

Two-Dimensional Infrared Correlation Spectroscopy Studies of Polymer Blends: Conformational Changes and Specific Interactions in Blends of Atactic Polystyrene and Poly(2,6-dimethyl-1,4-phenylene ether)

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Infrared spectra have been measured for the cast films of atactic polystyrene (PS), poly(2,6-dimethyl-1,4-phenylene ether) (PPE), and their blends of different compositions: PS/PPE = 90/10, 70/30, 50/50, 30/70, 10/90. Composition-dependent spectral variations of the blends have been analyzed by generalized two-dimensional (2D) correlation spectroscopy to study the conformational changes and specific interactions in the blends. The IR spectra have been divided into two sets for the 2D correlation: set S of high PS content (PS/PPE = 100/0, 90/10, 70/30) and set E of high PPE contents (PS/PPE = 50/50, 30/70, 10/90). The 2D synchronous correlation analysis in the CH stretching region of 3130–2810 cm^{-1} discriminates between the bands of PS and those of PPE. The 2D asynchronous correlation analysis identifies band variations that may be involved in the miscible blend formation. The specific interaction between PS and PPE in the blends is reflected in the frequency shift of the aryl CH “in-phase” out-of-plane wagging modes of PS and PPE, as well as in the intensity change of the “ring bands” of PPE and PS and of the methyl band of PPE. Thus, not only the aromatic rings of PS and PPE but also the CH_3 groups of PPE seem to play important roles in the formation of the miscible blends. The optimal packing between PS and PPE requires that the PPE chains adopt the conformation A or B (marked by the asymmetric ether stretching bands at 1187 and 1176 cm^{-1} , respectively), and the PS chains exist in a highly ordered state (marked by the CH_2 asymmetric stretching band at 2909 cm^{-1}). This paper demonstrates the usefulness of 2D IR spectroscopy for exploring the intermolecular interactions other than hydrogen bonding in polymer blends.

Introduction

Generalized two-dimensional (2D) correlation spectroscopy,¹ which is an extension of the original 2D correlation spectroscopy proposed by Noda in 1986,^{2–4} has received considerable attention in recent years. This novel 2D method can handle spectral fluctuations as an arbitrary function of time or any other physical variables, such as temperature, pressure, concentration, and composition. Generalized 2D correlation spectra emphasize spectral features not readily observable in conventional one-dimensional spectra. It can also probe the specific order of certain spectral events taking place with the development of a controlling physical variable.

Many applications of generalized 2D correlation spectroscopy have been reported,^{5–20} including temperature-dependent spectral variations,^{10–16} concentration-dependent spectral changes,^{17,18} 2D IR and Raman heterospectral correlation analysis,¹⁹ and 2D near-infrared (NIR) and mid-infrared heterospectral correlation analysis.²⁰ In this paper we present a 2D infrared correlation spectroscopic study on polymer blends.

Vibrational spectroscopic studies on polymer blends have been largely restricted to those containing hydrogen bonds and

have mainly used infrared spectroscopy.^{21–24} Hydrogen bonds are often employed to enhance the miscibility in polymer blends,^{25,26} and infrared spectroscopy is powerful in investigating hydrogen bonds.²⁵ In contrast, vibrational spectroscopic studies on the specific interactions in polymer blends without hydrogen bonding have been less often reported. Wellinghoff et al.²⁷ reported an infrared study on the composition-induced band shape change of the symmetric CH out-of-plane wagging mode at 856 cm^{-1} of PPE in PS/PPE blends. The lack of vibrational literature about polymer blends without hydrogen bonds may be due to the difficulty in identifying spectral signatures for the specific interactions between the component polymers. Generalized 2D IR correlation spectroscopy, which identifies various intra- and intermolecular interactions through selective correlation of bands,¹ may be able to pick up the characteristic features for the specific interaction in polymer blends.

In the present study, generalized 2D IR correlation spectroscopy has been applied to explore the intermolecular interactions without hydrogen bonding in blends of atactic polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene ether) (PPE) (Scheme 1). PS and PPE are well-known to be compatible at the molecular level without any hydrogen-bonding-based miscibility enhancers.^{27–32} Wellinghoff et al.²⁷ claimed that the dispersion interaction between the phenyl ring of PS and the phenylene ring of PPE is responsible for the blend compatibility. It was reported that a change in the shape of an infrared band of PPE

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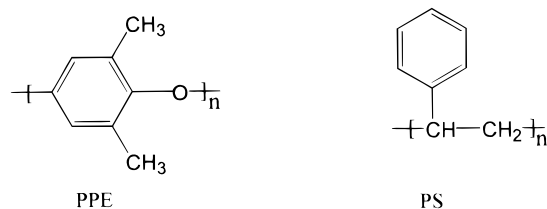
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SCHEME 1



at 856 cm^{-1} in PS/PPE blends is evidence for this interaction.²⁷ On the other hand, based upon NMR measurements of the blends, Djordjevic and Porter³² suggested that the specific interaction between the methyl groups of PPE and the phenyl ring of PS plays an important role in the compatibility between PS and PPE. Therefore, there is a controversy over the details of the interaction that seem to contribute to the compatibility of the blend system.

The feasibility of analyzing polymer blends using 2D correlation analysis has already been discussed in our previous paper.³³ We also reported 2D FT-Raman correlation studies on the composition-dependent spectral variations of PS/PPE blends.³⁴ In the latter paper³⁴ we introduced the idea of dividing the spectra of PS/PPE blends into two sets: one set with high PS content, another set with high PPE content. PS/PPE blends with high PS contents are known to have different mechanical properties and molecular environments in comparison to blends with high PPE content. The present 2D IR correlation analysis follows the previous Raman study, except that it uses thin cast films of the polymer blends. The IR spectra are also divided into two sets, set S with high PS contents and set E with high PPE contents.

Experimental Section

A high molecular weight atactic PS ($M_w = 240\,000$, $M_n = 112\,000$; Idemitsu Petrochemical Co., Ltd.) was mixed with additive-free PPE ($M_w = 36\,300$, $M_n = 13\,200$) in the desired portions in chloroform to form a blend solution. The blend solution of concentration about 1 wt % was kept in the dark for more than 1 week before casting. Then the blend solution was cast onto an aluminum plate and simply dried in air over 2 days. IR spectra were obtained for these simply dried films using a homemade film holder.

For fear of the existence of the last traces of solvent, the cast films were transferred onto Teflon plate and further dried at the glass transition temperature for 2 h under a nitrogen atmosphere. IR spectra were also obtained for these further dried films and compared with those of simply dried films. No significant spectral changes were observed.

The PS was proved to be atactic by both FT-IR and FT-Raman measurements.

The IR spectra of the PS/PPE blends were measured at a 2.0 cm^{-1} resolution and with 16 scans with a JASCO FT/IR-7300 spectrometer.

