Controllable specific interactions and miscibility in polymer blends: 5. Effect of crosslink density in interpenetrating polymer networks

Hong Xiao, Ming Jiang* and Tongyin Yu
Institute of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China
(Received 31 December 1993; revised 3 June 1994)

The effect of crosslink density in interpenetrating polymer networks (IPNs) with controllable hydrogen bonding composed of poly(butyl acrylate) (PBA) and polystyrene modified with hydroxyl-containing units [PS(OH)] on miscibility and morphology is studied. The results from d.s.c. and transmission electron microscopy (TEM) show that the crosslink density of PBA displays a two-fold effect on miscibility of the IPNs. For the IPNs made from immiscible polymer pairs with low hydrogen bonding density, crosslinking improves the degree of mixing, while for the IPNs composed of miscible polymer pairs due to hydrogen bonding, crosslinking causes microheterogeneity. An apparent discrepancy between the results of dynamic mechanical analysis and d.s.c. or TEM is observed and explained.

(Keywords: IPNs; hydrogen bonding; crosslink density)

INTRODUCTION

The motivation for studying interpenetrating polymer networks (IPNs) has been associated with the favourable effect of a crosslink structure on miscibility. Most polymer pairs are immiscible due to an unfavourable enthalpy of mixing and a small favourable entropy of mixing. However in the process of preparing an IPN system, the presence of the crosslink structure would retard the process of phase separation, resulting in some degree of phase mixing. This is called 'enforced miscibility'. A considerable body of experimental evidence leads to the conclusion that the apparent miscibility between the components characteristic of phase size and specific interface area in sequential IPNs gradually increases with increasing crosslink density of either the first or the second networks. Usually, the influence of the first network is more pronounced[1]. This problem has been studied by statistical thermodynamic considerations, i.e. Donatelli *et al.*[2] first derived an equation presenting the inverse proportionality of the domain size of the second polymer component to the crosslink density of the first network for semi-1 IPNs. Yeo *et al.*[3] developed a theory leading to similar conclusions applicable to both full and semi-IPNs. The significance of these experimental and theoretical studies is that the domain size, and hence some properties of an IPN, may be controlled for a given pair by changing the crosslink level of either component. However, in this context, a question naturally arises as to whether there is any limitation for improving miscibility just via crosslinking. In other words, whether it is possible to produce a single-phase IPN from a polymer pair just with the aid of crosslinking. We discuss this problem for two different cases. In the first, the polymer pair itself is immiscible due to dominant dispersion interactions and in the second, the polymer pair itself is miscible due to inherent or introduced specific interactions.

For the first case, the experimental results in the literature, as far as we know, seem to give a negative answer. So far there has been no work reporting that any full IPNs with a real single-phase can be prepared from a typical immiscible polymer pair, even for a polymer pair quite close to miscibility, e.g. polystyrene (PS) and poly(α-methyl styrene), which are mutually miscible under certain molecular weight conditions[4,5]. Recently, Widmaier[6] studied semi-IPNs composed of PS networks and linear poly(α-methyl styrene). In comparison with the corresponding blends of linear polymers, the IPNs displayed a much stronger tendency to phase separate, i.e. most IPNs showed two glass transition temperatures (T_gs) while the blends of the corresponding linear polymers with the same molecular weight possessed only one T_g. In contrast, some miscible IPNs are reported by Frisch *et al.*[7] based on immiscible polymer pairs. However, they are simultaneous IPNs in which both networks form in the same time period, so phase separation has been prevented.

For the second case, where a polymer pair itself is miscible due to specific interactions, no clear conclusion can be drawn with regard to miscibility in the IPNs based on the limited data in the literature. For the most studied miscible polymer pair of PS and poly(2,6-dimethyl-1,4-phenylene oxide), miscible simultaneous or semi-IPNs

---

* To whom correspondence should be addressed

0032-3861/94/25/5529-07

were reported[8] but for another well-known miscible blend of PS and poly(vinyl methyl ether), depending on the crosslink density of the PS networks, phase separation may take place[9,10]. For miscible blends of uncured epoxy resin and poly(ethylene oxide), phase separation occurred as crosslinking proceeded[11]. The IPNs studied by Nishi and Kotaka[12] were composed of the complex-forming polymer pair of polyoxyethylene and poly(acrylic acid). D.s.c. and dynamic mechanical analysis (d.m.a.) studies proved that complex formation was no longer possible between the tightly crosslinked networks. In the study of Kim *et al.*[13] on phenolic resin and methyl methacrylate (MMA) and Coleman *et al.*[14] on phenolic resin and a copolymer of ethylene and vinyl acetate (EVA), the disadvantageous effect of crosslinking on mutual miscibility was also reported.

