

# Fourier Transform Infrared Spectroscopic Studies of the Poly(styrene-*co*-acrylonitrile) and Poly(vinyl chloride-*co*-vinyl acetate) Blends

GAURAB DAS, A. N. BANERJEE

Department of Plastics and Rubber Technology, University Colleges of Science and Technology, Calcutta University, 92, A.P.C. Road, Calcutta -700009, India

Received 10 June 1996; accepted 23 August 1996

**ABSTRACT:** The Fourier transform infrared (FTIR) spectroscopic studies of the poly(styrene-*co*-acrylonitrile) (SAN) and poly(vinyl chloride-*co*-vinyl acetate) (VYHH) blends produced by different blending techniques, viz., solution blending, melt-blending, and also the co-precipitation methods of blending, were performed. In the case of miscible blend systems, substantial band shiftings took place, whereas immiscible blend systems showed slight or no band shifting. The miscible blends showed a substantial residual spectrum which was absent in the case of the immiscible system when a similar subtraction process was carried out. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 991–1000, 1997

**Key words:** polymer blend; dependency on method; FTIR-compatibility; residual spectrum; subtraction process

## INTRODUCTION

Usually, two different polymers will not mix on a segmental level but as an essentially favorable interaction between two polymers that can allow one to obtain homogeneous blends. FTIR is a potential tool for the investigation of the mutual compatibility of various polymers; the very small spectral changes which are introduced as a result of the interaction can be detected by this method. The inherent sensitivity and computational facilities of FTIR spectroscopy have been particularly valuable in characterizing the specific interactions between component polymers in several blend systems.<sup>1–10</sup>

If the component polymers are incompatible, the individual polymers do not recognize, in the infrared sense, the existence of the other polymer in the blend. In such a case, it is possible to digi-

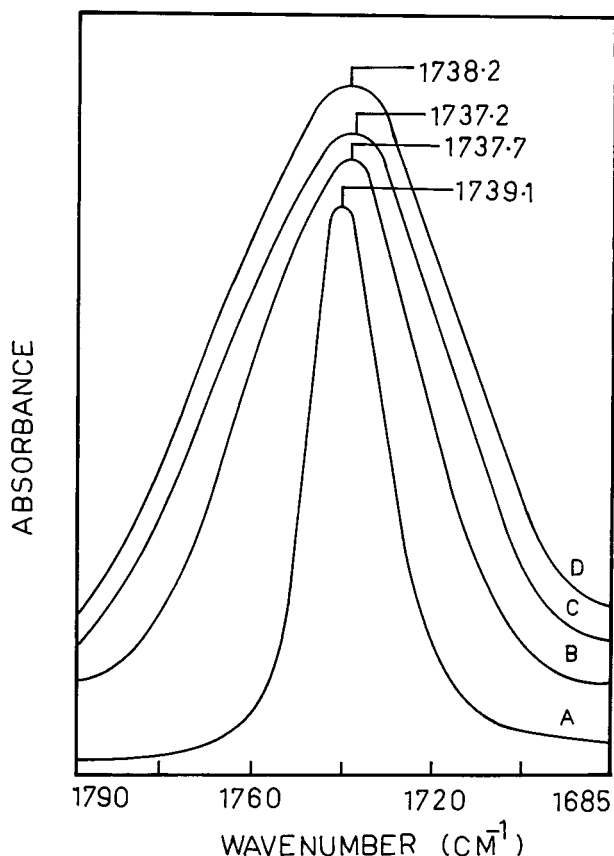
tally subtract from the spectrum of the blend the spectrum of one of the pure component polymers using an appropriate weighting factor and the residual spectrum thus obtained should be the same as the spectrum of the other polymer. However, specific interactions in miscible blends may result in a band shift, band broadening, or an intensity change of some of the absorption bands associated with one or both of the component polymers. In such cases, the residual spectrum obtained by digital subtraction of the spectrum of either one of the component polymers will be different from the spectrum of the other.<sup>11</sup>

Using FTIR spectroscopy, the presence of specific molecular interaction in miscible polymer blend systems and their absence in the phase-separated systems was observed. The interaction spectrum was obtained using the digital subtraction techniques. This article deals with FTIR spectroscopic studies of the VYHH/SAN blends produced by different blending techniques such as solution casting, melt-mixing, and coprecipitation methods of blending.

---

Correspondence to: A. N. Banerjee

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/080991-10



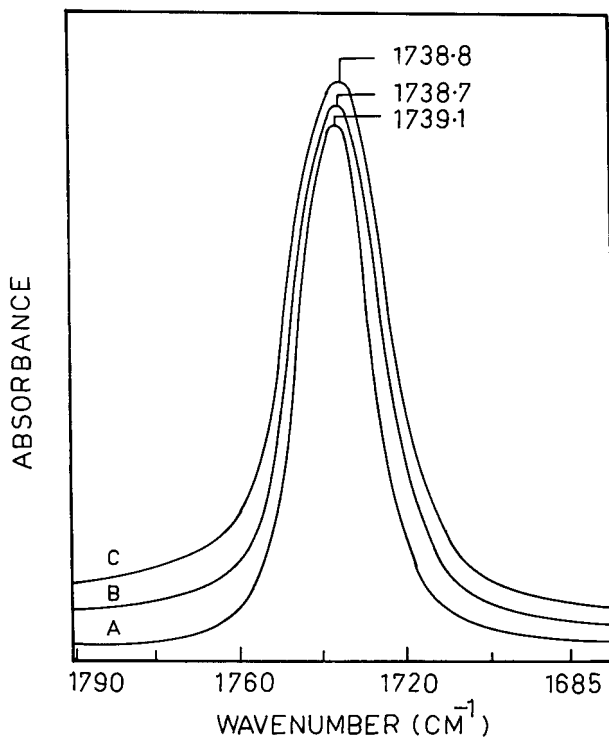
**Figure 1** FTIR absorption spectra in the region 1790–1685  $\text{cm}^{-1}$  of pure VYHH and VYHH/SAN blends cast from THF (A) pure VYHH, (B) 60 : 40, (C) 50 : 50, and (D) 40 : 60 VYHH/SAN blends.

