Correlating Miscibility of PVC/PMMA Blend with Polymer Chain Orientation

V. D. Deshpande, Umesh Singh

University Institute of Chemical Technology, Matunga, Mumbai 400019, India

ABSTRACT: Blends of poly (vinyl chloride) (PVC) and poly (methyl methacrylate) (PMMA) with varying concentrations of the polymers were prepared in a film form by standard solution casting method, using methyl ethyl ketone (MEK) as a common solvent. The miscibility of the blend was studied by dynamic mechanical analysis. The chain orientation behaviors of PVC and PMMA in the stretched blend films were studied by infrared dichroism method. Up to 60 wt % PVC concentration in the blend, PVC showed negative values for orientation function whereas PMMA showed independent positive values for its orientation function. On further increasing PVC concentration in the blend, the orientation function of PVC flipped to positive values, and both PVC and PMMA showed same magnitude and trend in orientation behavior. The chain orientation behavior of individual polymers in the immiscible compositions of the blend was observed to be independent, while there was a high degree of cooperation for chain orientation in the miscible composition. Change in the miscibility of the blend was simultaneously accompanied by conformational changes in PVC. The change in orientation behavior is interpreted in terms of curling of polymer chains in the immiscible phase. The polymer chain curling hypothesis used here is applicable independent of the type of polymers in the blend. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 624–630, 2006

Key words: PVC; PMMA; chain orientation; IR-dichroism; polymer blends; miscibility

INTRODUCTION

Polymer blends have been of great interest for quite some times, as polymer blending is a cheap and fast way of improving the properties of commercially available polymers without the laborious development of new polymers. However, the physical properties of the newly developed polymer blends are strongly dependent on the phase miscibility. Hence, study of miscibility and phase behavior of polymers has attracted intense investigation in both industry and academy.[1,2]

Many methods are available for determination of miscibility. Among these, differential scanning calorimetry and fourier transform infrared spectroscopy (FTIR) are the most popular methods; however, transmission electron microscopy (TEM) and Light scattering have also been used.[1–4] Recently, solid state C13 nuclear magnetic resonance (NMR) has also been used for investigating blend miscibility.[5]

As a different approach, we have undertaken the chain orientation study of a polymer blend; where polymer blend shows concentration dependent phase miscibility. The aim of our study was to see whether (a) the chain orientation behavior of individual polymers in the miscible and immiscible compositions is different; (b) whether the information of chain orientation behavior can be used to study miscibility of the polymer blends.

For this study, the blend of poly (vinyl chloride) (PVC) and poly (methyl methacrylate) (PMMA) were chosen. This blend was first studied by Shurer et al.[6], using dynamic mechanical analysis. Subsequently, the miscibility of the blend has been studied by thermally stimulated depolarization current method (TSDC),[7] fluorescence nonradiative energy transfer,[8] X-ray diffraction[9], and NMR.[10] Theoretical studies have also been undertaken for this blend.[11] The large number of these studies has established the composition dependent miscibility of this blend system. Because of its composition dependent miscibility, it forms an ideal system for undertaking chain orientation study to see whether any correlation exists between blend miscibility and polymer chain orientation.

Generally, uniaxial stretching induces anisotropy in the polymers because of alignment of polymer chains in the direction of stretching. This alignment or orientation is described by an orientation distribution function $f(\theta)$, where θ is the angle between the chain axis and the direction of stretching. The function, $f(\theta)$ is expressed as

Correspondence to: U. Singh (ups20@bath.ac.uk).
Present Address: Department of Biology and Biochemistry, University of Bath, Bath, BA2 7AY, UK.

$$f(\theta) = \tfrac{1}{2} \cdot \pi \sum_{n=0}^{\infty} (n + 1/2) < P_n(cos\ \theta) > P_n(cos\ \theta) \quad (1)$$

where P_n (cos θ) are Legendre polynomials.

For uniaxially oriented polymers, all the odd terms are zero. Also the higher order terms are insignificant. Hence, the orientation function can be approximated by

$$f(\theta) = P_2\ cos(\theta) = (3 < cos^2\theta > - 1)\ /\ 2 \quad (2)$$

where, P_2 cos (θ) is the second order moment of orientation function.