The spectra of PS and its blends with PPE were divided into two sets, as described in the Introduction. All the spectra employed in the 2D correlation analysis were normalized, with the integration in the whole spectral region equal to unity. The spectra in set S were arranged as PS \rightarrow SE91 (90% PS plus 10% PPE) \rightarrow SE73 (70% PS plus 30% PPE). Those in set E were arranged as SE55 (50% PS plus 50% PPE) \rightarrow SE37 (30% PS plus 70% PPE) \rightarrow SE19 (10% PS plus 90% PPE).

For the 2D correlation analysis we used a software named "2D Pocha", which was composed by Daisuke Adachi (Kwansei Gakuin University). The one-dimensional reference spectra

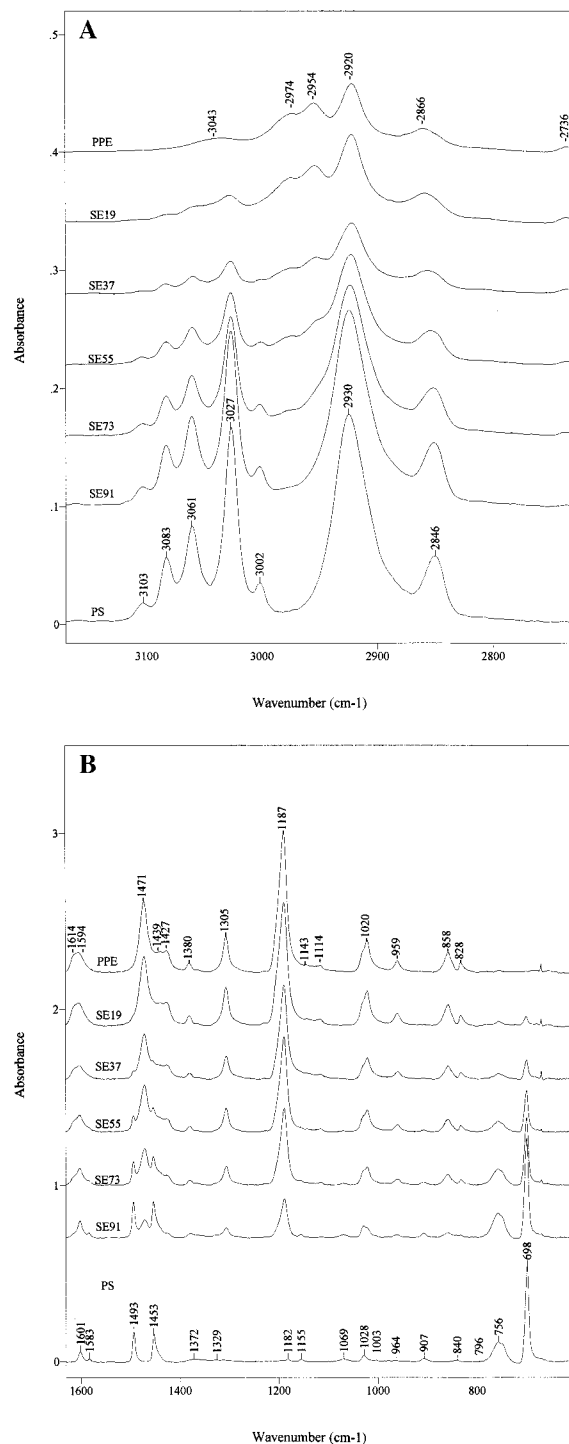


Figure 1. IR spectra in the region $3170\text{--}2700\text{ cm}^{-1}$ (A) and the region of $1630\text{--}600\text{ cm}^{-1}$ (B) of PS, PPE, and their blends of different compositions (PS/PPE = 90/10, 70/30, 50/50, 30/70, 10/90).

shown at the side and top of the 2D correlation maps are the average over three spectra in one set. In the 2D correlation maps shaded regions indicate negative correlation intensities, while unshaded regions indicate positive correlation intensities.

Results and Discussion

The IR spectra of PS, PPE, and their blends with different compositions are shown in Figure 1A,B for the regions of $3170\text{--}2700\text{ cm}^{-1}$ and $1630\text{--}600\text{ cm}^{-1}$, respectively. The bands of PS and PPE are assigned according to refs 35 and 36 and listed in Tables 1 and 2, respectively.

TABLE 1: Assignments of the Bands in the IR Spectrum of PS

frequency (cm ⁻¹)	intensity ^a	assignments (Wilson no.) ^b
3103	w	in-plane CH str (7b)
3083	m	in-plane CH str (20b)
3061	m	in-plane CH str (20a)
3027	s	in-plane CH str (2)
3002	w	in-plane CH str
2930	s	CH ₂ asymmetric str
2909	s	CH ₂ asymmetric str
2846	m	CH ₂ symmetric str
1601	m	ring str (8a)
1583	w	ring str (8b)
1543	vw	out-of-plane ring def at 698 cm ⁻¹ + out-of-plane CH def at 841 cm ⁻¹
1493	vs	ring str (19a)
1453	vs	CH ₂ bending
1372	w	CH ₂ wagging + methine CH def
1329	m	CH ₂ wagging + methine CH def
1182	w	in-plane CH def (9a)
1154	w	in-plane CH def (15)
1069	w	out-of-phase in-plane CH bending (18b)
1028	m	in-plane CH def (18a)
1003	w	in-plane ring def + in-phase ring def (12+5, 1)
981	w	out-of-phase out-of-plane CH wag (5)
964	w	out-of-phase out-of-plane CH wag (17a)
943	w	combination of out-of-plane ring def modes (4+16A)
907	m	out-of-phase out-of-plane CH wag (17b)
841	w	out-of-phase out-of-plane CH wag (10a)
756	s	in-phase out-of-plane CH wag (10b)
698	vs	out-of-plane ring def (11)
540	s	out-of-plane ring def (4)

^a Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak. ^b Key: def, deformation; str, stretching.

TABLE 2: Assignments of the Bands in the IR Spectrum of PPE^a

frequency (cm ⁻¹)	intensity	assignment (Wilson no.)
3043	w	in-plane CH asymmetric str
2974	m	in-plane CH symmetric str
2954	m	CH ₃ asymmetric str
2920	m	CH ₃ symmetric def due to Fermi Resonance
2866	m	CH ₃ symmetric str due to Fermi Resonance
1614	m	ring str (8a)
1594	m	ring str (8b)
1471	vs	ring str (19a)
1439	m	ring str (19b)
1427	m	CH ₃ asymmetric def
1380	w	CH ₃ symmetric def
1305	s	ring str (14)
1187	vs	asymmetric ether str
1143	w	in-plane CH def
1114	w	in-plane CH def (18b)
1020	s	in-plane CH def (18a)
959	m	in-plane CH wag
858	m	in-phase out-of-plane CH wag (17b)
828	m	out-of-phase out-of-plane CH wag (10a)

^a The phenylene ring of PPE is substituted at 1, 2, 4, and 6 sites and has C_{2v} symmetry.