## EXPERIMENTAL

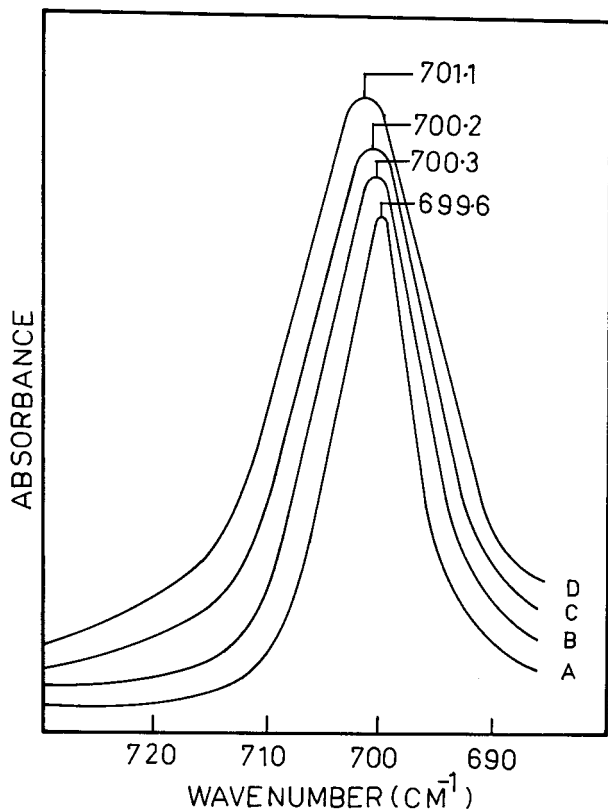
Poly(styrene-*co*-acrylonitrile) (SAN; Polylan 1000 IM-1) was supplied by Polychem (India) Limited. It had an acrylonitrile content of 22% by weight from elemental analysis. It was a random copolymer and had an average molecular weight of 95,000. The poly(vinyl chloride-*co*-vinyl acetate) (VYHH) was supplied by the Union Carbide International Co., USA, contained 87 wt % vinyl chloride and 13 wt % vinyl acetate, and had an intrinsic viscosity value (cyclohexanone at 20°C) of 0.53.

The individual polymer solutions were prepared by dissolving the individual polymers in solvents (such as in THF and chloroform), followed by stirring for approximately 24 h. The concentration of the solutions was 4% on a weight basis. The solutions were subsequently blended in the

proper proportions and stirred for approximately 24 h; then, the blend solutions were settled for 7 days. The resulting blend solutions were then cast onto the mercury surface at ambient temperature in order to get uniform film thickness; for all the cases, the same volume of the aliquots of the blends were poured on the same diameter of the mercury surface. The evaporation of the solvents was done slowly under reduced pressure at 100°C until the films reached constant weight. In this method, pure polymers and their blends were precipitated simultaneously from their solutions described above using the nonsolvent methanol. The latter, in a volume ratio of about 10 : 1 to the added solution, was continuously stirred in a beaker while the solution was added slowly. The precipitated powder was allowed to dry in a similar way as described in the solution-casting method. Melt-mixing was accomplished by melting the coprecipitated blends prepared by the coprecipitation method described above at about 150–170°C for 5 min depending on the composition of the blends. For the purpose of attaining the same



**Figure 2** FTIR absorption spectra in the region 1790–1685  $\text{cm}^{-1}$  of pure VYHH and of VYHH/SAN blends cast from chloroform: (A) pure VYHH and (B) 80 : 20 and (C) 40 : 60 VYHH/SAN blends.



**Figure 3** FTIR absorption spectra in the region 720–690  $\text{cm}^{-1}$  of pure SAN and of VYHH/SAN blends cast from (A) pure SAN and (B) 80 : 20, (C) 50 : 50, and (D) 20 : 80 SAN/VYHH blends.

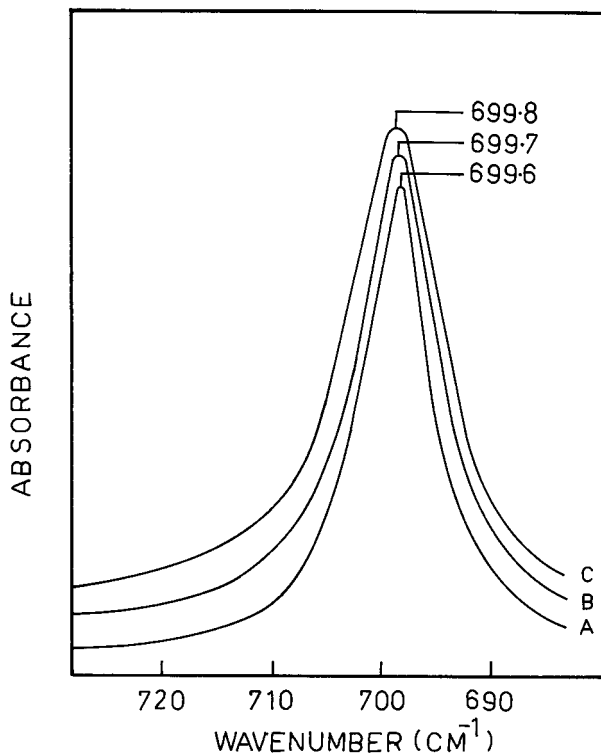
thermal history, two pure components were melted under identical conditions. In the case of melt-mixing, octyl tin mercaptide (2 wt % on the basis of the total polymer) was added as a stabilizer to avoid the thermal degradation of VYHH. Films were prepared by compression molding at a temperature 170°C for 5 min.

Infrared spectra were obtained on a Perkin-Elmer 1600 Series FTIR spectrophotometer. Sixty-four scans at a resolution of 4  $\text{cm}^{-1}$  were signal-averaged. The films were sufficiently thin so as to obey the Beer Lambert Law (absorbance less than 0.8). The digital subtraction process was carried out by attempting to zero-out selective bands of each of the two-component polymers, so as to obtain a zero base line over the entire region of interest. In the case of the blend powders obtained from melt-mixing and also from coprecipitation methods, powder samples were thoroughly mixed with KBr in a weight ratio of 1 : 50; then, a KBr

