

The effect of introduced hydrogen bonding on miscibility of polymer blends studied by excimer fluorescence

Ming Jiang*, Xianyi Cao, Wenjie Chen, and Tongyin Yu

Institute of Materials Science, Fudan University, Shanghai, People's Republic of China

Summary

Polymer-polymer miscibility in immiscible polymer blends can be considerably enhanced by introducing specific interactions between component polymers. In this paper, the effect of introduced hydrogen bonding in blends of modified polystyrene containing hydroxyl groups and copolymer of 2-vinyl naphthalene and methyl methacrylate is examined by excimer fluorescence. This technique is proved to be effective in monitoring the degree of mixing of the component polymer chains as functions of both intensity of hydrogen bonding and concentration of the guest polymer. The results also indicate the presence of heterogeneity of chain distribution on a very small scale which may be undetectable by routine techniques.

Introduction

In terms of phase behaviour, polymer blends can be roughly classified into miscible and immiscible categories. However, recent developments in exploring the role of specific interaction between component polymers on the miscibility have made the boundary between the two categories indistinct. Many experimental results in literature have proved that the miscibility in polymer blends can be substantially enhanced by introducing a certain amount of such chemical groups or ions, which are capable of establishing hydrogen bonding (1) or ion-ion (2) interaction between the polymers pairs. In the case of hydrogen bonding, the effect of such chemical modification of a component polymer on the miscibility is very remarkable, for example, only about 2 mole% of strong proton-donor groups introduced can make typical immiscible blends such as polystyrene (PS) and poly(ethyl methacrylate) completely miscible as seen by differential scanning calorimetry (DSC) (1). Recently, in our laboratory, attention has been paid on the effect of the chemically introduced specific interaction on the miscibility (3,4). For blends of PS and some of poly(acrylates) and poly(methacrylates), a regular and broad variation in miscibility and morphology of the blends with the amount of proton-donor-containing groups introduced in PS was observed. As far as the degree of mixing between the component polymers, this type of blend is of particular interest since its miscibility achieved is mainly caused by hydrogen bonding between proton-acceptor and proton-donor groups and the latter

*To whom offprint requests should be sent

may only exist in a few percent of repeating units in one modified component while the rest of the chains are substantially repulsive with the counter polymer chains. Better understanding of the degree of mixing needs characterization of the possible heterogeneity in spatial distribution of the two component segments on very small scale for the blends which may be shown to be miscible by the routine characterization techniques such as DSC and dynamic mechanical analysis. Solid NMR and fluorescence techniques including excimer formation and non-radiative energy transfer have been regarded as powerful methods for this purpose.

Among existing techniques capable of examining the miscibility in polymer blends, excimer fluorescence, which was first used for polymer-polymer miscibility study by Frank et al. (5,6), possesses the following advantages, i.e. first, concentration sensitivity sufficient for studying the miscibility of blend components at concentrations as low as 0.5 wt% or even less, and second, sensibility of excimer formation to the immediate environment of excimer-forming groups leading to the ability of monitoring molecular interpenetration at a scale much smaller than that in other conventional techniques. An apparent limitation of this technique is that the minor component in blends, which is usually called guest polymer, must consist of aryl fluorescence chromophores. In this method, the ratio of excimer to monomer emission intensities I_e/I_m is the main measured value. Two groups of blends have been studied systematically by Frank et al. For the first group consisting of a series of blends of Poly(2-vinyl naphthalene) (PVN) with PS or PMMA (5,6,7), I_e/I_m is proved to be effective in monitoring the influence of molecular weight of the two host polymers on the miscibility. The other group is the blends of PVN with members of a homologous series of poly(alkyl methacrylates) host polymers (8). I_e/I_m observed has shown its clear dependence on the type of host matrix and good correlation of this dependence with the difference in solubility parameters of the guest and host polymers. Although the achievements of this technique in miscibility study are apparent, the types of blends which have been examined by this method are still limited. In this communication, recent results of using the technique to study the effect of introduced hydrogen bonding on the miscibility of blends are reported. Instead of PVN homopolymer, copolymer of 2-vinyl naphthalene and minor amount of methyl methacrylate is used as the guest. This modification makes the guest possess both functions of fluorescence chromophore and proton-acceptor group.