Based on the above discussion, it is clear that in order to elucidate the role of crosslinking on miscibility in IPNs with strong intercomponent interactions, we need a system in which both crosslink density and intensity of the specific interaction are independently controllable over a broad range. The IPNs composed of a poly(acrylic ester) and PS(OH), in which a strong proton-donor-containing unit $-C(CF_3)_2OH$ is incorporated at will, can meet this requirement. In particular, since only ~2 mol% of the hydroxyl-containing units in PS(OH) can make its blends with poly(acrylic ester) miscible, introducing more hydroxyl into PS(OH), which is readily performed, may provide a much more favourable enthalpy of mixing than the need for making a miscible blend of linear polymers. Therefore, we may study the effect of crosslink density on miscibility at higher levels of interactions.

EXPERIMENTAL

The preparations of hydroxyl-containing monomer *p*-(1,1,1,3,3,3-hexafluoro-2-hydroxypropyl)-α-methyl styrene (HFMS) and IPNs composed of poly(butyl acrylate) (PBA) as the first network and PS(OH), i.e. a copolymer of styrene and HFMS, as the second network were reported in the preceding paper[15]. Characterization of the IPNs by turbidity measurements, d.s.c., TEM and d.m.a. were also described[15]. Turbidity τ was calculated through

$$\tau = -\ln(I/I_0)/L$$

where I/I_0 is the transmittance of the sample with thickness L.

As used in the preceding paper[15], in the sample codes of the IPNs, the numerals following B represent the type of the first network (PBA), whose number-average molecular weights between crosslinks (M_c) measured by swelling in toluene, methyl ethyl ketone (MEK) and tetrahydrofuran (THF), respectively, are listed in *Table 1*. The numerals following S represent the weight percentage of the crosslink agent in the PS(OH) network and the numerals in the middle represent the hydroxyl contents in PS(OH).

RESULTS AND DISCUSSION

First, we discuss the effect of crosslink density (*CD*) of network 1 (PBA) on turbidity at different hydroxyl contents (0, 1, 5 and 30 mol%) in PS(OH) (*Figure 1*). For the first two cases of low hydroxyl contents, when the corresponding blends of the linear polymers are immiscible, there exists an apparent dependence of transparency on *CD*. The increase in *CD* causes a substantial decrease of the turbidity, indicating an increase of the degree of phase mixing. However, the results for the cases with high hydroxyl contents (5 and 30 mol%) for which the corresponding linear blends are miscible, are quite different. These IPN films, independent of the *CD*, look transparent with very low turbidity (0.04–0.06). In fact, the influence of *CD* on turbidity here, if any, could not be detected. This means that phase separation in these samples may not exist or, if any, on a scale much smaller than visible light wavelengths. The real phase structure can only be detected by a combination of techniques, in particular d.s.c., TEM and d.m.a.

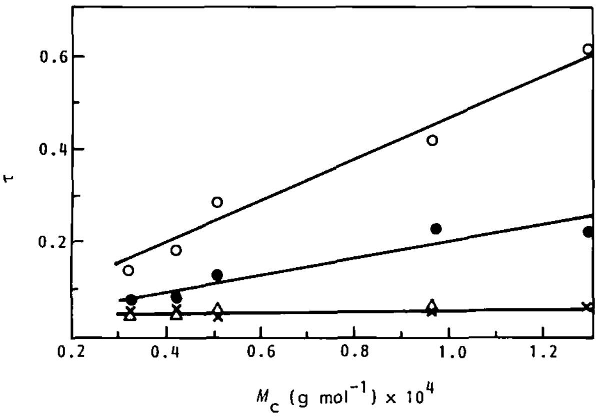

Figure 1 Dependence of the turbidity of IPNs on crosslink density of the PBA network at different levels of OH content in PS(OH): (○) 0; (●) 1; (△) 5; (×) 30 mol%

Table 1 Characterization data of PBA networks

	M_c in		
Sample code	Toluene	MEK[a]	THF
B1	16000	13000	14000
B2	14000	9700	12000
B3	6700	5100	4800
B4	5900	4200	4500
B5	5400	3200	3900

[a] In the text, only the values measured in MEK are used

For all the samples listed in *Table 2* covering a broad range of hydroxyl content (0–50 mol%) in PS(OH) and *CD* of PBA (M_c = 3200–13000) and PS(OH), the most remarkable feature of the d.s.c. results is that all the samples display two glass transitions indicating the existence of phase-separated structures. *Figures 2a–e* show the dependences of both the high T_g and the low T_g on the *CD*s of the PBA and PS(OH) networks. *Figure 2a* is for the case without any introduced hydroxyl-containing units, i.e. an ordinary IPN. The dependences of the high T_g and the low T_g on *CD* are different. For the high T_g, the shift to a lower temperature gradually increases with increasing *CD* of the PBA, while for the low T_g, being quite close to that of pure PBA, is almost independent of the *CD*. Therefore, the two transitions may be associated with a 'pure' PBA phase and a 'mixed phase' with comparable amounts of both components.