1. Interaction Spectra of PS/PPE Blends. The specific interactions in polymer blends have long been studied in line with “interaction spectrum”.^{25,37} The interaction spectrum of a blend is obtained by subtracting the spectra of the component polymers in the pure form from the blend spectrum, thus representing only the net interaction between the component polymers. The concept of the interaction spectrum has been effective in studying the specific interactions in polymer blends with hydrogen bonds. In the present study, however, it is found

that the traditional approach of studying the interaction spectrum is not very effective for the PS/PPE blends.

2. Backgrounds for 2D Correlation Analysis of Polymer Blends. The 2D IR study of the blends of PS and PPE has dual goals. One is to separate the bands of PS from those of PPE in the spectra of the blends. Another is to study the specific interaction between PS and PPE in the blends. The first goal is realized by synchronous 2D correlation analysis of the IR spectra. The intensities of the bands of PS are decreasing while those of PPE are increasing for both set S and set E. Using Φ to designate synchronous 2D correlation intensities between two bands, we have the following relations

$$\begin{aligned}\Phi[v(\text{PS}), v(\text{PS})] &> 0, & \Phi[v(\text{PPE}), v(\text{PPE})] &> 0, \\ \Phi[v(\text{PS}), v(\text{PPE})] &< 0, & \text{and} & \Phi[v(\text{PPE}), v(\text{PS})] < 0\end{aligned}$$

On the basis of these relations, we are able to ascribe bands in the spectra of the blends to PS or PPE.

The second goal is realized by asynchronous 2D correlation analysis of the IR spectra. An asynchronous correlation peak $\Psi[v_1, v_2]$ appears only if the intensity change of two bands at v_1 and v_2 has basically dissimilar or uncoordinated trends. 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 weight percentage of the component polymer. Such simple proportional changes alone do not give rise to asynchronous peaks.

The sign of an asynchronous correlation peak $\Psi[v_1, v_2]$ gives information about the sequential order of intensity change between two bands at v_1 and v_2 . According to Noda,¹ $\Phi[v_1, v_2] < 0$ and $\Psi[v_1, v_2] > 0$ implies that the intensity change at v_1 occurs at higher PPE contents compared to that at v_2 . So does $\Phi[v_1, v_2] > 0$ and $\Psi[v_1, v_2] < 0$. $\Phi[v_1, v_2] < 0$ and $\Psi[v_1, v_2] < 0$ imply that the intensity change at v_1 takes place at lower PPE contents than that at v_2 . So do $\Phi[v_1, v_2] > 0$ and $\Psi[v_1, v_2] > 0$. In this paper we shall use these relationships to determine the sequential order of intensity change between two bands.

The following rule will be applied to identify whether an asynchronous peak $\Psi[v_1, v_2]$ comes from the conformation change of PS and PPE or the specific interaction between PS and PPE. If the order of intensity variation between the bands at v_1 and v_2 in set S is opposite to that in set E, then the bands at v_1 and v_2 can be regarded as indicative of the specific interaction between PS and PPE. Otherwise, the asynchronous peak $\Psi[v_1, v_2]$ is assumed to be indicative of the polymer conformation change. The specific interaction between PS and PPE is relatively weak in the blends of SE91 and SE19 and reaches the strongest when the PPE content is in the range 30–50%.^{27–31} With the increase in the PPE content from 0% to 90%, the spectral variations resulting from the specific interaction first increase and then decrease. This means that the sequential order between v_1 and v_2 has opposite trends for set S (from SE91 to SE73) and set E (from SE37 to SE19). If the intensity variation at v_1 occurs before (after) that at v_2 in set S, it will take place after (before) that at v_2 in set E.

3. CH Stretching Bands. Bands in the spectral region from 3130 to 2810 cm⁻¹ of PS and PPE are all due to aromatic and aliphatic CH stretching vibrations, as listed in Table 1. Figure 2 shows the synchronous correlation map of set S in this region. The band at 3027 cm⁻¹ certainly comes from PS, as seen from Figure 1A. The synchronous peaks at (3027, 3103), (3027, 3083), (3027, 3061), (3027, 2930), and (3027, 2846) are unshaded, indicating that the band at 3027 cm⁻¹ has positive

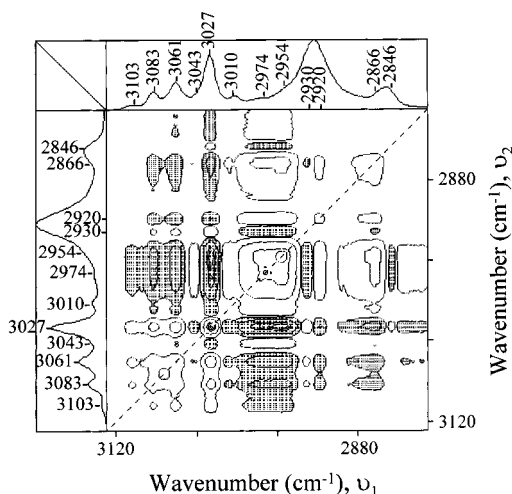


Figure 2. Synchronous 2D IR correlation spectrum in the range 3130–2810 cm^{-1} , constructed from the spectra of PS, SE91, and SE73 (set S).

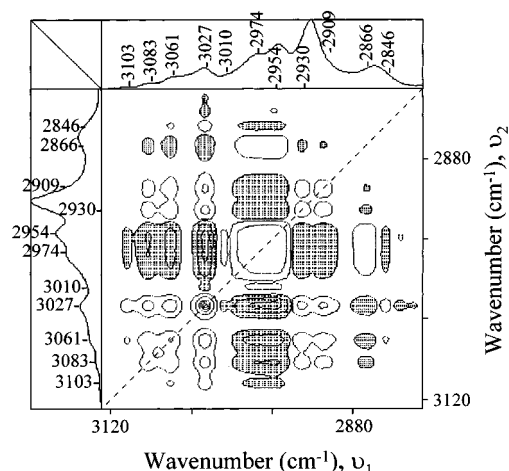


Figure 3. Synchronous 2D IR correlation spectrum in the range 3130–2810 cm^{-1} , constructed from the spectra of SE55, SE37, and SE19 (set E).

correlation intensities with the PS bands at 3103, 3083, 3061, 2930, and 2846 cm^{-1} . The synchronous peaks at (3027, 3043), (3027, 2974), (3027, 2954), (3027, 2920), and (3027, 2866) are shaded, indicating that the band at 3027 cm^{-1} has negative correlation intensities with the PPE bands at 3043, 2974, 2954, 2920, and 2866 cm^{-1} . The conclusions are consistent with the fact that the PS content decreases with the increase of the PPE content in the blends. The result clearly demonstrates that synchronous correlation analysis in the CH stretching region is powerful in separating bands of PS from those of PPE.

Figure 2 also detects a band at 3010 cm^{-1} that is not identifiable from the one-dimensional spectra of Figure 1. This band has negative synchronous correlation with the PS bands at 3083, 3061, and 3027 cm^{-1} , while positive correlation with the PPE bands at 2974, 2954, and 2866 cm^{-1} . It is thus ascribed to the aromatic CH stretching vibration of PPE.