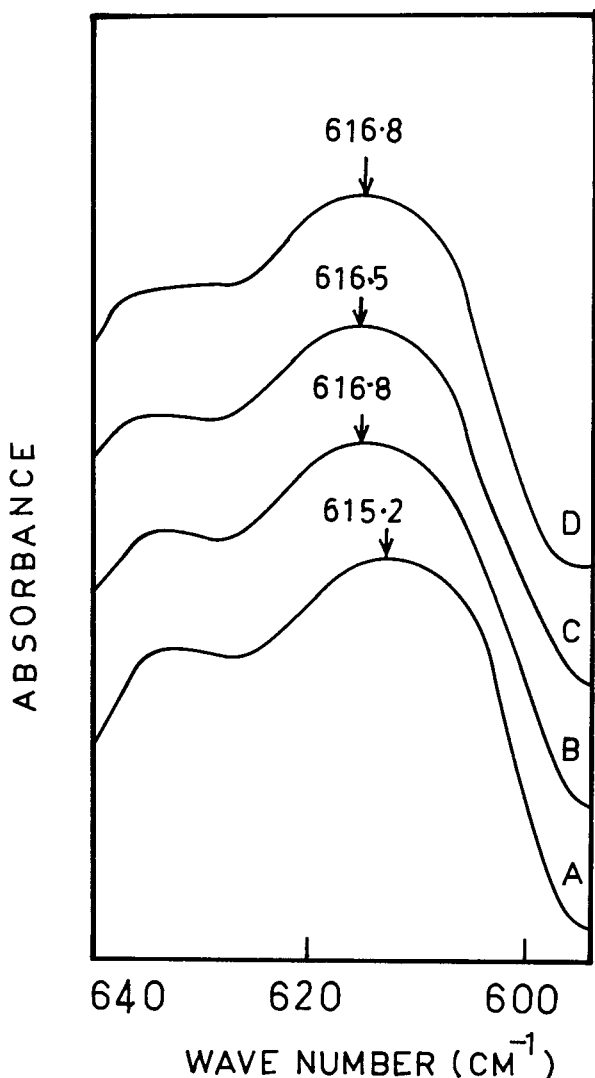
pellet was prepared and used for obtaining the IR spectra.

## RESULTS AND DISCUSSION

Figure 1 shows the FTIR absorption spectra in the region of 1790–1680  $\text{cm}^{-1}$  of the carbonyl stretching region for pure VYHH and its blends with SAN cast from THF at ambient temperature. The familiar shifting and broadening of the carbonyl band of VYHH was observed as a function of SAN content and was evidence for the presence of specific interaction between the components of the blends. Figure 2 shows the FTIR spectra of the carbonyl stretching band in the region 1790–1685  $\text{cm}^{-1}$  for the same blend cast from chloroform at ambient temperature. From Figure 2, it is observed that the slight or no shifting of the carbonyl bands took place, indicating the absence of the specific interaction between the components of the blend. It was found from our studies that



**Figure 4** FTIR absorption spectra in the region 720–690  $\text{cm}^{-1}$  of pure SAN and of VYHH/SAN blends cast from (A) chloroform, (B) pure SAN, and (C) 50 : 50 and 20 : 80 SAN/VYHH blends.



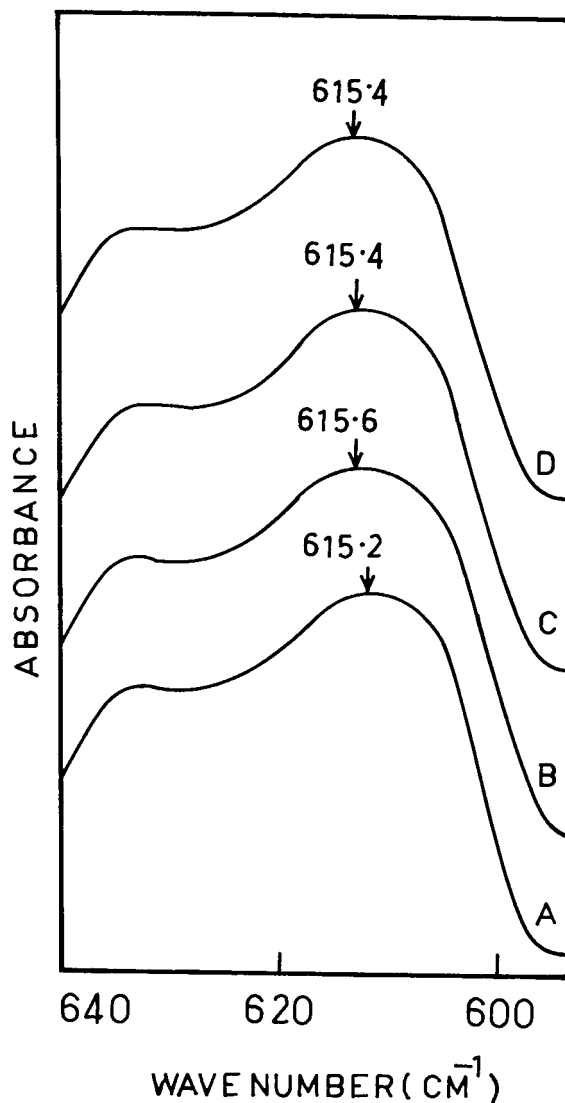
**Figure 5** FTIR absorption spectra in the region 640–600  $\text{cm}^{-1}$  of pure VYHH and of VYHH/SAN blends cast from THF (A) pure VYHH and (B) 80 : 20, (C) 50 : 50, and (D) 40 : 60 VYHH/SAN blends.

the SAN/VYHH blends cast from THF and MEK are compatible, whereas the blends cast from chloroform and dichloromethane are incompatible in nature.<sup>12</sup>

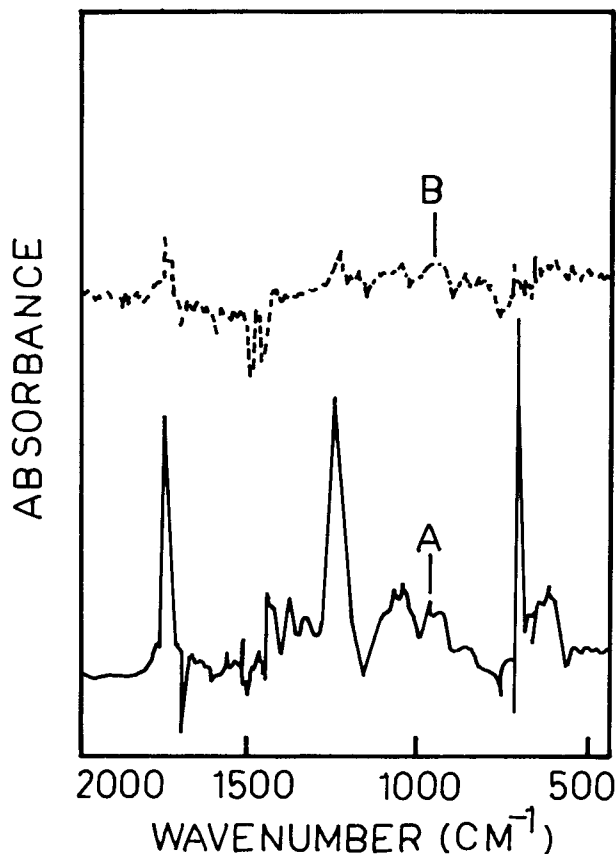
Naito et al.<sup>13</sup> showed that the interaction between poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) was manifested by a shift (approximately 10–15  $\text{cm}^{-1}$ ) in the stretching frequencies of the carbonyl group of PMMA, i.e., the 1739  $\text{cm}^{-1}$  stretching frequency of the carbonyl group of PMMA.