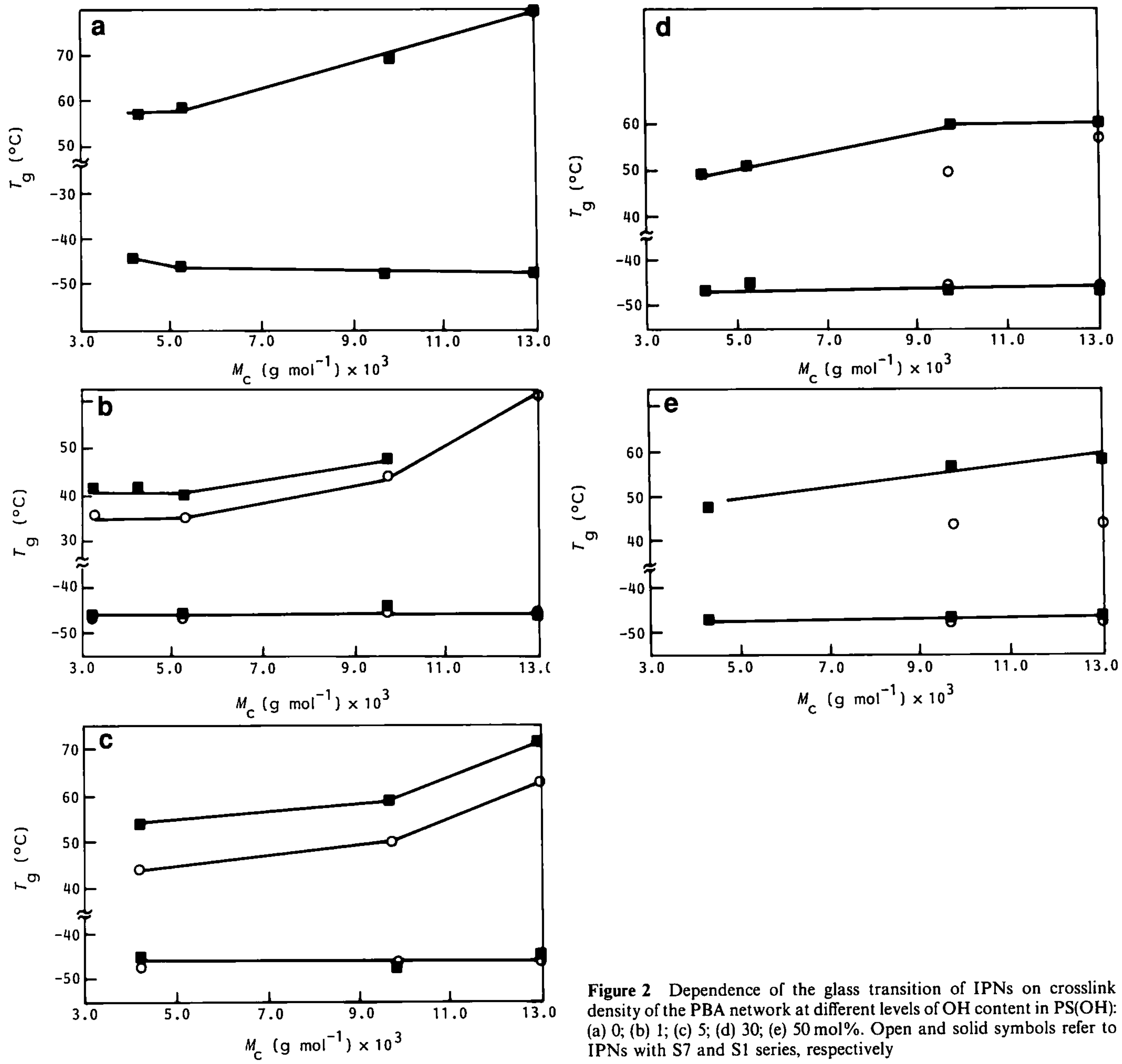

Figure 2 Dependence of the glass transition of IPNs on crosslink density of the PBA network at different levels of OH content in PS(OH): (a) 0; (b) 1; (c) 5; (d) 30; (e) 50 mol%. Open and solid symbols refer to IPNs with S7 and S1 series, respectively

This general feature is also found in the cases of hydroxyl contents being 1 and 5 mol% (*Figures 2b* and *c*). The decrease of the high T_g with increasing *CD* represents the general trend of miscibility enhancement caused by increasing the *CD* of the PBA. By comparing the results for the S1 series with those for the S7 series shown in *Figures 2b* and *c*, it can be found that, generally, an increase of the *CD* of the PS(OH) network causes an increased shift of the high T_g, but almost has no effect on the low T_g. *Figures 2d* and *e* are for the IPNs with higher (30 and 50 mol%) hydroxyl contents. Although the corresponding linear blends with high hydrogen bonding density are certainly miscible and even form a complex, the IPNs give two-phase structures. However, we cannot attribute this simply to the unfavourable effect of *CD* on miscibility. We still find some tendency for a decrease in the high T_g with increasing *CD*, although it is not as apparent as in *Figures 2a* and *b*. Therefore, in the IPNs with high contents of interpolymer hydrogen bonding, crosslinking has a complicated effect on miscibility. Its elucidation needs several approaches as discussed later.