The synchronous correlation map of set E in the region from 3130 to 2810 cm^{-1} is shown in Figure 3. It looks much like Figure 2 except for the band at 2909 cm^{-1} , which is absent in Figure 2. The band at 2909 cm^{-1} has a positive correlation with the PS bands at 3083, 3061, and 3027 cm^{-1} , and negative correlation with the PPE bands at 2974, 2954, and 2866 cm^{-1} . It is thus assignable to PS. Judging from its frequency, it must be due to the asymmetric stretching vibration mode of CH_2 along

the main chain. The band at 2909 cm^{-1} appears only for set E of low PS content, where most PS chains have the chance of interacting with PPE chains. Consequently, the band at 2909 cm^{-1} represents the chain conformation of PS in close contact with PPE chains. The band at 2930 cm^{-1} due to the asymmetric CH_2 stretching should represent the chain conformation of isolated PS domains in the blends. The favorable packing between PS and PPE chains shifts downward the asymmetric CH_2 stretching band by about 20 cm^{-1} .

The corresponding asynchronous maps (not shown) for set S and set E give cross-peaks that have minimal correlation intensity and poor signal-to-noise ratio. Therefore 2D correlation analysis in the CH stretching region is most suitable for detecting the coordinated intensity variations between two bands of the same component as well as between two bands due to different components; the 2D maps in this region are useful in separating PS bands from PPE bands in the blend spectra. This feature is the same as that obtained from 2D analysis of the diffuse reflectance near-infrared spectra of PS/PPE blends in pellets,³⁸ where we have concluded that the spectral regions of the first and second overtones of CH stretching vibrations (6200–5600 and 9000–8000 cm^{-1} , respectively) are most suitable for detecting the coordinated intensity variations between PS and PPE bands.

4. Ring Bands in the Region of 1630–1570 cm^{-1} . Bands in the spectral region from 1630 to 1570 cm^{-1} of PS and PPE are all due to aromatic ring C=C stretching vibrations, which are usually called “ring bands”.³⁵ The previous 2D FT-Raman studies³⁴ reveal that the “ring bands” are useful in detecting the strong specific interaction between PS and PPE. Unlike the aryl CH in-plane or out-of-plane vibrations, these “ring bands” are not prone to be influenced by weak intermolecular interactions. Figure 4A shows the synchronous correlation map of set S in this region. It is noticed that all cross-peaks are positive, implying that the bands at 1614, 1594, and 1575 cm^{-1} are all due to the same component. The 2D FT-Raman studies³⁴ confirm the tetra-substituted phenylene ring of PPE has two bands at 1614 and 1594 cm^{-1} . Therefore, the bands at 1614, 1594, and 1575 cm^{-1} should be all due to PPE.

The synchronous correlation map of set E in this region (Figure 5A) gives positive cross-peaks at (1614, 1594) and (1601, 1583), consistent with the assignment included in Tables 1 and 2. The pair of bands at 1601 and 1583 cm^{-1} comprises a feature of monosubstituted aromatic rings.

The asynchronous maps of set S and set E in the “ring bands” region give cross-peaks that have opposite signs, as can be seen by comparing Figure 4B with Figure 5B. The order of intensity variation between two bands of set S and set E is listed in Tables 3 and 4, respectively. The first rows of Tables 3 and 4 show that the event at 1614 cm^{-1} takes place before and after that at 1601 cm^{-1} in set S and set E, respectively. Thus, the asynchronous peak at (1614, 1601) in Figures 4B and 5B should arise from the specific interaction that may be responsible for the blend compatibility. The same conclusion is also reached for the asynchronous peak at (1594, 1601) by comparison of the second rows of Tables 3 and 4. Consequently, the “ring bands” at 1614 and 1594 cm^{-1} of PPE and at 1601 cm^{-1} of PS are indicative of the specific interaction between PS and PPE. The phenylene ring of PPE and the phenyl ring of PS seem to be involved in the miscible blend formation. The conclusion is the same as that proposed by Wellingshoff et al.²⁷

However, the third rows of Tables 3 and 4 show that the order of occurrence for the events at 1614 and 1583 cm^{-1} is the same for both set S and set E. The asynchronous peak at

TABLE 3: Synchronous and Asynchronous 2D Correlation Intensities and the Order of Intensity Variations between Two Bands of Set S

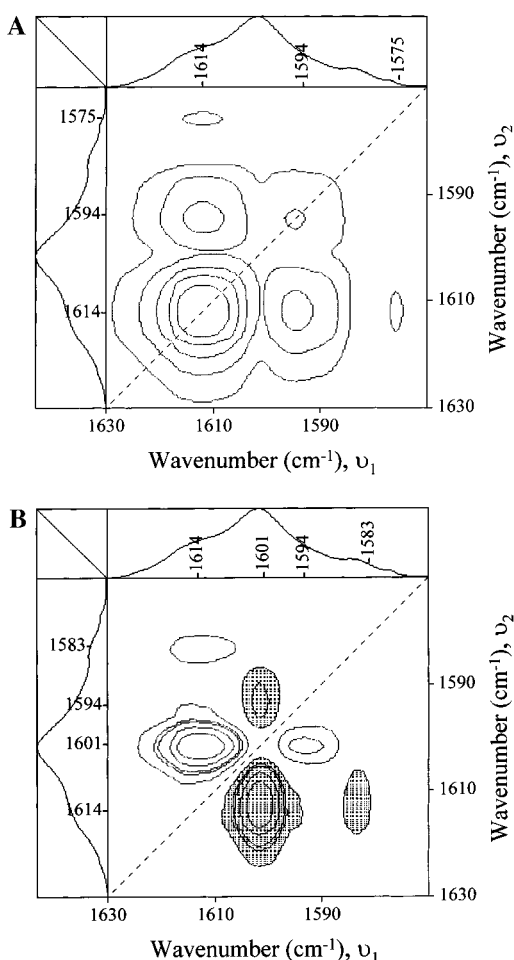
no.	Φ	Ψ	assignment	order ^a
1	$\Phi(1614, 1601) > 0$	$\Psi(1614, 1601) > 0$	(PPE, PS)	1614 before 1601 cm ⁻¹
2	$\Phi(1594, 1601) > 0$	$\Psi(1594, 1601) > 0$	(PPE, PS)	1594 before 1601 cm ⁻¹
3	$\Phi(1614, 1583) > 0$	$\Psi(1614, 1583) > 0$	(PPE, PS)	1614 before 1583 cm ⁻¹
4	$\Phi(1493, 1427) < 0$	$\Psi(1493, 1427) < 0$	(PS, PPE)	1493 before 1427 cm ⁻¹
5	$\Phi(1187, 1176) > 0$	$\Psi(1187, 1176) < 0$	(PPE, PPE)	1187 after 1176 cm ⁻¹

^a v_1 after (before) v_2 means the intensity change of the band at v_1 occurs at higher (lower) PPE contents than that at v_2 .

