cm^{-1} occurs before that at 5679 cm^{-1}. They are due to the two methyl groups of PPE. Most probably, the two bands at 5752 cm^{-1} and 5679 cm^{-1} may be associated essentially independently with each of the two methyl groups. Thus, blending with PS gives rise to different chemical environment for the two CH_3 of PPE. The bands at 5752 and 5679cm^{-1} are then assigned to "blend bands". Combining the 13th and 14th rows of Table III, it is also concluded that these bands are "blend bands".

The asynchronous peak at (5752, 5970) in Fig. 5B between two PPE bands reflects the configuration change of PPE when blended with PS. The face-to-face packing between the aromatic rings of PS and PPE certainly influences the orientation of the two methyl groups substituted on the phenylene ring of PPE. The band at 5752 cm^{-1} arises from the CH_3 while the band at 5970 cm^{-1} from the phenylene ring.

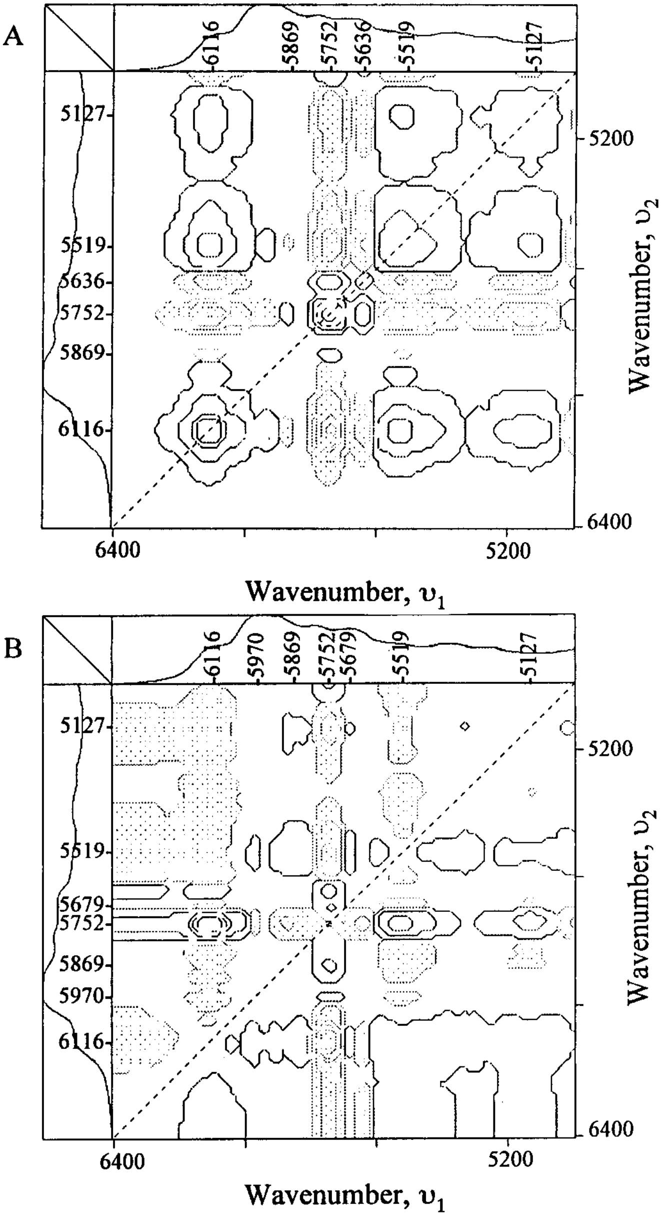

Fig. 5 Synchronous (A, top) and asynchronous (B, bottom) 2D NIR correlation spectra in the range of 6400-5000 cm^{-1}, constructed from composition-dependent spectral changes of five PS/PPE blends and PS