The morphological features of the IPNs studied by TEM support the conclusions of the d.s.c. studies. First, all the samples listed in *Table 2* show phase-separated structures. Some typical micrographs are shown in *Figures 3a–h*. Two-phase structures are even found for the IPNs in which the hydroxyl content is as high as 30 mol%. In this case the phase structure is extremely fine (< 10 nm, as shown in Figure 2d of ref. 15). By comparing *Figures 3a* and *b*, *c* and *d*, *e* and *f* and *g* and *h*, where each pair has the same *CD* of PS(OH) and the same OH content but different *CD*s of the PBA, one may see a relatively clear decrease of phase size with increasing

Table 2 Characterization data of IPNs

Sample code	PS(OH)/PBA	OH content in PS(OH) (mol%)	M_c of PBA network (kg mol^{-1})	Crosslink agent in PS(OH) (wt%)
B1-0-S1	49/51	0	13.0	1
B2-0-S1	48/52	0	9.7	1
B3-0-S1	49/51	0	5.1	1
B4-0-S1	48/52	0	4.2	1
B5-0-S1	48/52	0	3.2	1
B1-1-S1	48/52	1	13.0	1
B2-1-S1	49/51	1	9.7	1
B3-1-S1	49/51	1	5.1	1
B4-1-S1	48/52	1	4.2	1
B5-1-S1	48/52	1	3.2	1
B1-1-S7	48/52	1	13.0	7
B3-1-S7	49/51	1	5.1	7
B4-1-S7	49/51	1	4.2	7
B4-1-S7	47/53	1	4.2	7
B5-1-S7	48/52	1	3.2	7
B1-5-S1	49/51	5	13.0	1
B2-5-S1	49/51	5	9.7	1
B3-5-S1	48/52	5	5.1	1
B4-5-S1	47/53	5	4.2	1
B5-5-S1	48/52	5	3.2	1
B1-5-S7	47/53	5	13.0	7
B2-5-S7	48/52	5	9.7	7
B3-5-S7	48/52	5	4.2	7
B1-30-S1	48/52	30	13.0	1
B2-30-S1	46/54	30	9.7	1
B3-30-S1	47/53	30	5.1	1
B4-30-S1	47/53	30	4.2	1
B5-30-S1	48/52	30	3.2	1
B1-50-S1	47/53	50	13.0	1
B2-50-S1	46/54	50	9.7	1
B3-50-S1	46/54	50	5.1	1
B4-50-S1	47/53	50	4.2	1

CD of the PBA network. This can be regarded as evidence of an advantageous effect of the *CD* of the first network on miscibility.

The effect of the *CD* of network 2 [PS(OH)], in general, is not as apparent as that of network 1. By comparing *Figures 3a* and *e* containing the same *CD* of PBA network but different contents of the crosslink agent in the PS(OH) networks (1 and 7%, respectively) no apparent phase size variation can be detected. *Figures 3b* and *f* show the same result. This morphological study confirms the extremely fine two-phase structure of the systems with a high hydrogen bonding density (*Figures 3c, d, g* and *h*), where the hydroxyl content of PS(OH) is 5 mol%. In these IPNs, as reported previously[16], the free and self-associated hydroxyl groups totally disappear and all the hydroxyl groups are involved in hydrogen bonding with the carbonyl groups of the counter polymers. However, differing from the corresponding linear blends, which form single-phase structures due to this strong intercomponent interaction, these IPNs show extremely fine phase separation.

Summarizing the experimental results from d.s.c., turbidimetry and TEM, we may be able to conclude as follows. A favourable effect of crosslinking on miscibility is clearly shown by the decrease of turbidity, the shift of high glass transition to a lower temperature and the decrease of domain size for the IPNs with a low hydroxyl content (0, 1 mol%) in PS(OH), while the corresponding blends without crosslinking are immiscible. This advantageous effect, undoubtedly is caused by the retardation of phase separation in the process of IPN formation due to the restriction of the molecular mobility by the first network. However, for the PS(OH)s with high (5, 30 and 50 mol%) hydroxyl contents, the linear blends are definitely miscible, but the corresponding IPNs do show two phases with extremely fine structure. The reasons leading to this disadvantageous effect of crosslinking on miscibility on the segmental scale are complicated. For example, in the process of producing the IPNs composed of phenolic resins and carbonyl-containing polymers[13,14], crosslinking occurs at relatively high temperatures, which may cause dissociation of the