The infrared absorption spectra of the C—H

out-of-plane deformation band of the phenyl groups of SAN and SAN/VYHH blends cast from THF at ambient temperature are shown in Figure 3. The shifting of the C—H out-of-plane deformation band of the phenyl groups took place significantly with the blend composition. On the contrary, no significant shifting of the C—H out-of-plane deformation of the phenyl group took place with the blend composition in the case of the SAN/VYHH blends cast from chloroform at ambient temperature (Fig. 4).



**Figure 6** FTIR absorption spectra in the region 640–600  $\text{cm}^{-1}$  of pure VYHH and of VYHH/SAN cast blends from (A) chloroform and (B) pure VYHH 80 : 20, (C) 40 : 60, and (D) 20 : 80 VYHH/SAN blends.

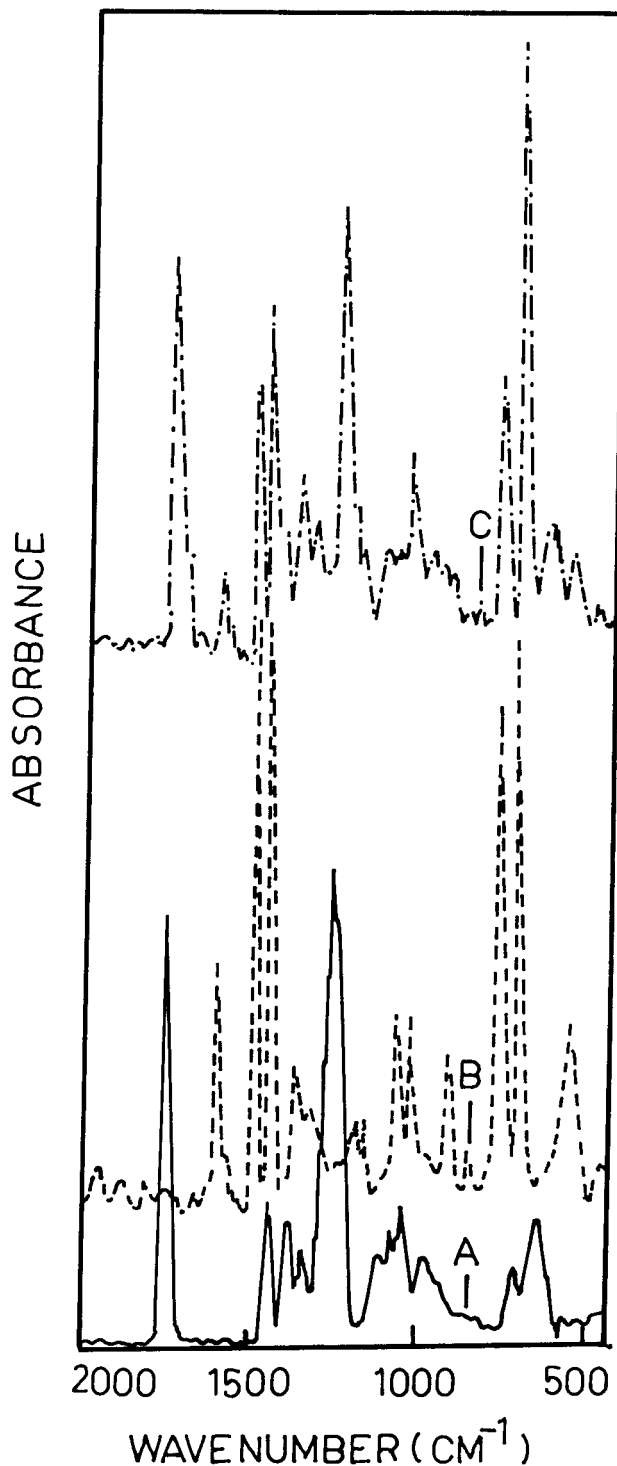


**Figure 7** (A) Interaction spectrum in the region 2000–500  $\text{cm}^{-1}$  of 50 : 50 VYHH/SAN miscible blend cast from THF (the spectrum was magnified by a factor of 20). (B) Interaction spectrum in the region 2000–500  $\text{cm}^{-1}$  of 50 : 50 VYHH/SAN immiscible blend cast from chloroform (the spectrum was magnified by a factor of 20).

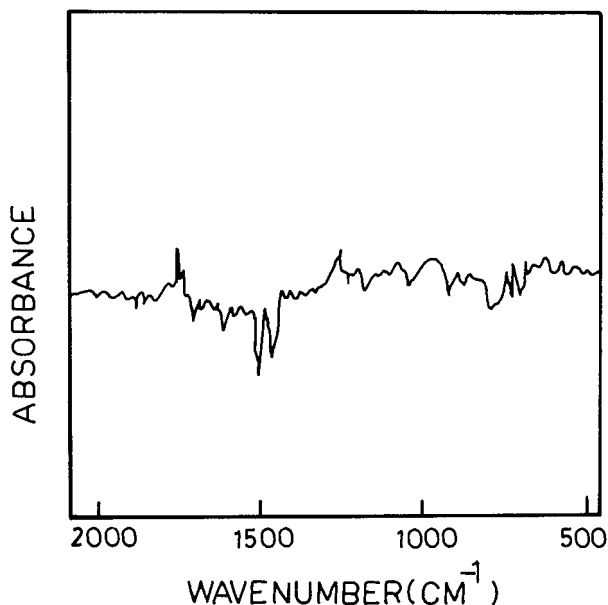
Feng et al.<sup>14</sup> reported that there were strong intermolecular interactions between the phenyl groups of styrene–maleic anhydride copolymers (SMA, 50 wt % maleic anhydride) and the carbonyl groups of PMMA. They concluded that it was the intermolecular interactions, instead of intramolecular repulsion forces within the SMA copolymers, that made the SMA/PMMA blends miscible.