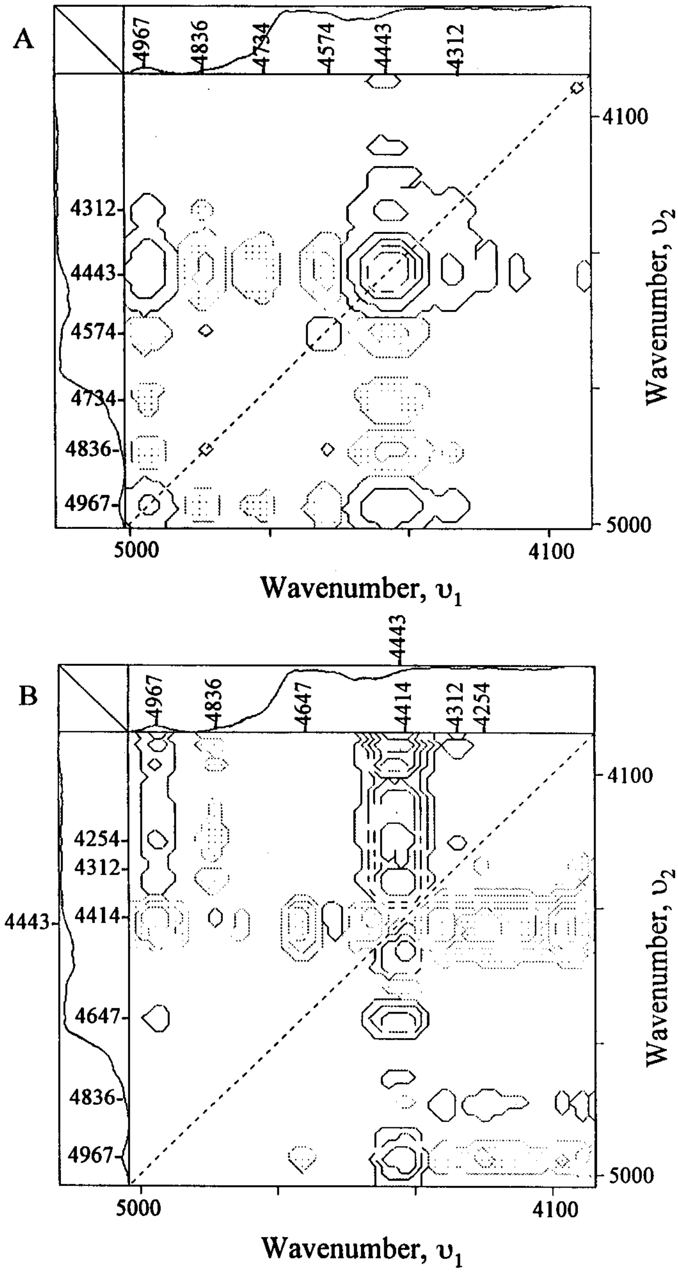

Fig. 6 Synchronous (A, top) and asynchronous (B, bottom) 2D NIR correlation spectra in the range of 5000-4000 cm^{-1}, constructed from composition-dependent spectral changes of five PS/PPE blends and PS

Fig. 6A shows the synchronous 2D NIR correlation spectrum in the region of 5000-4000 cm^{-1}. The 4967 cm^{-1} band in the average spectrum is certainly due to PPE (see Fig. 2). The signs of cross peaks between this band and other bands show that bands at 4836, 4734 and 4574 cm^{-1} are due to PS, while those at 4443 and 4312 cm^{-1} are ascribed to PPE.

Many pairs of cross peaks appear in the corresponding asynchronous spectrum (Fig. 6B). The cross peak at (4967, 4414) between two PPE bands reflects the conformational change of PPE, since the band at 4414 cm^{-1} contains contributions from both the methyl group and the phenylene ring. The cross peak at (4967, 4647) between two PPE bands of the phenylene ring is strange. Most probably, the band at 4647 cm^{-1} is a "blend band" of PPE. As shown in Table II, it contains contributions from the band at 1700 cm^{-1} characteristic of the tetra-substituted phenylene ring. The band at 1700 cm^{-1} is the first overtone of the CH in-phase out-of-plane wag mode at 856 cm^{-1} (Ref. 19). The band at 856 cm^{-1} has been used by Wellinghoff et al (Ref. 19) to identify the specific interaction between PS and PPE.

The cross peak at (4836, 4254) between two PS bands of the phenyl ring is also strange. The band at 4836 cm^{-1} may be a "blend band". As listed in Table I, it contains the aromatic summation band at 1800 cm^{-1}, which in turn contains some out-of-plane C-H vibrations. In addition, the asynchronous peaks at (4836, 4254) and (4312, 4254) both reflect the specific interaction in the blends.

CONCLUSION

2D NIR correlation analysis separates the bands of PS from those of PPE and detects several "blend bands". The asynchronous peaks have been ascribed to either the conformational changes or the specific interaction of PS and PPE. It seems that not only the phenyl rings of PPE and PS but also the CH_3 groups of PPE are responsible for the compatibility of the blends.

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