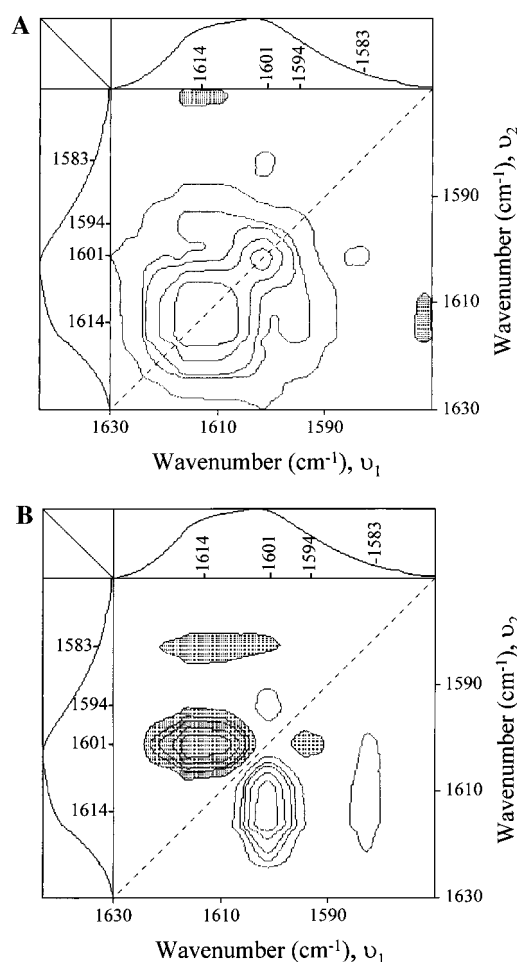
TABLE 4: Synchronous and Asynchronous 2D Correlation Intensities and the Order of Intensity Variations between Two Bands of Set E

no.	Φ	Ψ	assignment	order ^a
1	$\Phi(1614, 1601) > 0$	$\Psi(1614, 1601) < 0$	(PPE, PS)	1614 after 1601 cm ⁻¹
2	$\Phi(1594, 1601) > 0$	$\Psi(1594, 1601) < 0$	(PPE, PS)	1594 after 1601 cm ⁻¹
3	$\Phi(1614, 1583) < 0$	$\Psi(1614, 1583) < 0$	(PPE, PS)	1614 before 1583 cm ⁻¹
4	$\Phi(1493, 1427) < 0$	$\Psi(1493, 1427) > 0$	(PS, PPE)	1493 after 1427 cm ⁻¹
5	$\Phi(1187, 1176) < 0$	$\Psi(1187, 1176) < 0$	(PPE, PPE)	1187 before 1176 cm ⁻¹

^a v_1 after (before) v_2 means the intensity change of the band at v_1 occurs at higher (lower) PPE contents than that at v_2 .

**Figure 4.** Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1630–1570 cm⁻¹, constructed from the spectra of PS, SE91, and SE73 (set S).

(1614, 1583) in Figures 4B and 5B is not indicative of the specific interaction. The band at 1583 cm⁻¹ is known as a unique feature of monosubstituted aromatic rings. Therefore, the monosubstitution of the phenyl ring of PS may not be a prerequisite for the blend compatibility. In other words, polysubstituted phenyl rings may also be compatible with PPE. The intensity variation of the band at 1583 cm⁻¹ may represent a persistent conformational change of PS in the blends for PPE contents from zero to 90%.

**Figure 5.** Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1630–1570 cm⁻¹, constructed from the spectra of SE55, SE37, and SE19 (set E).

As a summary, 2D correlation in the spectral region of aromatic C=C stretching vibrations is useful in detecting the specific interaction in PS/PPE blends, but not suitable for separating PS bands from PPE bands.

5. Ring Bands in the Region of 1510–1400 cm⁻¹. The aromatic bands in this region are also “ring bands”. However, methyl and methylene bending vibrations contribute to this spectral region significantly. The synchronous correlation map of set S in this region gives well-coordinated intensity variations

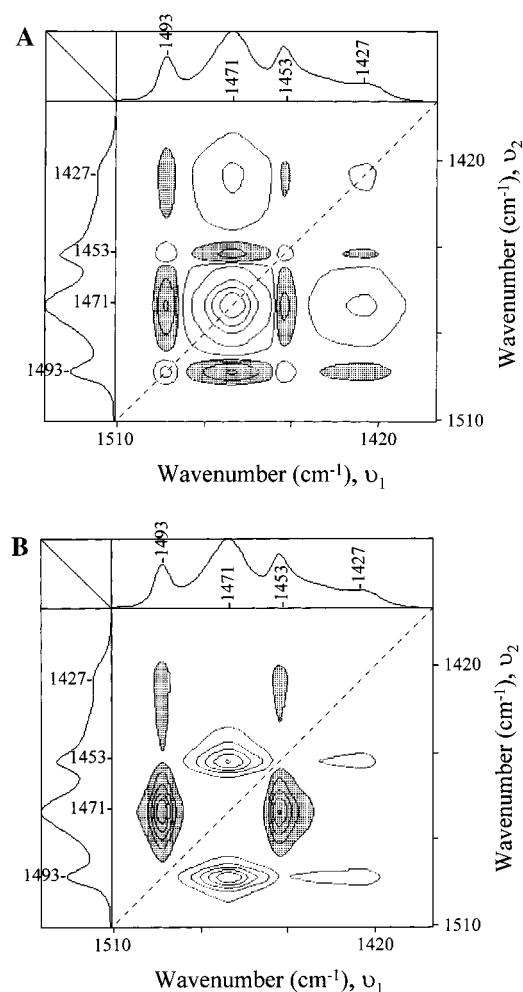


Figure 6. Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1510–1400 cm^{-1} , constructed from the spectra of PS, SE91, and SE73 (set S).

between PS bands and PPE bands, as shown in Figure 6A. The signs of all cross-peaks reflect the assignment that bands at 1493 and 1453 cm^{-1} are due to PS, while bands at 1471 and 1427 cm^{-1} are from PPE. The synchronous correlation map (Figure 7A) of set E in the same region also gives well-coordinated intensity variations between PS bands and PPE bands. The bands at 1480 and 1464 cm^{-1} must arise from PPE, since they have a negative correlation with the PS bands at 1493 and 1453 cm^{-1} and positive correlation with the PPE band at 1427 cm^{-1} . Comparing Figure 6A with Figure 7A, it is evident that the bands at 1480 and 1464 cm^{-1} of set E are due to splitting of the band at 1471 cm^{-1} of set S. Most probably, this splitting results from the partial crystallization of PPE, when the PPE content is high in the blends.²⁷