Experimental

materials Preparation of Hydroxyl group-containing monomer p-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)- α -methyl styrene and its copolymers with styrene were described previously (4). The copolymers obtained are denoted by PS(OH) followed by figures referring to the mole fraction of the hydroxyl-containing units. The average molecular weights of PS(OH) with

hydroxyl contents varied from 0 to 30 mole% are in the range of 30 to 100 Kg/mole. Details are described in ref.4. Copolymers of 2-vinyl naphthalene and methyl methacrylates were prepared by copolymerization of carefully purified 2-vinyl naphthalene and methyl methacrylate in benzene with azobisisobutyronitrile as initiator at 60°C in ampoules. The products were reprecipitated in dichloromethane/methanol for three times. The compositions of the copolymers were measured by UV spectroscopy. The copolymers are denoted as PVN-M followed by figures, if necessary, referring to the mole fraction of MMA units. Two samples having 8.2 and 9.0 MMA mole% and molecular weights 102 and 59 Kg/mole respectively were used in this study.

Low molecular weight polystyrene was prepared by routine ionic polymerization. Polystyrene with proton-donor end group was obtained by terminating the living ionic polystyrene with hexafluoroacetone.

Excimer fluorescence measurements A Spex 1212 Spectrofluorometer was used. Measurements were performed with exciting irradiation at 290 nm and the fluorescence intensities at 340 nm and 400 nm were taken as the monomer and excimer emission respectively. The samples for fluorescence measurements were solvent casting films from toluene. Prior to measuring, the films were kept in a vacuum oven at 90°C for 12 hours.

DSC measurements A Dupont 10908 Thermal Analyzer was used. The related experimental conditions were mentioned in ref.4.

Results and Discussion

Glass transition behaviour of a series of blends of PVN-M and PS(OH) in weight compositions of PVN-M/PS(OH) 30/70 and 50/50 was examined by DSC. Part of the results shown in Table 1. indicate that PVN-M8.2 is immiscible with homopolymer PS, PS(OH)1.9 and PS(OH)2.8 in the blends with weight composition 50/50 as two T_gs associated with the guest-rich and host-rich phases respectively are detected. However, more hydroxyl groups incorporated into PS make the blends miscible as only single T_g is observed for the blends comprising PS(OH)9.7 and PS(OH)29. The results for blends of PVN-M9 with PS(OH) in composition of guest/host 30/70 lead to the similar conclusion.

PVN-M8.2	blends of PVN-M8.2 with				
	PS	PS(OH)1.9	PS(OH)2.8	PS(OH)9.7	PS(OH)29
145	102,145	106,143	107,138	134	142

Tab.1 Glass transition temperature (°C) for PVN-M8.2 and its blends with PS(OH) (w/w 50/50)

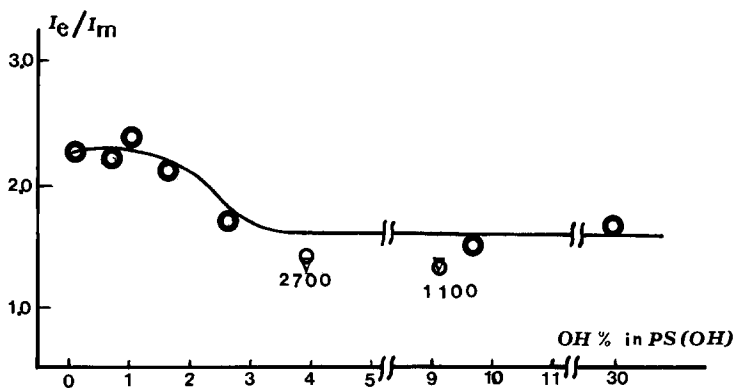


Fig.1 Dependence of I_e/I_m for blends of PVN-M8.2/PS(OH) (w/w 0.5/99.5) on hydroxyl content in PS(OH) (●), I_e/I_m values for blends of PVN-M8.2 and low molecular weight PS with (○) and without (▽) the proton-donor end-group.

Fig.1 shows the excimer fluorescence results of PVN-M8.2 in its blends with PS(OH) at very low guest concentration of 0.5 wt%. In this figure the values of I_e/I_m are recorded as a function of hydroxyl content in PS(OH). It is clearly seen that I_e/I_m appears to be unchanged for the host polymers having hydroxyl groups less than 2 mole%, then I_e/I_m apparently decreases as the hydroxyl content is increased from 2 to 3 mole%, and finally, I_e/I_m keeps constant at a lower level for all the blends having hydroxyl contents greater than 3%. Considering our DSC results that all the blends at higher concentrations of PVN-M (30 wt% and 50wt%) comprising PS(OH) with higher hydroxyl contents, i.e. 6.0, 8.2, 9.0, and 29 mole%, present only one glass transition, it is clear that, the blends with very low guest concentration giving low I_e/I_m plateau values in Fig.1 are miscible pairs while those corresponding to the high plateau I_e/I_m values are actually two phase systems. The area in between these two corresponds to the blends in which the level of interpenetration of unlike chains changes dramatically with the specific interaction. This result proves that excimer fluorescence may be qualified as a molecular probe for miscibility as a function of specific interaction in blends even when the blend composition is extremely unsymmetrical.