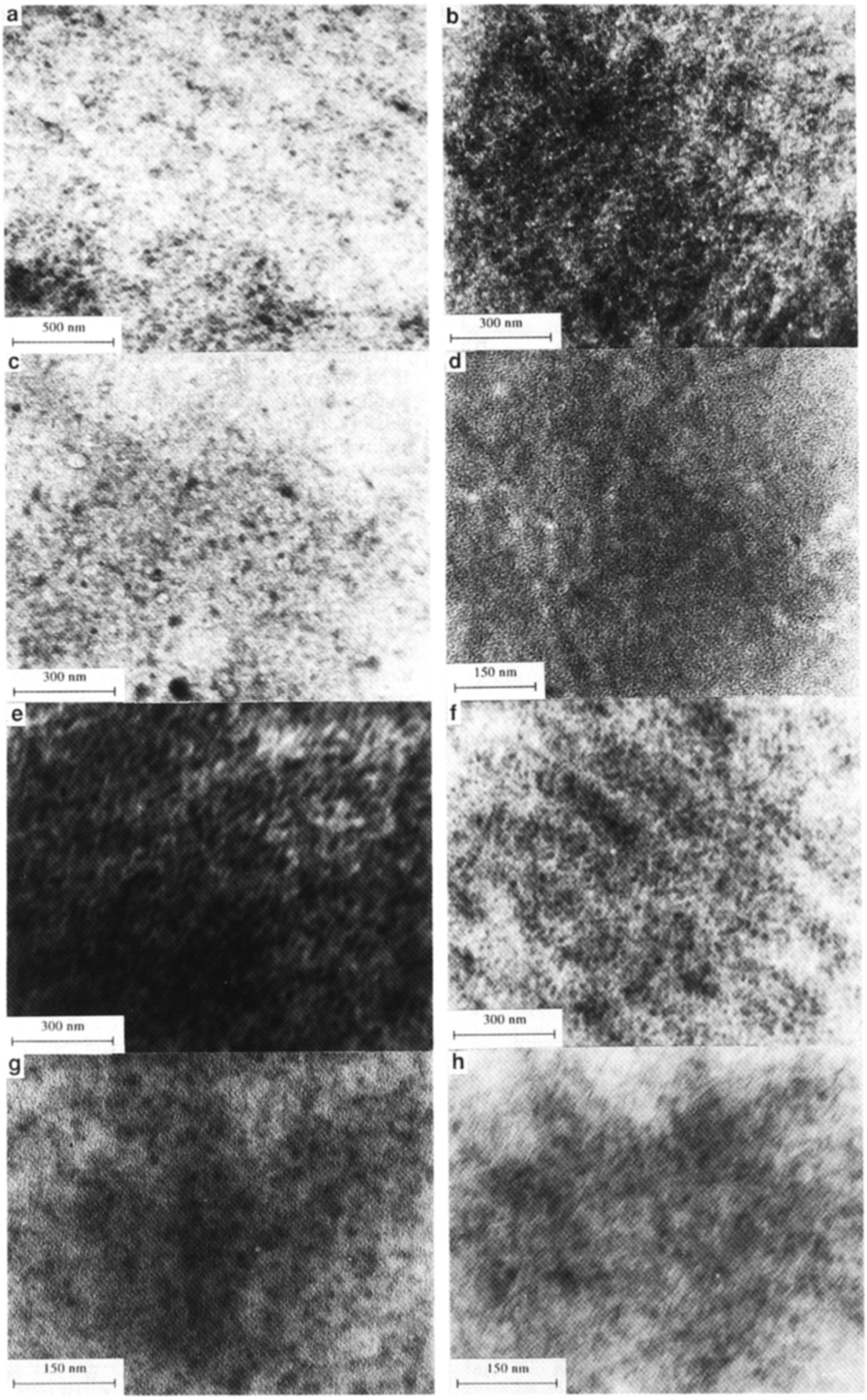

Figure 3 Transmission electron micrographs of IPNs showing the effect of crosslink density of the PBA network on morphologies: (a) B2-1-S1; (b) B5-1-S1; (c) B2-5-S1; (d) B4-5-S1; (e) B2-1-S7; (f) B5-1-S7; (g) B2-5-S7; (h) B4-5-S7