The magnitude of the orientation function f (θ) is positive when $cos^2\ \theta > 1/3$, i.e., when the average angle between the chain axis and the stretch direction (θ) < 54.74° and f (θ) is negative when $cos^2\ \theta < 1/3$ i.e., when the average angle $\theta > 54.74°$. Because of anisotropy in the oriented polymer, the absorption of plane polarized light in the parallel and the perpendicular directions are different. This is described by a quantity called dichroic ratio, which is given by

$$D = A_{/\!/}\ /\ A_{\perp}$$

where $A_{/\!/}$ and $A_{\perp}$ are absorbance in parallel and perpendicular directions, respectively. The second order moment of orientation function is related to the dichroic ratio by

$$P_2 cos(\theta) = f(\theta) = [(D - 1)/(D + 2)][(D_0 + 2)/(D_0 - 1)] \quad (3)$$

where, $D_0 = 2\ cot^2\alpha$

α = angle between the transition moment vector and the chain axis. The details can be found elsewhere.[12–14]

EXPERIMENTAL

Materials

Atactic poly (methyl methacrylate) (PMMA) having weight-average molecular weight(M_w) of 101,000 (cat. No. 18,224) was obtained from Aldrich Chemical Company (Milwaukee, WI). The poly (vinyl chloride) (PVC) in the pure form was kindly provided by Prof. A.K. Kalker of the Institute of Chemical Technology, University of Mumbai. The viscosity-average molecular weight (M_v) of PVC, as determined by intrinsic viscosity measurement in tetrahydrofuran at 25°C, was 47,000.

Blend preparation

The films of pure PVC, PMMA, and the blends were prepared by slow evaporation of 3% w/v solution in methyl ethyl ketone (MEK), (spectroscopic grade, S. D. Chemicals, Mumbai) in an oven at 55°C. To remove the last traces of solvent, the films were further annealed at 65°C for 6 h and stored in dry atmosphere. The films obtained were transparent, homogeneous and were around 40 μm in thickness. The amorphous films were uniaxially drawn to various draw ratios on an Instron Tensile Tester (model 1026) at a temperature of 120°C (fixed) at a nominal strain rate of 0.008 s^{-1}. A minimum of 10 min was allowed for sample to attain the desired temperature before drawing. The drawn samples were quenched in ice. Each time a maximum of 2 s passed between the end of drawing and quenching.

Viscoelastic measurements (dynamic mechanical analysis)

The viscoelastic measurements were obtained on a direct reading Rheovibron, DDV-II Rheo-200 Dynamic Tensile Tester (Toyo Measuring Instruments Ltd. Japan). The measurements were taken at a frequency of 11 Hz. A heating rate of 1–2°C/min was used. All the measurements were made on unoriented solution cast films.

Infrared dichroism/FTIR studies

The polarized spectra were recorded on a PYE-Unicam Infrared Spectrometer (PU 9612). The polarization was achieved by Perkin–Elmer wire-grid polarizer in the recombinant beam at 45° to the slit direction.[15] Samples instead of the polarizer were rotated to get the parallel and perpendicular readings. The orientation results were further checked by recording 128 superimposed polarized spectra of the films on FTIR Spectrometer (Bruker IFS 88). The absorbance values obtained in both cases were same (with in +/− 10% experimental error). The FTIR spectra of unoriented blend samples were obtained on the same spectrometer with a resolution of 2 cm^{-1} with a total of 128 scans.

