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Miscibility behaviour of poly(styrene-*co*-*N*-maleimide)s with poly(methyl methacrylate)

I. Vermeesch* and G. Groeninckx†
Katholieke Universiteit Leuven, Laboratorium voor Macromoleculaire Structuurchemie, Celestijnenlaan 200F, 3001 Heverlee, Belgium
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Various maleimide-containing copolymers have been studied with respect to their miscibility behaviour towards poly(methyl methacrylate) (PMMA) by differential scanning calorimetry (d.s.c.). Poly(styrene-*co*-*N*-maleimide)s (NMIs) with maleimide contents between 8 and 21 wt% were shown to be completely miscible with PMMA, whereas a blend containing 45 wt% maleimide in the NMI was not miscible with PMMA. In contrast to the miscible blend NMI-21/PMMA, a NMI-21-MMA polymer containing 21 wt% maleimide, 40 wt% methyl methacrylate, 35 wt% styrene and 4 wt% maleic anhydride proved to be immiscible with PMMA. By means of d.s.c. and Fourier transform infra-red spectroscopy measurements on the polymer blends and their model compounds, it was possible to account for the miscibility behaviour in terms of competing equilibria and concentration effects.

(Keywords: poly(styrene-*co*-maleimide); poly(methyl methacrylate); miscibility; hydrogen bonding)

INTRODUCTION

Blends of poly(methyl methacrylate) (PMMA) and polystyrene (PS) homopolymers are immiscible. Thornton *et al.*[1] confirmed the presence of two phases in PMMA/PS blends by means of glass transition temperature (T_g) measurements using differential scanning calorimetry (d.s.c.). Brannock *et al.*[2] found copolymers of maleic anhydride and styrene to be miscible with PMMA when the maleic anhydride (MA) content in the copolymer was varied in the range 8–47 wt%. The miscibility of the blends was explained by the 'mean field binary interaction or repulsion model'. According to this model[3–5], the mutual repulsive force between dissimilar segments in the copolymer can lead to the negative heat of mixing necessary to obtain miscibility. This model has also been applied to various systems where hydrogen bonding does occur[6–10].

It is interesting to investigate whether poly(styrene-*co*-*N*-maleimide)s (NMIs), which were prepared by modification of poly(styrene-*co*-maleic anhydride) with primary amines by reactive extrusion[11], and only differ by an NH group instead of an oxygen in the maleic anhydride group, are miscible with PMMA. In a previous paper[12], it was pointed out that a poly(styrene-*co*-*N*-maleimide) containing 14 wt% maleimide (denoted NMI-14) self-associated through hydrogen bonding between the carbonyl and the NH groups of the maleimide moieties. When specific interactions are present in blends, miscibility is generally obtained when the inter-association exceeds the self-association[13]. In the present study, NMI polymers with various maleimide contents have been blended with PMMA and their miscibility behaviour has been studied by d.s.c. As both self- and inter-association kinetics are in competition with each other, this study will enable us to find out at which copolymer composition the inter-association exceeds the self-association or vice versa.

EXPERIMENTAL

NMI-8 and NMI-14 are experimental poly(styrene-*co*-*N*-maleimide) copolymers containing 8 and 14 wt% maleimide, respectively. Both copolymers were prepared by reactive extrusion at the Monsanto Company, USA.

The copolymer NMI-21 has been prepared by reactive extrusion, as described in a previous article[11], from an SMA containing 25 wt% MA and 75 wt% styrene (St). The tetracopolymer NMI-21-MMA was prepared by the same way from an SMA containing 25 wt% MA, 40 wt% methyl methacrylate (MMA) and 35 wt% St. NMI-45, containing 45 wt% maleimide groups and 55 wt% styrene, has been prepared by the free radical route as described in ref. 14. The intrinsic viscosities of these NMI polymers are reported in *Table 1*; they have been measured with an Ubbelohde viscometer (capillary diameter 0.63 mm) at 25°C in *N*,*N*′-dimethylformamide starting from a 20 mg ml^{-1} solution. Determination of the molecular weight by gel permeation chromatography (g.p.c.) was not possible as the maleimide groups contain an acid imide proton which interacts with the styrene–divinylbenzene columns of the g.p.c. The atactic PMMA (Diakon MG 102), received from ICI, has a weight-average molecular weight of 72 500 and a polydispersity of 1.7, as measured by g.p.c.