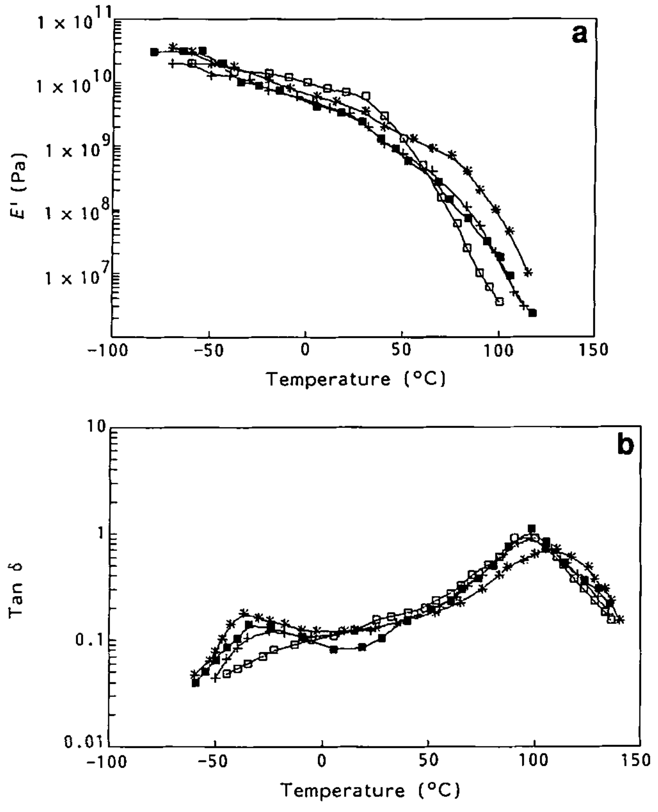

Figure 4 (a) Storage modulus E' and (b) tan δ of IPNs without hydrogen bonding plotted against temperature showing the effect of crosslink density of PBA: (∗) B2-0-S1; (■) B3-0-S1; (+) B4-0-S1; (□) B5-0-S1

hydrogen bonds. This obviously results in a decrease of the degree of mixing. In the present case, the IPNs of PS(OH)/PBA studied here were produced at 60°C[15,16], which was much lower than the lower critical solution temperature of the corresponding linear blends as reported by Pearce *et al.*[17], Cao[18] and He *et al.*[19]. Therefore, it is not reasonable to attribute this unfavourable effect of crosslinking on miscibility to dissociation of the hydrogen bonds. In contrast, i.r. studies have provided evidence that in the IPNs, all the hydroxyl groups in PS(OH) are involved in hydrogen bonding[16]. Therefore, we are inclined to attribute this disadvantageous effect of crosslinking on miscibility to the presence of inherent microheterogeneity of the networks themselves, which was evidenced by d.m.a. studies.

D.m.a. has been extensively used in characterizing IPNs for exploring their phase relationships and phase composition. In this study, the effect of *CD* of the PBA network on the phase structure at different levels of hydrogen bonding has been studied by d.m.a. *Figures 4a* and *b* illustrate the effect of crosslinking of the PBA network on the behaviour of the storage modulus (E') and loss factor (tan δ) against temperature for the IPNs without hydrogen bonding. All the IPNs, with the exception of B5-0-S1 with the highest *CD* of PBA, show two glass transitions associated with a PBA phase and a 'mixed phase'. The existence of two phases is expected since there is no hydrogen bonding. Increasing the *CD* of PBA, i.e. M_c values changing from 9700 to 5100, make the high T_g shift to a lower temperature, but no further apparent shift is observed with a further decrease of *CD*. It is interesting to note that increasing the *CD* of PBA causes a progressive decrease of the tan δ peak height of

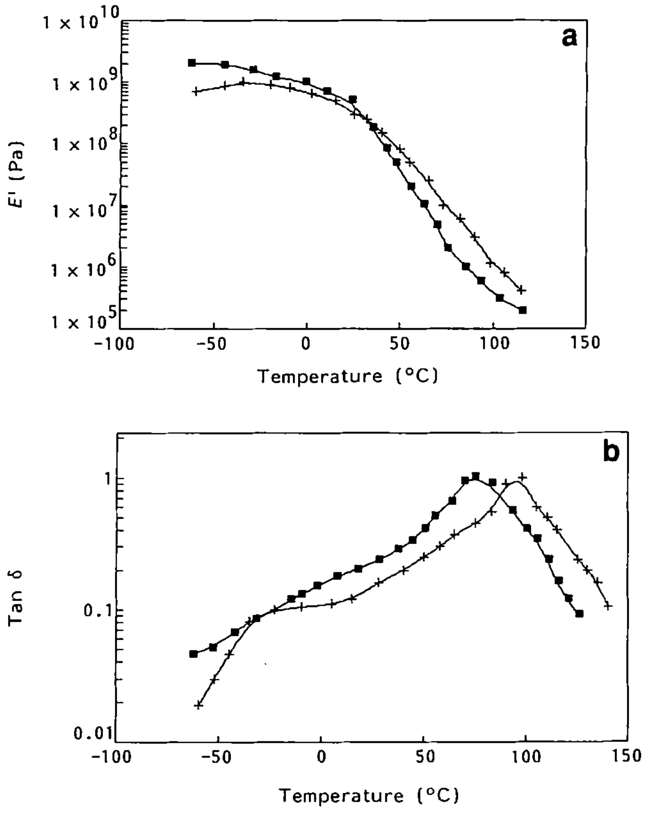

Figure 5 (a) Storage modulus E' and (b) tan δ of IPNs with 1 mol% OH plotted against temperature showing the effect of crosslink density of PBA: (+) B2-1-S1; (■) B3-1-S1