RESULTS AND DISCUSSIONS

Thermal studies

The results of dynamical mechanical analysis (DMA) on unoriented films are shown in the Figure 1. Here, the glass-transition temperature (Tg) of PVC/PMMA blend is plotted against the PVC composition in the blend. The glass transition of PVC and PMMA were found to be 86 and 112°C, respectively. The blends below 50 wt % show two distinct T_g's while a single Tg is obtained for blends containing 50 wt % and higher PVC concentration in the blend. If different phases are present in the blend having single T_g, each phase will
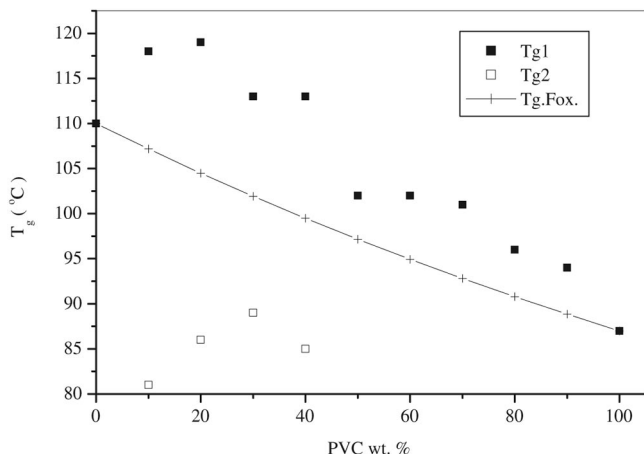
Figure 1 DMA results of PVC, PMMA, and their blends.

have its own characteristic transition peak. If peaks are close to each other they may overlap increasing the peak width of the transition. In such case, width of the transition may reflect the magnitude of local compositional fluctuations in polymer blends giving qualitative information regarding the relative homogeneity or the miscibility of the system. Hence, for the blends showing single glass transitions, the half width of the glass-transition peak at half peak height (hwhm), were plotted against PVC concentration (Fig. 2). As can be seen, the width of the transition peak corresponding to the 50 wt % PVC is considerably higher than that of the individual components. This suggests that even the blend 50 wt %PVC is immiscible. Homogeneity of the blends containing 60 wt % and higher PVC concentration is similar to the pure components, hence they are considered miscible.

The PVC/PMMA blends system has been studied by many workers. Vorenkamp et al.[16] in their heat of mixing studies of low molecular mass analogues of the PVC and PMMA have found that the heat of mixing is negative. The cloud point curve for the PVC/PMMA blend lies between 190 and 230°C with a minimum just above 190°C for approximately 30 wt % PVC. Saito et al.[15] have reported that the volume change on mixing, Δv, and the enthalpy of mixing, ΔH, are negative over entire composition range for this blend. They showed that the miscibility of this blend system is composition dependent and that the maximum negative change for Δv in the blend is at about 80 wt % PVC composition. Earlier, Shurer et al.[6] and Jager et al.[17] showed that PVC and atactic-PMMA form a homogeneous blend with a single T_g if prepared from a suitable solution. Heating the sample resulted in phase separation above 190°C for compositions below 60 wt % PVC. Above 60 wt % PVC no phase separation was observed. Recently, theoretical study by Honeycutt[11] has also shown that the miscibility of this blend system is composition dependent. The blend is

predicted to show higher miscibility for higher compositions of PVC, which agrees with most of the experimental results so far. The reason for miscibility has been attributed to the C—H..O type of interaction between C_α—H of PVC and —C=O of PMMA.[6,18] The NMR studies of these blends have also suggested existence of such hydrogen bonding interaction.[10] Earlier Li et al.[18] have studied two model sytems where they compared blends of chlorinated atactic polypropylene (cPP) with ethylene vinyl-acetate copolymer (EVA) and with PMMA. They found that while cPP/EVA blend is miscible in the whole composition range, cPP/PMMA shows composition dependent miscibility. This difference in miscibility was attributed to weaker H-bonds in the later. It was argued that the ester —C=O of PMMA being close to the back bone is sterically hindered, and therefore, has low H-bond acceptor potential and hence make weaker H-bonds. In comparison, —C=O of EVA is somewhat away from the backbone and is sterically not hinderd and hence can make good hydrogen bonds. Hence, we believe that C—H..O interaction, which is as such a weak interaction, should be very weak in PVC/PMMA system also due to steric hindrance of —C=O of PMMA. The enthalpy contribution of this H-bond is perhaps not good enough for making the blend miscible at all compositions. Our FTIR studies on PVC/PMMA blends also showed that the magnitude of the H-bonding interaction is composition dependent and is more effective for higher concentrations of PVC in the blend.[19] All these studies establish that the miscibility of PVC/PMMA blend is composition dependent and that the miscibility increases with higher composition of PVC in the blend. Our thermal studies give similar results for the miscibility of this blend system.
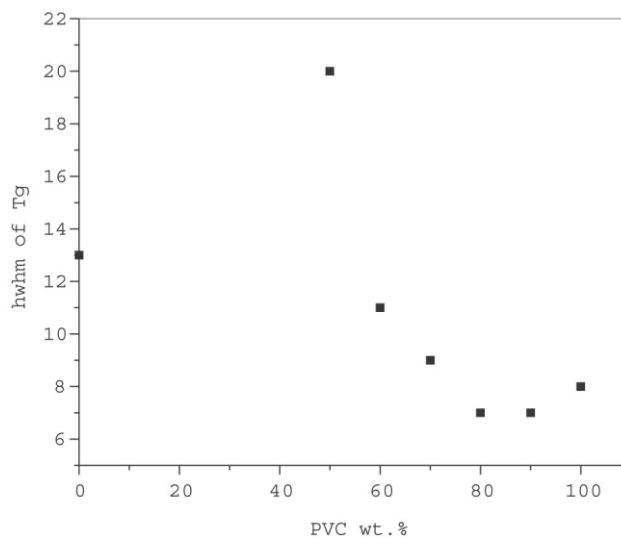