This feature of the curve in Fig.1 is quite similar to the results given by Frank et al (6,7) for the variation of I_e/I_m of PVN guest vs. molecular weight of host polymers. The common feature of the results is that for the variants, i.e. molecular weight in Frank's work and hydroxyl content in the present paper, to be either very low or high, I_e/I_m appears almost constant at different levels and I_e/I_m changes apparently with the variants as the latter assumes some medium values. Although it has been known that for a given guest-host system, I_e/I_m value depends on two main factors associated with

the degree of mixing in a blend, i.e. the number of intermolecular excimer sites and the efficiency of energy migration along the guest chains, there is still not sufficient knowledge to analyse the results quantitatively in terms of the two factors. However, the variation of I_e/I_m shown in Fig.1 does reflect the change of molecular morphology of the blends i.e. the distribution of the two types of the component polymer chains. In other words, this common feature reflects the variation of the degree of mixing with the thermodynamic driving forces, i.e. in Frank's case, the entropy change with molecular weight and in our case, the enthalpy change with the content of the introduced hydroxyl groups.

Besides the general trend of the miscibility variation with the specific interactions, this excimer fluorescence study presents some information useful for detecting the possible heterogeneity on a very small scale. I_e/I_m values for four blends of PVN-M8.2 with low molecular weight polystyrene are shown in Fig.1. It is interesting that the I_e/I_m value (1.46) for the blend with PS of molecular weight 1100 is almost the same as that (1.40) for the blend with PS having the same molecular weight but terminated with $(CF_3)_2-C(OH)-$. Furthermore, both PS species of molecular weight 2700 with and without the proton-donor end-groups give the similar I_e/I_m values (1.48, 1.38). These low values given by the four blends indicate that they are miscible blends and the presence of the proton-donor end-group in PS does not make any effect on the level of mixing. Clearly, the relatively large entropy of mixing due to the low molecular weight of PS in the blends constitutes the main part of driving force for mixing. In comparison with the low plateau value of I_e/I_m (1.65) for the blends in which PS(OH) having higher molecular weight and hydroxyl contents, the values given by the four blends are lower. The difference is slight but is larger than the experimental error. This difference, in our opinion, may reflect the disparity in the degree of mixing between the two kinds of blends. For the blends consisting of low molecular weight PS, the driving force from favourable entropy makes the unlike chains to interpenetrate each other closely while for the blends with high molecular weight, miscibility is caused by the favourable hydrogen bonding, which is only sparsely distributed along the chains while the most part of the unlike chains are inherently repulsive. Therefore, for the latter case, it is understandable that unlike chains may distribute more uniformly near hydrogen bonds but not so in the area relatively far from these bonds. However, this heterogeneity may exist on a scale smaller than that detectable by the routine techniques such as DSC. This preliminary result shows a nice prospect of excimer fluorescence in exploring the degree of mixing in polymer blends on a scale, say, much smaller than 10 nm.

Fluorescence study carried out in this laboratory on the effect of concentration on the observed I_e/I_m provides more

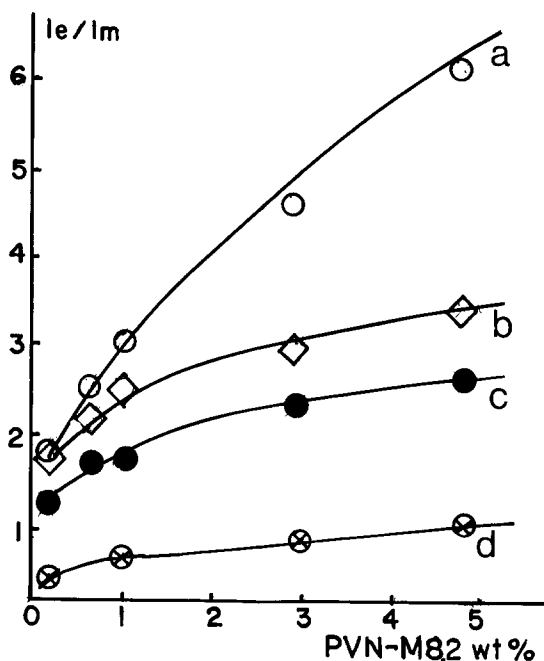


Fig.2 Dependence of I_e/I_m on concentration of PVN-M in PS(OH)/PVN-M blends
OH mole % in PS(OH):
a - 0, b - 1.9, c - 2.8,
d - 6.0