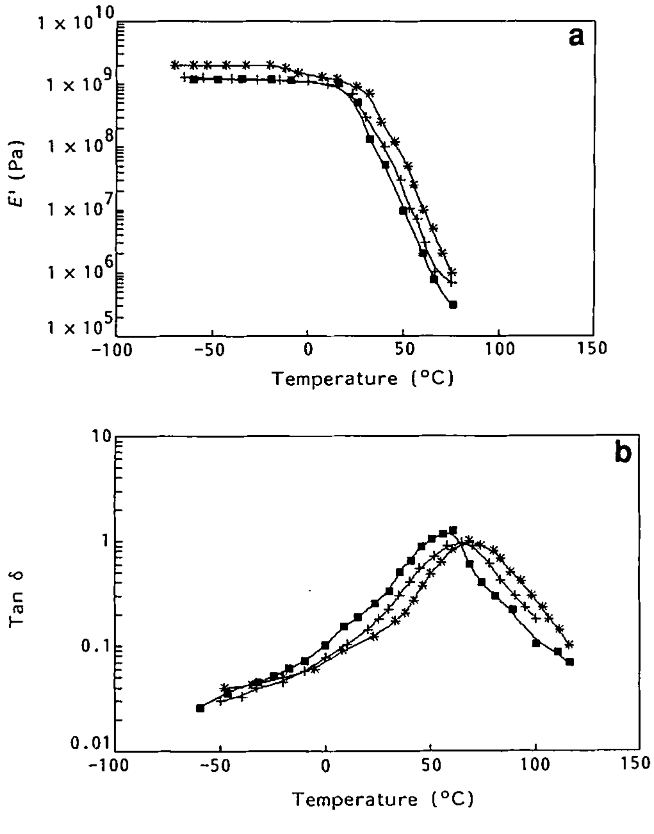

Figure 6 (a) Storage modulus E' and (b) tan δ of IPNs with 5 mol% OH plotted against temperature showing only one glass transition: (■) B2-5-S1; (+) B3-5-S1; (∗) B4-5-S1

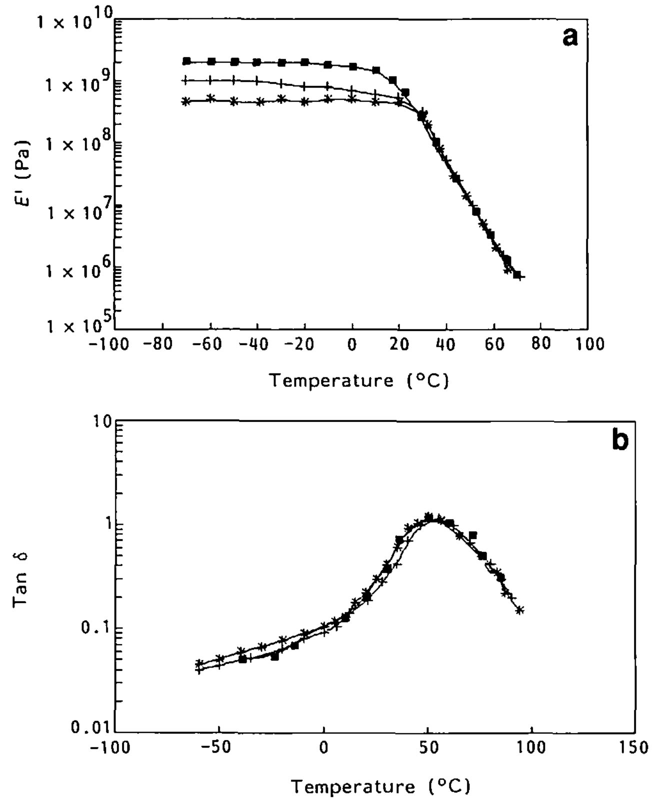

Figure 7 (a) Storage modulus E' and (b) $\tan\delta$ of IPNs with 30 mol% OH plotted against temperature showing only one glass transition: (■) B2-30-S1; (+) B3-30-S1; (*) B4-30-S1

the corresponding transition. For B5-0-S1, with the highest *CD* of PBA, the peak almost disappears. Since there are no introduced hydrogen bonds, this disappearance cannot be regarded as an indication of complete miscibility. In fact, this phenomenon is common for crosslinked polymers. Houston and Zia[20] reported that the $\tan\delta$ peak of poly(methyl acrylate) networks progressively decreases as the *CD* increases. It seems that increasing the *CD* results in a progressively larger fraction of repeat units being restrained and unavailable for the loss process. Consequently, the intensity of the $\tan\delta$ peak would decrease with increase in *CD*.