Figure 2 Half width analysis of Tg peaks of PVC, PMMA, and their blends.
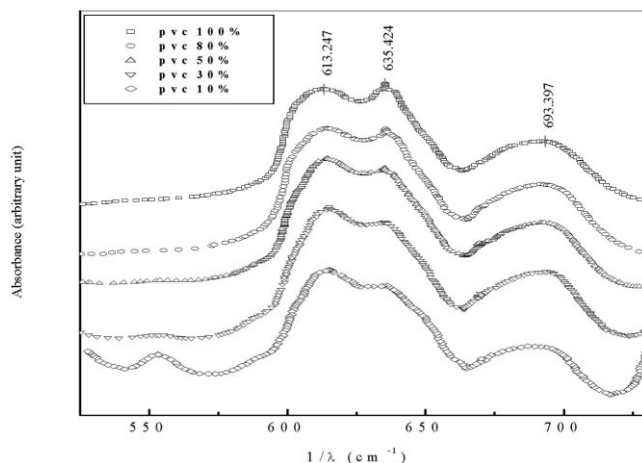
Figure 3 IR absorbance of PVC–PMMA blends.

FTIR studies

The C—Cl stretching vibration of PVC is very sensitive to conformational changes in the PVC backbone. This fact has been used in the past to monitor the conformational changes occurring in the PVC on thermal treatment[20] and upon plasticization.[21] The PVC bands centered at 615 and 636 cm^{-1} are believed to be due to short uncoupled planar zigzag (TT) and long coupled planar zigzag (TTTT) structures of the syndiotactic sequences.[21] Krimm et al.[22] have attributed the 680–700 cm^{-1} carbon chlorine stretching vibration to noncrystalline structures in PVC. They found that this band was separable into two bands centered at 685 and 693 cm^{-1} and was assigned to S$_{CH}$ mode where the subscripts denote atom trans to Cl. The 685 cm^{-1} band was assigned to more stable (TGTG) of the two conformations possible for the isotactic segment, while the 693 cm^{-1} band was assigned to the least stable of the two conformations for the syndiotactic pairs of the adjacent chlorine containing units. The latter band is reported to give parallel dichroism (D > 1) upon stretching, which was never observed in our study for pure PVC. The 685 cm^{-1} peak on the other hand, is reported to give only perpendicular dichroism.[22,23] Therefore, for the present study, the 693 cm^{-1} peak has been assumed to originate from mostly isotactic chains with the S$_{CH}$ conformation. Our interpretation of this peak is in agreement with that of other workers.[21,24]