Comparing the asynchronous correlation maps of set S (Figure 6B) and set E (Figure 7B) in this spectral region, it is seen that the cross-peak at (1493, 1427) has opposite signs in the two sets. The fourth rows of Tables 3 and 4 reveal that the order of occurrence of the events at 1493 and 1427 cm^{-1} has opposite trends from set S to set E. Consequently, the “ring band” of PS at 1493 cm^{-1} and the methyl band of PPE at 1427 cm^{-1} must be indicative of the specific interaction between PS and PPE at the molecular level. In other words, the rings of PS and the methyl groups of PPE seem to be responsible for the blend compatibility. This feature is consistent with that claimed by Djordjevic and Porter.³²

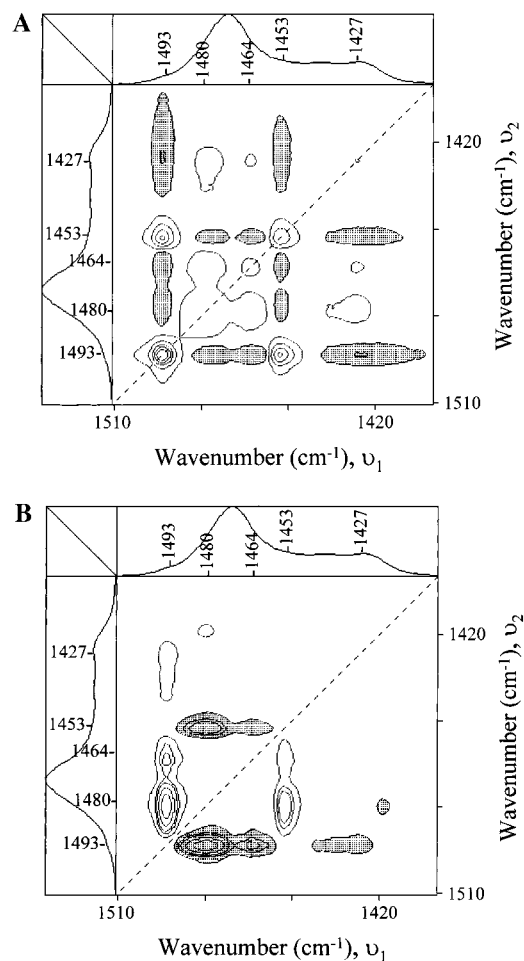


Figure 7. Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1510–1400 cm^{-1} , constructed from the spectra of SE55, SE37, and SE19 (set E).

As a summary, the region of 1510–1400 cm^{-1} is useful both in separating PS bands from PPE bands and in identifying spectral symptoms of the specific interaction in PS/PPE blends.

6. Ether Band around 1200 cm^{-1} . The asymmetric ether stretching band of PPE around 1200 cm^{-1} is very intense, while bands due to PS contribute little to the region 1220–1170 cm^{-1} . It is reasonable to attribute to PPE all bands from 1220 to 1170 cm^{-1} picked by 2D analysis. The ether bond of PPE mainly has three conformations (Scheme 2): C, A, and B, where the phenylene ring is in conjugation with two, one, and no neighbor rings, respectively.²⁷ The maximum conjugation between two rings occurs through the central oxygen when the two rings are coplanar with the central C–O–C plane. Conformation A of moderate conjugation is the most possible for PPE. The infrared frequency of the asymmetric ether stretching band is the highest for conformation C and the lowest for conformation B. The synchronous correlation map in Figure 8A of set S in this frequency region gives only one auto-peak at 1187 cm^{-1} , which is assigned to the conformation A.

The asynchronous maps of set S and set E in Figures 8B and 9B depict two cross-peaks at (1187, 1176) of opposite signs. The fifth rows of Tables 3 and 4 show that the order of events at 1187 and 1176 cm^{-1} has opposite trends from set S to set E. The bands at 1187 and 1176 cm^{-1} may be involved in the blend formation. The band at 1176 cm^{-1} has the lowest frequency among all the ether bands picked by 2D analysis and is ascribed to the conformation B. Consequently, conformations A and B are both present in the compatible blends of PS and PPE. This

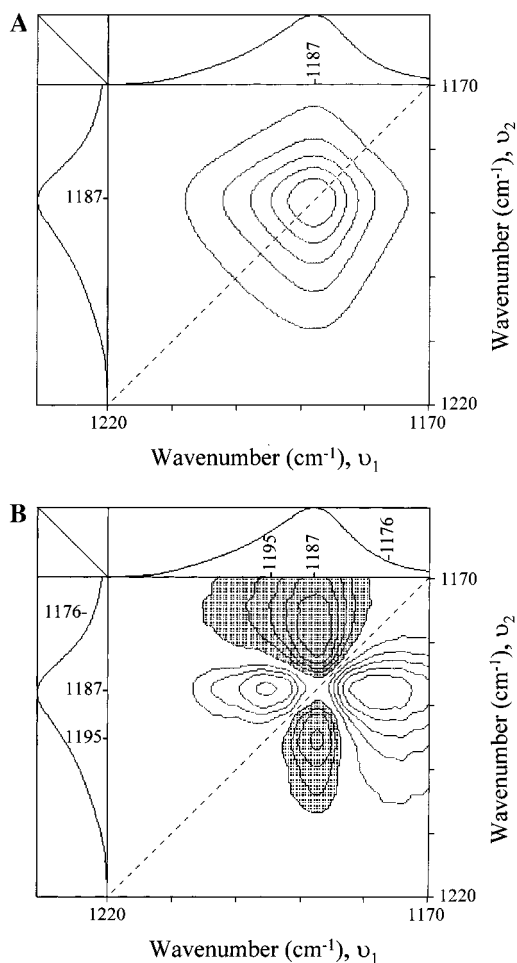
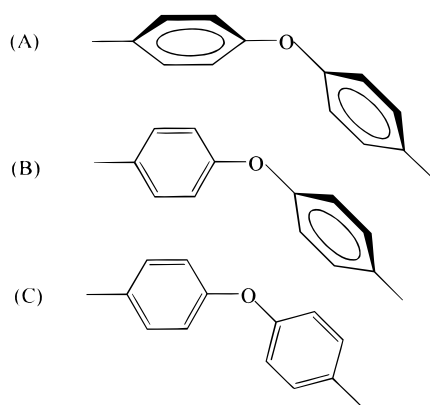


Figure 8. Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1220–1170 cm^{-1} , constructed from the spectra of PS, SE91, and SE73 (set S).

SCHEME 2



conclusion is in sharp contrast to the claim by Wellinghoff et al.²⁷ that the completely unconjugated B structure is not attainable in the blends. They studied the cast films of PS/PPE blends of different compositions using conventional one-dimensional infrared spectroscopy but did not detect spectral features below 1186 cm^{-1} . We have studied the cast films using the high-resolution two-dimensional spectroscopy and identified the band at 1176 cm^{-1} .