The variations of E' and $\tan\delta$ as functions of temperature for the IPNs with 1 mol% hydroxyl in PS(OH) are shown in *Figures 5a* and *b*, respectively. Two transitions can be seen for the case of low *CD* (B2-1-S1, $M_c = 9700$), but the peak around the transition area of the PBA network turns into a broad shoulder when the *CD* increases (B3-1-S1, $M_c = 5100$). An apparent shift of the high T_g to a lower temperature is observed by comparing the two curves of $\tan\delta$ *versus* temperature.

A remarkable change of dynamic mechanical behaviour is observed by comparing the results mentioned above with those shown in *Figures 6* and *7*, where the hydroxyl contents in PS(OH) reach the higher values of 5 and 30 mol%, respectively. The transition at low temperature completely disappears resulting in a single-transition feature. There is a slight dependence of the transition temperature on the *CD* of PBA when the hydroxyl content in PS(OH) is 5 mol% (*Figure 6*). The samples with high (30 mol%) hydroxyl content show a transition independent of *CD*. If the d.s.c. and TEM results had not been available, this feature of d.m.a. might lead to the conclusion of complete miscibility of the system. However, the absence of the transition around the T_g range of PBA shown in *Figures 6* and *7*, in our opinion, does not mean the absence of the related phase. This may be attributed to the insensitivity of d.m.a. to the highly crosslinked domains.

The presence of microheterogeneity in polymer networks is widely accepted. It is caused by, for example, the difference in reactivities of monomer and crosslinking agent[21] in copolymerization. In a simple model, it is assumed that a network actually composes loosely crosslinked and tightly crosslinked domains. If this assumption can be used to roughly describe the PBA networks used in this study, we may expect that PS(OH) with hydroxyl content higher than a critical value may be able to solubilize the loosely crosslinked areas forming a 'mixed phase' but not the tightly crosslinked PBA domains. The glass transition of these tightly crosslinked domains cannot be detected by d.m.a. due to the reason discussed above. Therefore, why are d.s.c. measurements still able to detect the glass transition of the highly crosslinked area? Although we may not be able to present a convincing theoretical elucidation, a number of experimental results in the literature can readily be found showing the same phenomenon. For example, a series of epoxy resin samples, covering quite a broad range of *CD*, show almost the same change of heat capacity in the d.s.c. curves associated with the glass transition[22].

ACKNOWLEDGEMENTS

The authors are grateful to the National Natural Science Foundation of China and Stiftung Volkswagenwerk (Germany) for their financial support of this project. We also thank Dr T. Pakular under whose guidance the d.m.a. measurements were performed at the Max-Planck Institute of Polymer Research, Mainz, Germany.

REFERENCES

1 Sperling, L. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981, Ch. 6
2 Donatelli, A., Sperling, L. and Thomas, D. *J. Appl. Polym. Sci.* 1977, **21**, 1189
3 Yeo, J., Sperling, L. and Thomas, D. *Polymer* 1983, **24**, 307
4 Saeki, J., Cowie, J. and McEwen, I. *Polymer* 1983, **24**, 60
5 Cowie, J. and McEwen, I. *Polymer* 1985, **26**, 1622
6 Widmaier, J.-M. *Macromolecules* 1991, **24**, 4209
7 Frisch, H. in 'Recent Development in PU and IPN's' (Ed. K. C. Frisch), Detroit University, Detroit, 1990, p. 16
8 Frisch, H., Klempner, D., Yoon, H. and Frisch, K. *Macromolecules* 1980, **13**, 1016
9 Bauer, B., Briber, R. and Han, C. *Macromolecules* 1989, **22**, 940
10 Felisberti, H., Lucca Freitas, L. and Stadler, R. *Polymer* 1990, **31**, 1440
11 Gao, Q., Peng, X. and Wang, Z. *Polym. Bull.* 1989, **21**, 593
12 Nishi, S. and Kotaka, T. *Macromolecules* 1985, **18**, 1519
13 Kim, H., Pearce, E. and Kwei, T. K. *Macromolecules* 1989, **22**, 3374
14 Coleman, H., Serman, C. and Painter, P. *Macromolecules* 1987, **22**, 226
15 Xiao, H., Jiang, M. and Yu, T. *Polymer* 1994, **35**, 5523
16 Jiang, M., Xiao, H., Jin, X. and Yu, T. *Polym. Bull.* 1990, **23**, 103
17 Pearce, E., Kwei, T. and Min, B. *Macromolecules* 1991, **24**, 464
18 Cao, X. *PhD Thesis* Fudan University, 1988
19 He, M., Fang, Y., Jiang, M. and Han, C. C. *Macromolecules* 1991, **24**, 464
20 Houston, D. and Zia, Y. *J. Appl. Polym. Sci.* 1983, **28**, 3849
21 Dusek, K. in 'Developments in Polymerization-3' (Ed. R. Haward), Applied Science Publishers, London, 1982, pp. 143–206
22 Fawa, R. *Polymer* 1968, **9**, 137