The conformational changes induced by blending of PVC with PMMA have been studied in the 600–725 cm^{-1} region of IR spectrum (Fig. 3). It is seen that for pure PVC, both 615 cm^{-1} and 635 cm^{-1} peaks are prominent. For lower PVC concentrations, 635 cm^{-1} peak becomes less pronounced. Although it is usually possible to measure changes in the conformational structure of polymers by FTIR difference spectroscopy, digital subtraction was inapplicable owing to

the considerable overlap of conformationally insensitive 2960 cm^{-1} band of PVC with that of C—H stretching vibrations of PMMA. The problem was further complicated by the small but definite wave number shift of some $\nu_{(C-Cl)}$ stretching vibrations in blended PVC with respect to the pure PVC. Hence, for the conformational analysis, the ratio of the peak height of 636 cm^{-1} (TTTT) with respect to the 615 cm^{-1} peak (short TT) were plotted against the PVC composition in the blend (Fig. 4). Similar results were obtained for 693 cm^{-1} peak (not shown). The choice of 615 cm^{-1} band as reference was made as other choices (693 and 636 cm^{-1}) gave inconsistent results with the dichroism studies. This is discussed further in later sections. As can be seen from the Figures 3 and 4, the intensity of 636 and 693 cm^{-1} decreases with respect to the 615 cm^{-1} peak as the PVC composition is decreased (i.e., when the blend composition is changed from miscible to immiscible compositions). These changes can be attributed to the progressive breaking down of the stable syndiotactic long planar zigzag TTTT and isotactic TGTG structures, as the PVC concentration is reduced and the blend becomes immiscible. Here, the changes in the *gauche* conformations could not be confirmed by IR spectra directly because of the nonresolution of the absorption bands at 647 and 680 cm^{-1}, corresponding to *gauche* conformations in PVC. However, our interpretation of the IR results is in agreement with the dichroism studies, which shows definite conformational changes in the isotactic region represented by the 693 cm^{-1} peak.

Conformationally sensitive band has been reported for PMMA in the IR region of (800–900 cm^{-1}) by Spevacek et al.[25] Our FTIR studies did not reveal any noticeable change in this region for the different compositions of the blend. However, this difference could be due to the difference in tacticity of the PMMA
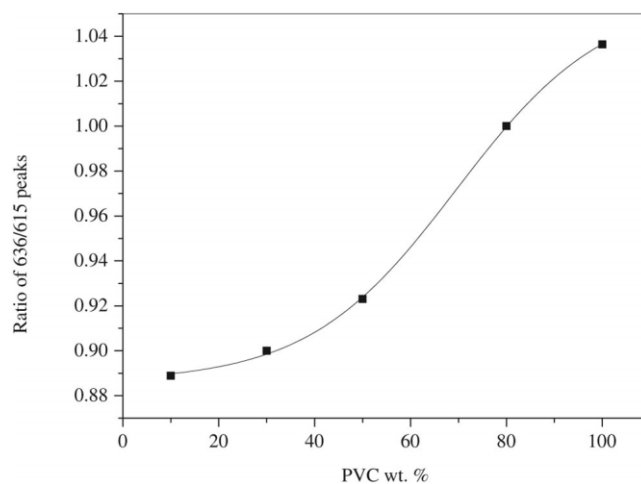

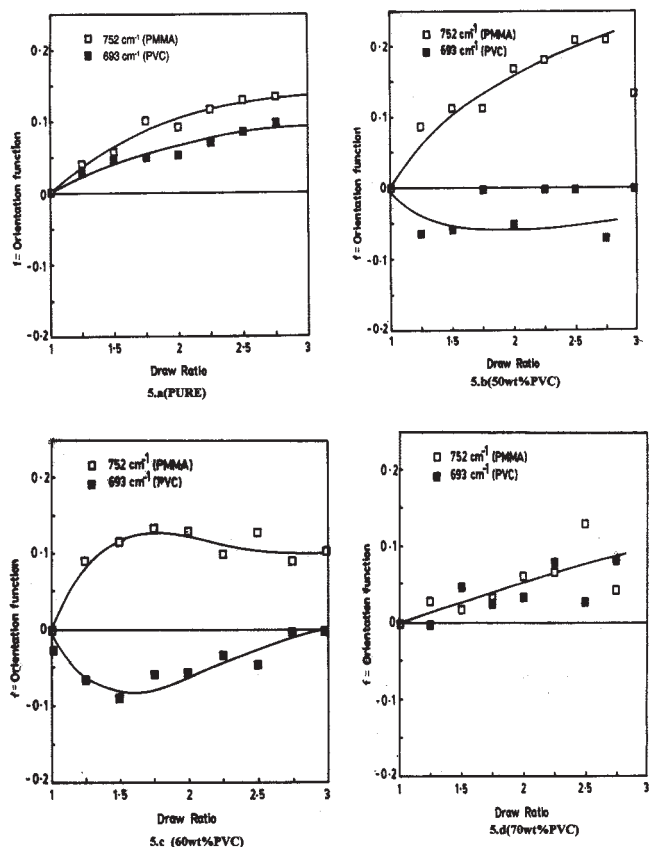**Figure 4** Variation of ratio TTTT structures to TT structures with PVC% in the blends.