In the IR spectrum of polystyrene (PS),<sup>15</sup> a number of bands showed small changes in position or shape when PS was blended with poly(vinyl methyl ether) (PVME). The band most sensitive to phase compatibility was located near 700  $\text{cm}^{-1}$ . This band was generally assigned to the C—H out-of-plane bending vibration. It was

found at 699.5  $\text{cm}^{-1}$  for film cast from toluene solutions containing equal amounts of PS and PVME. This is to be compared to the peak maxi-



**Figure 8** FTIR absorption spectra in the region 2000–500  $\text{cm}^{-1}$  of (A) pure VYHH, (B) pure SAN, and (C) 50 : 50 VYHH/SAN blend cast from THF.



**Figure 9** The difference spectrum of sequentially cast VYHH and SAN samples from THF (the spectrum has been magnified by 20 times) in the region of 2000–500  $\text{cm}^{-1}$ .

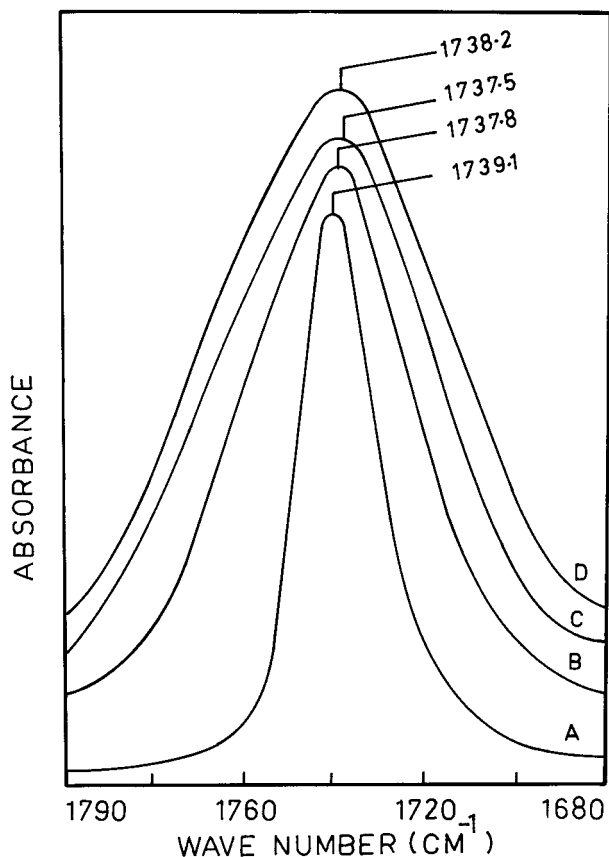
mum located at  $697.7 \text{ cm}^{-1}$  in pure PS. For incompatible blends of PS/PVME, such as the films cast from trichloroethylene (TCE) solutions, the peak maximum is usually found at an intermediate position between two extremes. Similar changes in frequency for this vibration were also observed for PS blended with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).<sup>16</sup> Figure 5 shows the FTIR absorbance spectra of the syndiotactic C—Cl stretching vibration band between 600 and  $640 \text{ cm}^{-1}$  for VYHH and VYHH/SAN blends cast from the THF solution and significant shifting of the band took place with the blend composition. But in the case of the same blend, i.e., the VYHH/SAN blend cast from chloroform, no prominent shifting of the syndiotactic C—Cl stretching band took place as a function of SAN content (Fig. 6), indicating that the solvent has played a vital role in the miscibility of the polymer components in the blends.

Chattopadhy and Banerjee<sup>17</sup> observed the shifting of a syndiotactic C—Cl stretching vibration band in the case of miscible blends of a vinyl chloride–vinyl acetate maleic acid terpolymer (VMCH) and nitrocellulose (NC) cast from THF and cyclohexanone, but no significant change was

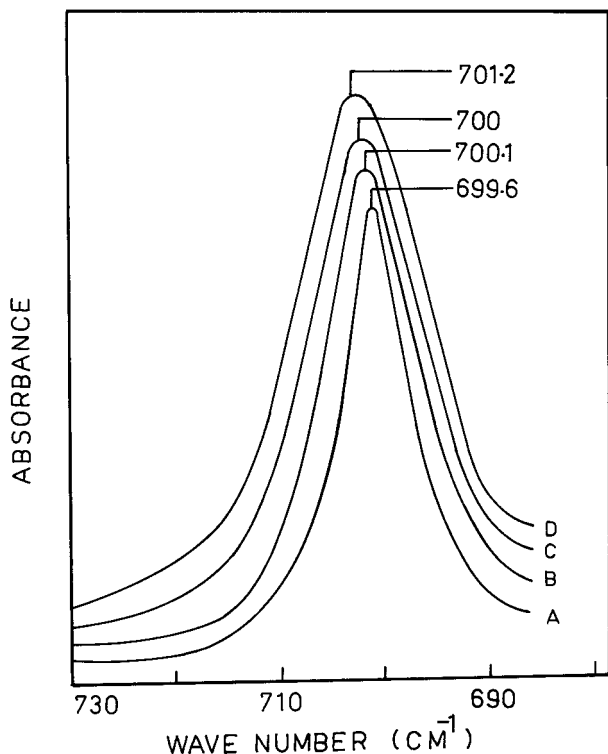
observed in the case of the same blends which were immiscible in nature cast from acetone.

An interaction spectrum was observed in the case of the miscible system, which was absent in the case of the immiscible system. Figure 7(A) and (B) shows the interaction spectrum in the region 2000–500  $\text{cm}^{-1}$  of the 50 : 50 VYHH/SAN miscible blend cast from THF and from chloroform, respectively. The spectra were magnified by factor 20 because the interaction spectra are small. The miscible blends showed substantial residual absorbance when approaching zero out of the bands of VYHH and SAN. In the phase-separated system, by comparison, only a minimal residue was observed when a similar subtraction process was carried out. The IR spectra of pure VYHH, pure SAN, and their blends are shown in Figure 8.

According to Garcia,<sup>18</sup> the residue observed



**Figure 10** FTIR absorption spectra in the region 1790–1680  $\text{cm}^{-1}$  of coprecipitated blends of VYHH/SAN: (A) VYHH and (B) 35 : 65, (C) 50 : 50, and (D) 80 : 20 VYHH/SAN blends.