Comparing Figure 8B with Figure 9B, it seems that the band at 1195 cm^{-1} of set S moves to 1205 and 1199 cm^{-1} for set E. Shift of the ether band to higher frequencies in set E implies that the self-packing of PPE chains favors a higher conjugation between adjacent phenylene rings. Set S has low PPE contents,

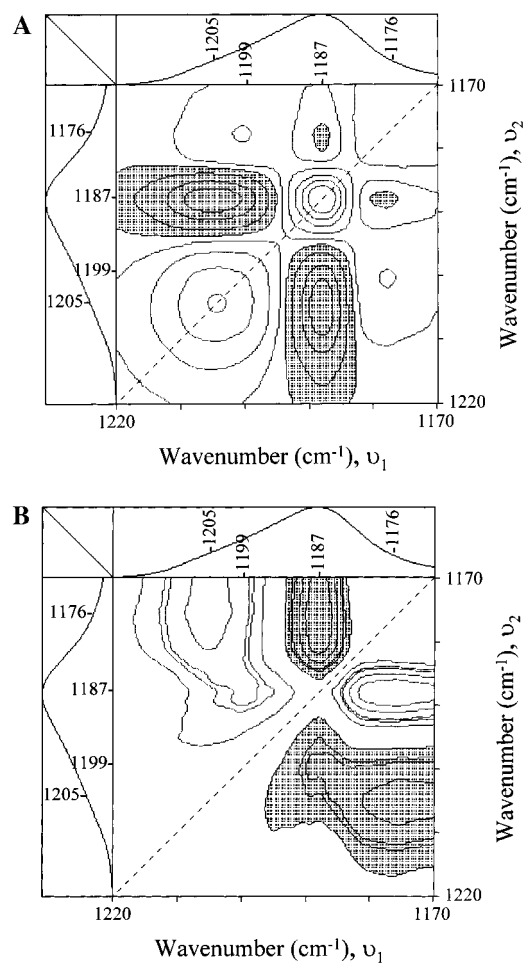


Figure 9. Synchronous (A) and asynchronous (B) 2D IR correlation spectra in the range 1220–1170 cm^{-1} , constructed from the spectra of SE55, SE37, and SE19 (set E).

and most PPE segments can achieve close contact with PS chains. Set E contains the blends SE19 and SE37 of high PPE content, for which some PPE segments have to pack by themselves, as would result in a partial crystallization. Wellinghoff et al.²⁷ observed an increase in the high-frequency shoulder of the ether band with the increase of the partial crystallinity in PPE. The band at 1205 cm^{-1} has the highest frequency and is ascribed to the conformation C, while the bands at 1199 and 1195 cm^{-1} are ascribed to the conformations somewhere between C and A. In other words the average angle between the phenylene ring plane and the C–O–C plane is perfectly zero for the conformation represented by the band at 1205 cm^{-1} , while in the range 0–45° for the conformation represented by the bands at 1199 and 1195 cm^{-1} . In Figure 9A the cross-peak at (1205, 1187) is negative, indicating that the increase of PPE segments existing in conformation C has occurred at the expense of those in conformation A.

In summary, 2D correlation analysis in the asymmetric ether stretching region reveals that favorable packing between PS and PPE requires that the PPE chain have the conformation A or B, i.e., high angles between the phenylene ring plane and the C–O–C plane. The packing between PPE segments favors the conformation C. The interaction between the phenyl ring of PS and the phenylene ring of PPE in the blends has taken place of the conjugation between the phenylene rings of PPE.

7. Aryl In-Phase CH Wag Band. The in-phase out-of-plane wagging mode of the monosubstituted phenyl ring of PS is located at 756 cm^{-1} , while that of the tetrasubstituted phenylene

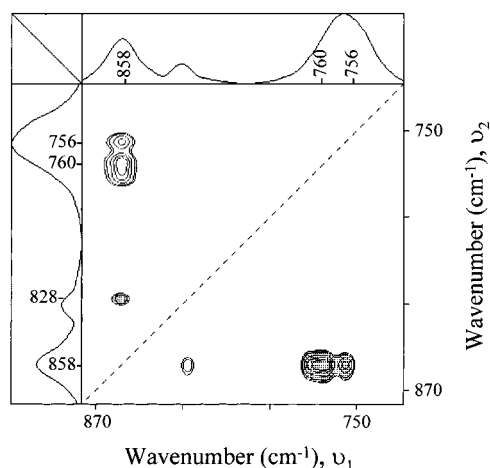


Figure 10. Asynchronous 2D IR correlation spectra in the range 880–730 cm^{-1} , constructed from the spectra of PS, SE91, and SE73 (set S).

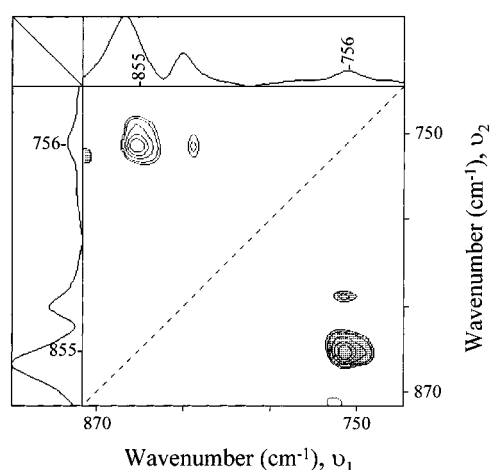


Figure 11. Asynchronous 2D IR correlation spectra in the range 880–730 cm^{-1} , constructed from the spectra of SE55, SE37, and SE19 (set E).

ring of PPE occurs at 858 cm^{-1} .³⁵ Here, “in-phase” means all the hydrogen atoms move in the same direction. Wellinghoff et al.²⁷ claimed that the band shape change at 858 cm^{-1} with the PPE composition in the blends is indicative of the specific interaction in the blends. The face-to-face packing of the aromatic rings of PS and PPE can result in a systematic frequency shift of the “in-phase” bands of both PS and PPE. While Wellinghoff et al.’s conclusion was drawn by one-dimensional observation of the band shape change, the high-resolution 2D analysis is able to resolve closely located bands embedded under the band shape change.

The asynchronous relationship between the “in-phase” bands of PS and PPE in set S and set E is depicted in Figure 10 and Figure 11, respectively. Figure 10 resolves two bands at 760 and 756 cm^{-1} for the “in-phase” mode of PS, while Figure 11 produces only one band at 756 cm^{-1} . Set A has high PS content, and some phenyl rings of PS cannot interact with the phenylene rings of PPE. Set B has lower PS content, and most of the phenyl rings of PS can interact with the phenylene rings of PPE. The band at 756 cm^{-1} should reflect the situation where the phenyl ring of PS is in contact with the phenylene ring of PPE, while the band at 760 cm^{-1} should represent the case where the phenyl rings of PS pack by themselves. The same reasoning can be extended to the “in-phase” mode of PPE, which shifts from 858 cm^{-1} in Figure 10 to 855 cm^{-1} in Figure 11. The band at 855 cm^{-1} thus reflects the situation where the phenylene ring of

PPE is in contact with the phenyl rings of PS, while the band at 858 cm^{-1} represents the case where the phenylene rings of PPE pack by themselves.