Figure 5 Behavior of orientation function with draw ratio for PVC/PMMA at different wt % of PVC.

samples used by them (*syndiotactic*) and our sample, which was *atactic*.

Orientation measurements

For the study of blends by infrared dichroism, it is required to have nonoverlapping absorption bands in the infrared region. In this study, the nonoverlapping bands of PVC and PMMA at 693 cm^{-1} and 752 cm^{-1}, respectively, were selected. The PVC band at 693 cm^{-1} is associated with TGTG conformation of isotactic segments, while the 750 cm^{-1} band of PMMA is assigned to the skeletal vibrational motion affected by CH$_2$ rocking vibration.[26] The angle between the chain axis and the transition moment vector for the 750 cm^{-1} vibration of PMMA is measured to be at 17°.[26] For pure PVC this angle was taken as 90°.[27]

Results of orientation study are plotted as values of orientation function $f(\theta)$ versus apparent draw ratio. [Fig. 5(a)] shows the orientation behavior of pure PVC and PMMA. As seen from the figure, both PVC and PMMA show increase in $f(\theta)$ with draw ratio. The values of orientation function for these two polymers have the same order of magnitude as obtained by other coworkers.[15,26,27] The orientation behavior of PVC/PMMA blend with PVC wt % changing from 10

to 90%, were studied. Figures 5(b)–5(d) show orientation behaviors of PVC and PMMA in the blends containing 50, 60, 70 wt % of PVC, respectively. As shown in Figure 5(b), PVC shows negative values of $f(\theta)$ with draw ratio, whereas PMMA shows positive values, which increase monotonically with draw ratio. Similar negative behavior for PVC was noted for all blends containing lower wt. % of PVC. It was also noted that for the lower concentration of PVC in the blend, its orientation function showed higher degree of fluctuations with draw ratio when compared with that of PMMA, probably because of random distribution of minor phase-separated PVC domains. In the blend containing 60 wt % PVC, [Fig. 5(c)], both PVC and PMMA show change in the trend of orientation behavior at higher draw ratio. Initially, there is increase in $f(\theta)$ value of PVC up to the draw ratio of 1.5, thereafter the value starts decreasing continuously. A similar trend, although less pronounced, is observed for PMMA. As the concentration of PVC is increased to 70 wt %, the orientation behavior of PVC flips. Now it gives positive values with draw ratio instead of negative ones [Fig. 5(d)]. Interestingly, at this composition both PVC and PMMA show same magnitude and trend of orientation with draw ratio. Similar cooperative behavior of orientation function with draw ratio was observed for all blends containing more than 70 wt % PVC. The variation of orientation function of PVC and PMMA with PVC wt. % in the blend at a fixed draw ratio of 2.75 is shown in the Figure 6. Here, PMMA shows increasing trend till 50 wt % and shows a transition between 50 and 60 wt % PVC in the blend achieving a constant value for blends containing 70 wt % and higher concentration of PVC. PVC shows negative values of $f(\theta)$ up to 60 wt % PVC concentration and shows positive values at higher concentrations. For PVC, a typical 'S'-shaped curve is obtained which cuts the x-axis between 60 and 70 wt % PVC concen-
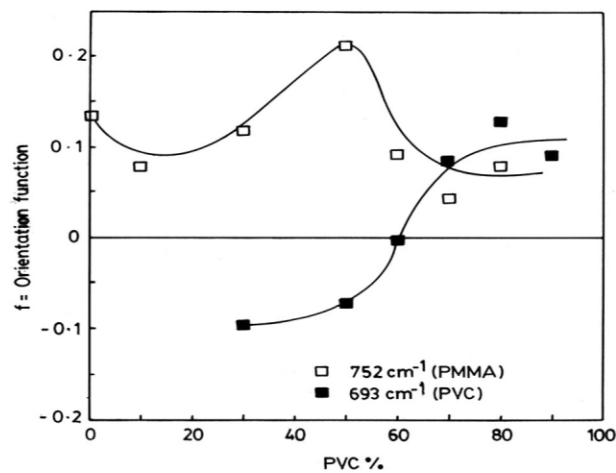