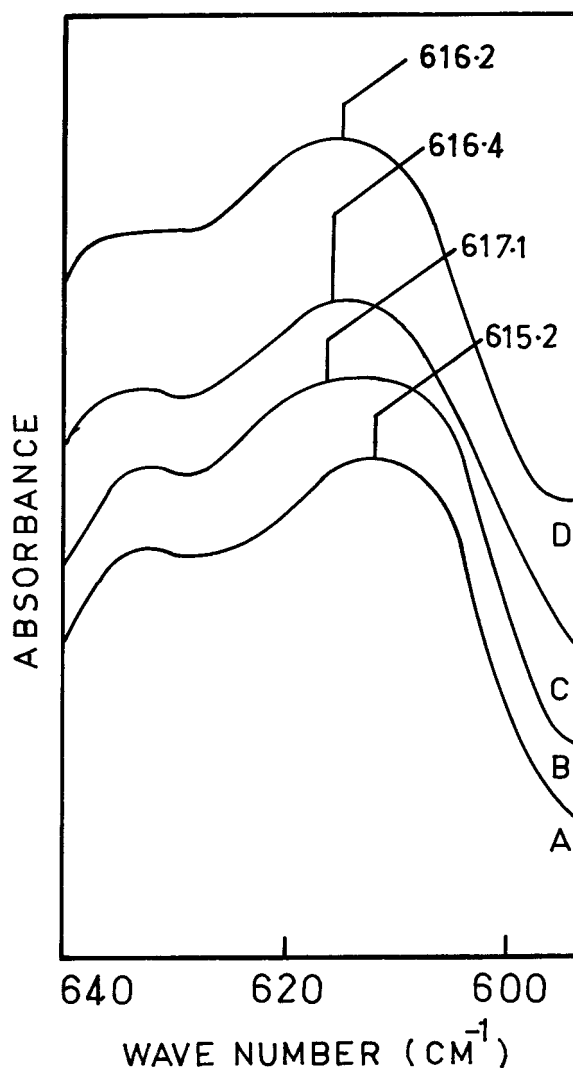
**Figure 11** FTIR absorption spectra in the region  $720\text{--}690\text{ cm}^{-1}$  of coprecipitated blends of VYHH/SAN: (A) pure SAN and (B) 70 : 30, (C) 50 : 50, and (D) 30 : 70 SAN/VYHH blends.

for the phase-separated blend may be due to a number of effects such as scattering, dispersion, interfacial effects, and the nature of the phase separation and small-scale partial miscibility. The dispersion effect results from the change in the real part of the refractive index of the blend as compared to the pure components. According to the work of Allara,<sup>19</sup> the residual absorbances are of the order of 5% of the initial intensity, which is in good qualitative agreement with the 2–4% residual absorbance observed for the phase-separated system. It is difficult to attribute this small residue to any one of the above-mentioned effects—most likely, it is a combination of all.

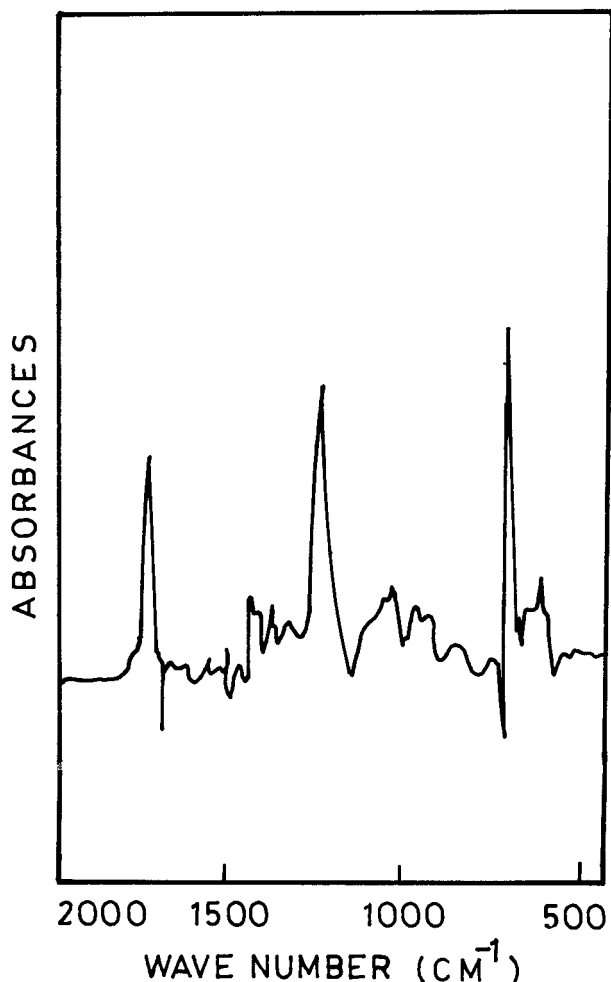
Garcia<sup>18</sup> and Lu et al.<sup>20</sup> separately studied the miscible and immiscible blends of PS/PVME by FTIR spectroscopy. They separately reported that the miscible PS/PVME blends showed strong evidence of molecular interaction, whereas no molecular interaction was detected for phase-separated PS/PVME blends. The interaction spectrum was

obtained by digital subtraction techniques. In view of these results, they concluded that molecular interaction must play a role in the compatibility of the two polymers.

Looking at the interaction spectra, it has been seen that most of the changes were associated with the VYHH bands in the  $1739.1\text{ cm}^{-1}$  (which is due to the carbonyl C=O stretching band) and  $615.2\text{ cm}^{-1}$  (which is due to the syndiotactic C—Cl stretching vibrational band) spectral region and with the SAN bands in the  $699.6\text{ cm}^{-1}$  (which is due to the C—H out-of-plane deformation band). From the above stud-



**Figure 12** FTIR absorption spectra in the region  $640\text{--}600\text{ cm}^{-1}$  of the coprecipitated blends of VYHH/SAN: (A) pure VYHH and (B) 80 : 20, (C) 50 : 50, and (D) 20 : 80 VYHH/SAN blends.



**Figure 13** Interaction spectrum of coprecipitated blends of VYHH/SAN (50 : 50) in the region of 2000–500  $\text{cm}^{-1}$  (the spectrum was magnified by a factor of 20).