In conclusion, the specific interaction produces a downward shift of the aryl CH “in-phase” out-of-plane wagging modes of PPE and PS by 3 and 4 cm^{-1} , respectively. The corresponding synchronous maps for set S and set E in the region of 880–730 cm^{-1} only indicate the consistent but less informative result that when the PPE band around 858 cm^{-1} is increasing, the PS band around 756 cm^{-1} is decreasing. Hence they are not shown.

Conclusions

Generalized 2D IR correlation spectroscopy has been applied to the study of the conformational changes and specific interactions in blends of atactic PS and PPE. The PS/PPE blends have been divided into two sets: set S of high PS content and set E of high PPE content. The 2D synchronous correlation analysis in the spectral region of 3130–2810 cm^{-1} due to CH stretching vibrations proves to be powerful in separating the bands of PS from those of PPE. It is found that the main chain of PS, which packs favorably with PPE in the blends, exists in a highly organized state, as marked by the CH_2 asymmetric stretching vibration mode at 2909 cm^{-1} .

The 2D asynchronous correlation analysis reveals that the “ring bands” at 1614 (PPE), 1602 (PS), 1594 (PPE), and 1493 cm^{-1} (PS) and the methyl band at 1427 cm^{-1} (PPE) are indicative of the specific interaction in the blends. The favorable packing between PS and PPE requires that the PPE chains adopt conformation A or B. The asymmetric ether stretching vibration has frequencies at 1187 and 1176 cm^{-1} for ether bonds of PPE chains in contact with PS chains and has frequencies at 1205, 1199, and 1195 cm^{-1} for PPE chains in their isolated domains. The specific interaction in the blends shifts the aryl CH “in-phase” out-of-plane wagging mode of PPE from 858 to 855 cm^{-1} and that of PS from 760 to 756 cm^{-1} . It is concluded from the asynchronous spectra that 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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References and Notes

- (1) Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1329.
- (2) Noda, I. *Bull. Am. Phys. Soc.* **1986**, *31*, 520.
- (3) Noda, I. *J. Am. Chem. Soc.* **1989**, *111*, 8116.
- (4) Noda, I. *Appl. Spectrosc.* **1990**, *44*, 550.
- (5) Ozaki, Y.; Noda, I. *J. NIR Spectrosc.* **1996**, *4*, 85.
- (6) Gustafson, T.; et al. In *Time-Resolved Vibrational Spectroscopy V*; Lau, A., Siebert, F., Eds.; Springer-Verlag: Berlin, 1994; pp 131–135.
- (7) Noda, I.; Liu, Y.; Ozaki, Y.; Czarniecki, M. A. *J. Phys. Chem.* **1995**, *99*, 3068.
- (8) Sefara, N. L.; Magtoto, N. P.; Richardson, H. H. *Appl. Spectrosc.* **1997**, *51*, 536.
- (9) Czarniecki, M. A.; Wu, P.; Siesler, H. W. *Chem. Phys. Lett.* **1998**, *283*, 326.
- (10) Nabet, A.; Pezolet, M. *Appl. Spectrosc.* **1997**, *51*, 466.
- (11) Liu, Y.; Ozaki, Y.; Noda, I. *J. Phys. Chem.* **1996**, *100*, 7327.
- (12) Noda, I.; Liu, Y.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 8665.
- (13) Ozaki, Y.; Liu, Y.; Noda, I. *Macromolecules* **1997**, *30*, 2391.
- (14) Müller, M.; Buchet, R.; Fringeli, U. P. *J. Phys. Chem.* **1996**, *100*, 10810.
- (15) Ozaki, Y.; Liu, Y.; Noda, I. *Appl. Spectrosc.* **1997**, *51*, 526.
- (16) Czarniecki, M. A.; Maeda, H.; Y. Ozaki; Suzuki, M.; Iwahashi, M. *J. Phys. Chem. A* **1998**, *102*, 9117.
- (17) Wang, Y.; Murayama, K.; Myojo, Y.; Tsenkova, R.; Hayashi, N.; Ozaki, Y. *J. Phys. Chem. B* **1998**, *102*, 6655.
- (18) Ren, Y.; Shimoyama, M.; Ninomiya, T.; Matsukawa, K.; Inoue, H.; Noda, I.; Ozaki, Y. *Appl. Spectrosc.*, submitted.

- (19) Noda, I.; Liu, Y.; Ozaki, Y. *J. Phys. Chem.* **1996**, *100*, 8674.
- (20) Schultz, C. P.; Fabian, H.; Mantsch, H. H. *Biospectroscopy* **1998**, *4*, 19.
- (21) Dong, J.; Ozaki, Y. *Macromolecules* **1997**, *30*, 286.
- (22) Fawcett, A. H. *Polymer Spectroscopy*; John Wiley & Sons: Chichester, U.K., 1996.
- (23) Jo, W. H.; Cruz, C. A.; Paul, D. R. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1057.
- (24) Koenig, J. L.; Tovar, M. J. M. *Appl. Spectrosc.* **1981**, *35*, 543.
- (25) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
- (26) Utracki, L. A. *Polymer Alloys and Blends, Thermodynamics and Rheology*; Carl Hanser: Munich, 1989.
- (27) Wellinghoff, S. T.; Koenig, J. L.; Baer, E. *J. Polym. Sci., Polym. Phys.* **1977**, *15*, 1913.
- (28) Shultz, A. R.; Gendron, B. M. *J. Appl. Polym. Sci.* **1972**, *6*, 461.
- (29) Wellinghoff, S. T.; Baer, E. *Prepr.—Am. Chem. Soc., Div. Org. Coatings Plast. Chem.* **1976**, *36*, 140.
- (30) Palmer, R. A.; Gregoriou, V. G.; Chao, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 1222.
- (31) Boscoletto, A. B.; Checchin, M.; Tavan, M.; Camino, G.; Costa, L.; Luda, M. P. *J. Appl. Polym. Sci.* **1994**, *53*, 121.
- (32) Djordjevic, M. B.; Porter, R. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1981**, *22*, 323.
- (33) Ren, Y.; Ozaki, Y.; Murakami, T.; Nishioka, T.; Nakashima, K. *Macromol. Symp.*, in press.
- (34) Ren, Y.; Ozaki, Y.; Murakami, T.; Nishioka, T.; Nakashima, K.; Noda, I. *Macromolecules*, in press.
- (35) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press Inc.: San Diego, 1991: page 12 about the effect of Fermi resonance on the frequency of CH₃ symmetric stretching mode of methyl-substituted benzene; pages 279–282 about “the 1620–1400 cm⁻¹ ring bands” and page 284 about the in-phase out-of-plane CH wagging vibrations of monosubstituted and 1,2,3,5-substituted aromatic rings.
- (36) Nyquist, R. A.; Putzig, C. L.; Leugers, M. A.; McLachlan, R. D.; Thill, B. *Appl. Spectrosc.* **1992**, *46*, 981.
- (37) Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1992; p 125.
- (38) Ren, Y.; Ozaki, Y.; Murakami, T.; Nishioka, T.; Nakashima, K.; Noda, I. *J. Phys. Chem. B*, submitted.