Figure 6 Behavior of orientation function with PVC wt % in blends for draw ratio 2.75.

tration. This indicates a possible conformational transition of PVC taking place in the blend around this composition. Similar results were obtained at all draw-ratios. However, more pronounce effects are observed only at higher draw ratios.

As shown by our thermal studies, the PVC/PMMA blend is immiscible up to 50 wt % of PVC in the blend, our study of conformation analysis shows that as the concentration of PVC in the blend reduces, there is a progressive breaking down of the stable syndiotactic long planes zigzag TTTT and isotactic TGTG structures. Up to this composition, the PMMA forms a continuos matrix in which the PVC molecules are distributed like solute. When phase separated, PVC molecules curl up and form spherical domain to reduce the surface area of interaction. This curling of molecules is achieved by the introduction of turns in long syndiotactic planar zigzag (TTTT) and long isotactic (TGTG) sequences. This could be achieved by change of *trans* conformations to *gauche* conformations at suitable sites. The conformational changes in the syndiotactic short planar zigzag (TT) sequences are assumed to be minimum. This could be justified as the bends along the chain length can be easily achieved without breaking of such short sequences, which are otherwise stable. In the immiscible blends, because of curling of the PVC molecules by introduction of turns along the chain, the value of the angle α drastically changes. As can be seen from eq. (3), the value of this angle is considered as constant for calculation of the orientation function $f(\theta)$. Hence, any drastic change in the angle α will be reflected in terms of sudden change in the values of the PVC orientation with composition as the same value of the angle $\alpha = 90°$ has been used through out for calculation of $f(\theta)$. We would like to mention that the negative values of $f(\theta)$ in the immiscible blend need not mean that the molecules are oriented at angles greater than 54.74° with the draw axis as the exact value of angle α in immiscible blends is not known for calculations. It probably only indicates a different conformation for PVC in immiscible blends. As the blend composition changes from immiscible to miscible, the normal conformation of PVC is restored, which contains relatively more long syndiotactic planar zigzag (TTTT) and long isotactic (TGTG) sequences when compared with immiscible blends. This restores the normal value of angle α, which is reflected in the transition of $f(\theta)$ in going from immiscible to miscible composition. Thus, we interpret the transition in $f(\theta)$ with composition to be due to change in miscibility of the blend accompanied by simultaneous change in PVC conformation. The higher degree of extended PVC structure in the miscible blends allows greater interaction between PVC and PMMA molecules, which leads to greater cooperativeness in their chain orientation function.

The slight difference in the interpretation of miscibility by the DMA and orientation studies could be due to considerable overlapping of the two transition bands in DMA, which are very close together as explained earlier. This difference in the interpretation of miscibility by thermal method and the orientation method highlights the more subtle nature of the orientation method and its advantage over thermal method for detecting miscibility.

It may be noted that the behavior of $f(\theta)$ of PMMA also indicates progressive conformational changes within immiscible blend as the PMMA composition decreases continuously. A sharper transition in $f(\theta)$ occurs upon miscibility, which is expected to behave like PVC in the miscible blend. However, as pointed earlier, we could not see any changes in the conformationally sensitive IR region of PMMA, which lies between 800 and 900 cm^{-1}.[25] This we believe could be due to less sensitivity of this peak to detect the conformational changes occurring in atactic PMMA, which was used in the present study. In the absence of independent evidence, we find it difficult to speculate about the nature of conformational changes in PMMA in the blend.