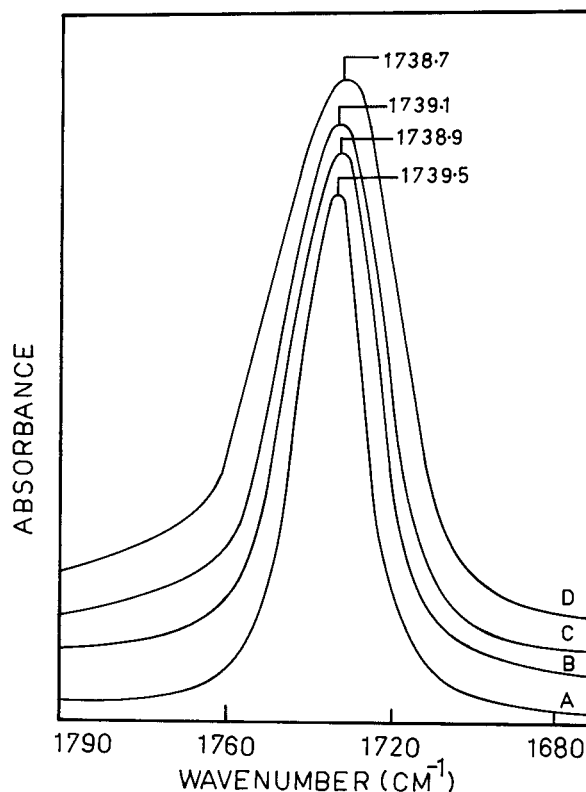
ies, it was observed that a significant band shift took place in the case of miscible blends, while no band shift took place in the case of immiscible blends. These band shifts suggested and confirmed the interactions between the blend components.<sup>11</sup>

Specific interactions between certain aromatics and chlorinated compounds have been found in the literature.<sup>21–24</sup> Evidence for this is seen in exothermic mixing,<sup>21</sup> NMR chemical shifts,<sup>22</sup> and shift in the infrared band for the C—H out-of-plane deformation of the aromatics.<sup>23</sup> This interaction is believed to lead to a weak complex, and the mechanism has been attributed to (a) a dipole-induced dipole interaction,<sup>22</sup> (b) hydrogen-bond formation between

the  $\pi$ -electron of the aromatics and the  $\alpha$ -hydrogen of chlorohydrocarbon,<sup>21</sup> or (c) aromatic quadrupole-hydrogen-induced dipole interaction.<sup>24</sup>

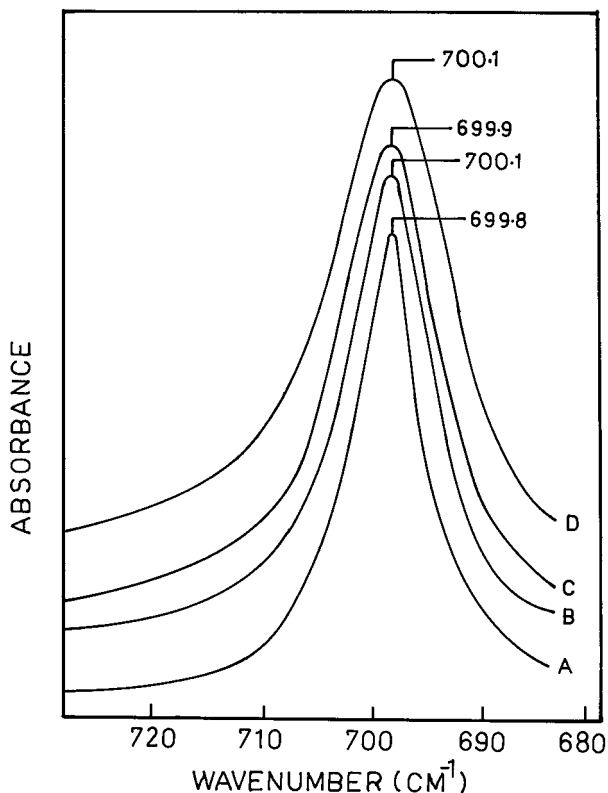
Instead of mixing the VYHH with SAN in THF and casting a film of the miscible blend, each component was cast separately on the same salt plate with the plate dried before the second component was applied. No interaction spectrum was found, as expected, indicating that the interaction is intrinsic to the blend and not associated in any way with the artifact of the two components (Fig. 9).

The shifting of the carbonyl stretching band, the C—H out-of-plane deformation band, and also the syndiotactic C—Cl stretching band of the coprecipitated blends are shown in Figures 10–12, respectively. The interaction spectrum of the coprecipitated blends (i.e., the blend was coprecipitated from chloroform solution by methanol) is given in Figure 13. The interaction spectrum of



**Figure 14** FTIR absorption spectra in the region 1790–1680  $\text{cm}^{-1}$  of the melt-mixed SAN/VYHH blends: (A) pure VYHH and (B) 30 : 70, (C) 50 : 50, and (D) 70 : 30 VYHH/SAN blends.





**Figure 15** FTIR absorption spectra in the region 720–600  $\text{cm}^{-1}$  of melt-mixed SAN/VYHH blends: (A) pure VYHH and (B) 30 : 70, (C) 50 : 50, and (D) 70 : 30 VYHH/SAN blends.

the coprecipitated blend was similar to that of the blend cast from the THF solution.

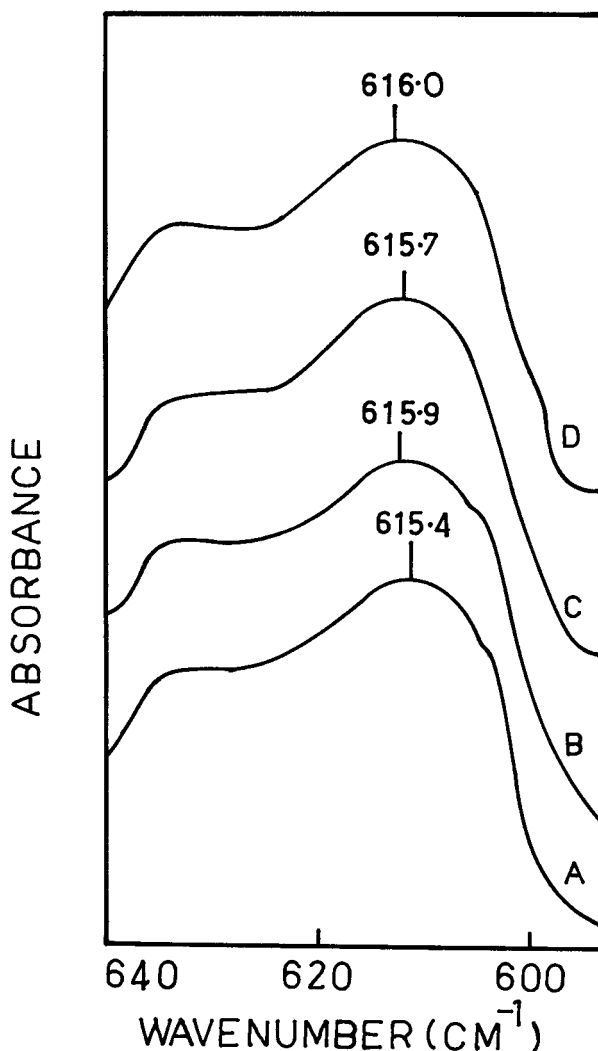
The IR spectra of the carbonyl band, C—H out-of-plane deformation band, and syndiotactic C—Cl stretching band are shown in Figures 14–16, respectively. From Figures 14–16, it was observed that no or only slight band shifts took place, indicating the absence of polymer–polymer interaction in the blends. The interaction spectrum of the melt-mixed blends is shown in Figure 17. The interaction spectrum is similar to that obtained in the case of incompatible blends cast from chloroform solutions. It was found from our previous studies<sup>12</sup> that the coprecipitated blends of VYHH/SAN are compatible in nature, whereas the melt-mixed blends of VYHH/SAN are incompatible in nature.