information on the miscibility of the systems. Fig.2 shows variation of I_e/I_m of guest polymer PVN-M as a function of concentration of the guest in host polymer PS(OH) with different hydroxyl content. Generally, as expected, I_e/I_m increases with the guest concentration in spite of hydroxyl content in PS(OH), since the number of excimer-forming sites between naphthalene rings on different molecular chains i.e. intermolecular excimer, increases with the guest concentration. All the curves in Fig.2 show linearity in the range of concentration from 2% to 5% PVN-M. A remarkable feature of these curves is that the slope for the blend of PVN-M and homopolymer PS is much larger than those for the others. Frank et al.(8) studied the effect of guest PVN concentration for blends of PVN and members of poly(methyl acrylates) and found apparent dependence of the slope on the difference in the solubility parameters of the guest and host. According to Frank et al.(8), in the case of complete miscibility, the guest segments uniformly pervade in matrix, I_e/I_m should be varied with guest concentration (C) linearly i.e. $I_e/I_m = AC$, where A is a proportional constant. However, for immiscible systems, clustering of the guest segments causes the local concentration to increase relative to that of the bulk, and obviously the degree of clustering is associated with Flory-Huggins interaction parameter χ . Combining both the effects of uniform and clustered distribution of guest segments, the dependence of I_e/I_m on the concentration may be written as $I_e/I_m = A(1+B\chi/A)C$ where B is a constant. Apparently, $B\chi$ represents the slope increment due to the chain clustering relative to uniform distribution of the guest chains. Since this increment is proportional to parameter χ , it may conclude that, the poorer the guest-host interaction, the more serious the local aggregation of the guest chains, and the

larger the slope of I_e/I_m against the guest concentration. The results shown in Fig.2 for the blends in which the miscibility is caused by hydrogen bonding between the guest and host polymers, are generally in accordance with this simplified model. That the largest slope associated with the case of homopolymer PS being the matrix is understandable because of the absence of hydrogen bonding. They are immiscible systems although it can not be judged by DSC due to low concentration of the guest. However, chain aggregation of PVN-M guest decreases apparently as small amount of hydroxyl groups are introduced, which is monitored by the dramatical decrease of the slope. Curves b, c and d are almost parallel each other indicating the same extent of uniformity of the guest chain distribution in the blends. Because DSC has shown single-phase structure for the blends of PS(OH)6 with higher concentration of PVN-M (30% and 50%), it is believed that the blends of PS(OH)6/PVN-M at much low guest concentration range as shown in curve d must be miscible ones. Therefore, the blends associated with curves b and c, which have the same slope as that of curve d are probably miscible systems, although the hydroxyl contents here are only 1.9 and 2.8 mole% respectively. Nevertheless, it can not infer that complete miscibility would be kept for the blends with higher guest concentration. In fact, two glass transition regions are observed by DSC for the blends comprising host PS(OH)1.9 and PS(OH)2.8 with PVN-M concentrations of 30% and 50%. In addition, preliminary experiments in this lab have shown that the slopes of curve b and c turn to higher values at higher guest concentration which may be associated with transition from uniformity to aggregation of the guest chains. This phenomenon will be discussed in the coming papers.

Acknowledgement

The authors are very grateful to The National Natural Science Foundation of China and Stiftung Volkswagenwerk for their financial support to this project.

References

1. See e.g. Pearce, E., Kwei, T.K., Min, B., J. Macromol. Sci., Chem. A21, 1181 (1984)
2. See e.g. Simmons, A., Eisenberg, A. Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 27(1), 341 (1986)
3. Jiang, M., Cao, X., Yu, T., IUPAC Macro 88, p.383, Kyoto (1988)
4. Cao, X., Jiang, M., Yu, T., Makromol. Chem. in press
5. Semerak, S.N., Frank, C.W., in "Polymer Blends and Composites in Multiphase Systems" ed. C.D. Han, Am. Chem. Soc., 77 (1984)
6. Semerak, S.N., Frank, C.W., Macromolecules, 17, 1148 (1984)
7. Semerak, S.N., Frank, C.W., Macromolecules, 14, 443 (1981)
8. Frank, C.W., Gashigari, M., Chutikamontham, P., Haverly, V.J., in "Structure and Properties of Amorphous Polymers" ed. by A.G. Walton, Elsevier Sci. Pub. Co. Amsterdam, 187 (1978)