CONCLUSIONS

Our study suggests that the chain orientation behavior of individual polymers in the immiscible blend is independent of each other as they are in different phase separated domains while there is high degree of cooperativeness in miscible blends. Conformational changes occur in at least one of the blend components when blend changes its phase from immiscible to miscible, which is reflected in transition of its orientation function. Hence, the chain orientation studies of the blends can provide useful information about the miscibility of the polymer blends at molecular level. Since, immiscible blends show phase-separated domains with coiling of chains of at least that polymer forming minor domain, the curling model used here to explain the behavior may be applicable to other systems as well for study of miscibility at the molecular level.

References

1. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer-Polymer Miscibility; Academic Press: New York, 1979.
2. Kwei, T. K.; Wang, T. T. In Polymer Blends; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1978.
3. Walsh, D. J.; Rostami, S. Adv Polym Sci 1985, 70, 119.

4. Utracki, L. A. Polymer Alloy and Blends; Hanser: Munich, 1989.

5. Wang, J.; Cheung, M. K.; Mi, Y. L. Polymer 2001, 42, 3087.

6. Schurer, J. W.; Boer, A. D.; Challa, G. Polymer 1975, 16, 201.

7. Vanderschueren, J.; Janssens, A.; Ladang, M.; Niezette, J. Polymer 1982, 23, 395.

8. Albert, B.; Jerome, R.; Teyssie, P.; Baeyensvolant, D. J Polym Sci Polym Chem 1986, 24, 551.

9. Wlochowicz, A.; Janicki, J. J Appl Polym Sci 1989, 38, 1469.

10. Kogler, G.; Mirau, P. A. Macromolecules 1992, 25, 598.

11. Honeycutt, J. D. Macromolecules 1994, 27, 5377.

12. Ward, I. M. Structure and Properties of Oriented Polymers; Applied Science: New York, 1975.

13. Lunn, A. C.; Yannas, I. V. J Polym Sci Part B: Polym Phys 1972, 10, 2189.

14. Jasse, B.; Koenig, J. L. J Polym Sci Part B: Polym Phys 1979, 17, 799.

15. Saito, H.; Inoue, T. J Polym Sci Part B: Polym Phys 1987, 25, 1629.

16. Vorenkamp, E. J.; Tenbrinke, G.; Meijer, J. G.; Jager, H.; Challa, G. Polymer 1985, 26, 1725.

17. Jager, H.; Vorenkamp, E. J.; Challa, G. Polym Commun 1983, 24, 290.

18. Li, W. S.; Shi, L. H.; Shen, D. Y.; Wu, Y. S.; Zheng, J. Polymer 1989, 30, 604.

19. Deshpande, V. D.; Singh, U. M. Macromolecules-New Frontiers, Vol. II; In IUPAC Symposium on Advances in Polymer Science and Technology, Chennai, India, January 1998.

20. Koenig, J. L.; Antoon, M. K. J Polym Sci Part B: Polym Phys 1977, 15, 1379.

21. Theodorou, M.; Jasse, B. J Polym Sci Part B: Polym Phys 1983, 21, 2263.

22. Krimm, S.; Folt, V. L.; Shipman, J. J.; Berens, A. R. J Polym Sci 1963, A-1, 2621.

23. Shimonachi, T.; Tsuchiya, S.; Mizushima, J. J. J Chem Phys 1959, 30, 1365.

24. Hubbell, D. S.; Cooper, S. L. J Polym Sci Part B: Polym Phys 1977, 15, 1143.

25. Spevacek, J.; Schneider, B.; Dybal, J.; Stokr, J.; Baldrian, J. J Polym Sci Part B: Polym Phys; 1984, 22, 617.

26. Zhao, Y.; Jasse, B.; Monnerie, L. Polymer 1989, 30, 1643.

27. Chabot, P.; Prudhomme, R. E.; Pezolet, M. J Polym Sci Part B: Polym Phys 1990, 28, 1283.