## CONCLUSIONS

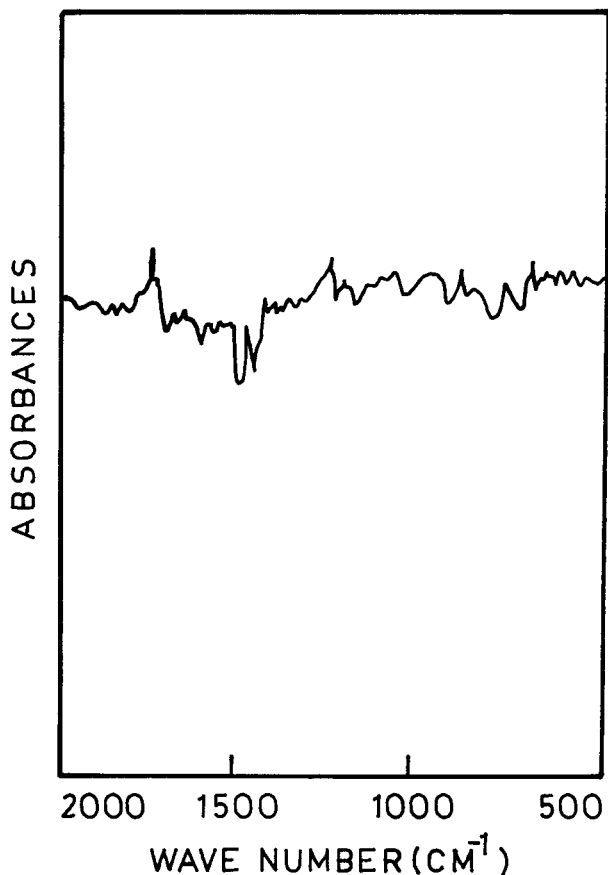
In the case of the miscible blend systems, significant band shifting was observed, indicating the

presence of specific molecular interactions in the blend, but in the case of immiscible blend systems, no or only slight band shifting has taken place, indicating the absence of specific molecular interactions in the case of immiscible blend systems. Using FTIR spectroscopy, a substantial interaction spectrum was observed which was absent in the case of the phase-separated systems.

The award of a CSIR, an Indian Fellowship (SRF), to G.D. is sincerely acknowledged.



**Figure 16** FTIR absorption spectra in the region 640–690  $\text{cm}^{-1}$  of the melt-mixed SAN/VYHH blends: (A) pure VYHH and (B) 30 : 70, (C) 50 : 50, and (D) 70 : 30 VYHH/SAN blends.



**Figure 17** Interaction spectrum in the region 2000–500  $\text{cm}^{-1}$  of melt-mixed blends of VYHH/SAN (50 : 50) (the spectrum was magnified by a factor of 20).

## REFERENCES

1. M. M. Coleman, J. Zarian, D. F. Varnell, and P. C. Painter, *J. Polym. Lett. Ed.*, **15**, 749 (1977).
2. M. M. Coleman and J. Zarian, *J. Polym. Sci. Polym. Phys. Ed.*, **17**, 837 (1979).
3. M. M. Coleman and D. F. Varnell, *J. Polym. Sci. Polym. Phys. Ed.*, **18**, 1403 (1980).
4. D. F. Varnell and M. M. Coleman, *Macromolecules*, **14**, 1350 (1981).
5. D. F. Varnell, J. P. Runt, and M. M. Coleman, *Polymer*, **24**, 37 (1983).
6. V. Janarthanan and G. Thyagarajan, *Polymer*, **30**, 3593 (1992).
7. J. C. Lim, J. K. Park, and H. Y. Song, *J. Polym. Sci. Polym. Phys. Ed.*, **32**, 29 (1994).
8. R. Xie, B. Yang, and B. Yang, *J. Polym. Sci. Polym. Phys. Ed.*, **33**, 25 (1995).
9. Y. T. Lee, S. Y. Lee, and S. H. Goh, *Eur. Polym. J.*, **31**, 39 (1995).
10. D. F. Varnell and M. M. Coleman, *Polymer*, **22**, 1324 (1981).
11. G. M. Venkatesh, R. D. Gillbert, and R. E. Fornes, *Polymer*, **26**, 45 (1985).
12. G. Das, A. N. Banerjee, and B. C. Mitra, *Eur. Polym. J.*, **32**, 179 (1996).
13. K. Naito, G. E. Johnson, D. L. Allara, and T. K. Kwei, *Macromolecules*, **11**, 1260 (1978).
14. H. F. Feng, L. Shen, and Z. Feng, *Eur. Polym. J.*, **31**, 243 (1995).
15. S. L. Hsu, F. J. Lu, and E. Benedetti, in *Polymer Blends and Composites in Multiphase Systems*, C. D. Hans, Ed., American Chemical Society, Washington, DC, 1984, p. 101.
16. S. T. Welligton, J. L. Koenig, and E. Baer, *J. Polym. Sci. Polym. Phys. Ed.*, **1**, 1913 (1977).
17. S. Chattopadhy and A. N. Banerjee, *Polym. Adv. Technol.*, **2**, 191 (1991).
18. D. Garcia, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 107 (1984).
19. D. L. Allara, *Appl. Spectrosc.*, **33**, 358 (1979).
20. F. J. Lu, E. Benedetti, and S. L. Hsu, *Macromolecules*, **16**, 1525 (1983).
21. L. Abello, *J. Chem. Phys.*, **70**, 1355 (1973).
22. W. G. Schneider, *J. Phys. Chem.*, **66**, 2653 (1962).
23. I. R. Hill, D. Steele, and J. Jindale, *Spectrochem. Acta*, **37a**, 667 (1981).
24. M. W. Hanna and D. E. Williams, *J. Am. Chem. Soc.*, **90**, 5338 (1968).