NMI/PMMA blends at various compositions were prepared from 2 wt% solutions in anhydrous tetrahydrofuran (THF) and were precipitated in n-hexane,

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* Present address: ICI Europe, Everslaan 45, 3078 Everberg, Belgium
† To whom correspondence should be addressed

Table 1 Intrinsic viscosities for the various NMI copolymers

NMI copolymer	$[\eta]$ (dl g^{-1})	Standard error
NMI-8	0.624	0.049
NMI-14	0.550	0.055
NMI-21	0.386	0.018
NMI-45	0.679	0.048
NMI-21-MMA	0.413	0.026

except for the NMI-45/PMMA blends which were precipitated in methanol. The samples were filtered and dried overnight in a vacuum oven at 80°C. Glass transition temperatures of the blends were measured on a Perkin-Elmer DSC-7 at a heating rate of 10°C min^{-1}; the second run was used to determine T_g. Fourier transform infra-red (*FT*i.r.) spectroscopy was performed using a Nicolet 680 DSP instrument at a resolution of 2 cm^{-1}; a minimum of 16 scans were signal averaged and stored on a magnetic disk. Polymer films were prepared by solution casting onto KBr windows from a 2 wt% solution in THF. To ensure a constant film thickness, a saturated THF environment was maintained during the evaporation process. The films were dried in a vacuum oven at 80°C overnight and stored in a desiccator prior to use. The low molecular weight analogue model compounds α-methyl-α-phenylsuccinimide and methylisobutyrate were used without further purification. Solutions of the model compounds were prepared in anhydrous CCl_4; the concentration of α-methyl-α-phenylsuccinimide was kept constant at 0.05 M while the concentration of the methylisobutyrate was varied in 1:1, 1:2 and 1:3 ratios. *FT*i.r. spectra of the model compounds and their blends were recorded on a Nicolet 680 DSP with the use of a liquid cell at a resolution of 2 cm^{-1}.

Transparent films for cloud point determination were prepared by compressing slightly some blend powder between glass slides at a temperature approximately 20°C above T_g. The samples were then introduced in a Mettler oven; using an optical microscope (Olympus BH-2), light was transmitted through the samples every 2 min. The light intensity decrease was measured as a function of temperature (1°C min^{-1}) by a charge-coupled device IVC500 camera, mounted onto the light microscope and connected to a personal computer.

RESULTS AND DISCUSSION

Influence of maleimide content in NMI/PMMA blends

The miscibility of PMMA with NMI copolymers containing 8 to 45 wt% maleimide was studied by d.s.c. *Figures 1* to *4* present d.s.c. thermograms of the NMI/PMMA blends as a function of the various imide levels in the copolymer. NMI-8/PMMA blends have been subjected to enthalpy relaxation experiments because of the closeness of the glass transitions of the two components. It is well known that these experiments are very useful to evaluate blend miscibility when the glass transition temperatures are virtually coincident[15]. In the most simple case, the ageing kinetics of an immiscible blend will be representative of those of the pure polymers superimposed upon each other. The samples were heated at 190°C for 5 min to erase all previous thermal history and were subsequently annealed at 104°C for 4 days. The enthalpy relaxation that occurs at this stage is recovered during reheating and is visible as an endothermic peak in the d.s.c. thermogram. Each polymer has its own individual ageing behaviour reflected in the position and the magnitude of the recovery peak. Single endotherms were observed for all blend compositions on heating at 10°C min^{-1}, indicating miscibility of the NMI-8/PMMA blends (*Figure 1*). NMI-14 was found to be miscible with PMMA at all blend compositions (*Figure 2*), as also were the NMI-21/PMMA blends (*Figure 3*). D.s.c. scans of the NMI-45/PMMA blends showed two T_gs, indicating the presence of two phases (*Figure 4*). Note that the decrease in baseline for the pure PMMA and blends beyond 250°C is believed to result from degradation of the PMMA compound. Poly(*N*-maleimide) (NMI-100)/PMMA blends were not prepared because proper characterization of the T_g of pure poly(*N*-maleimide) was not possible and degradation of PMMA would occur at these high temperatures. The experimental T_g values of all miscible blends were plotted *versus* the weight fraction of PMMA in the blend (*Figure 5*). From a comparison of the experimental values with the calculated

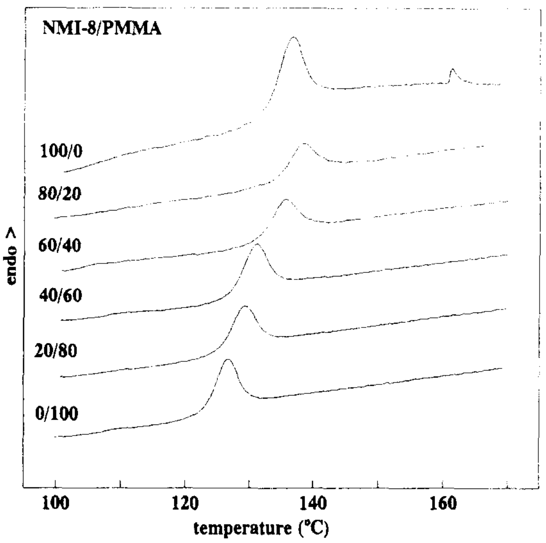

Figure 1 Enthalpy relaxation measurements of NMI-8/PMMA blends

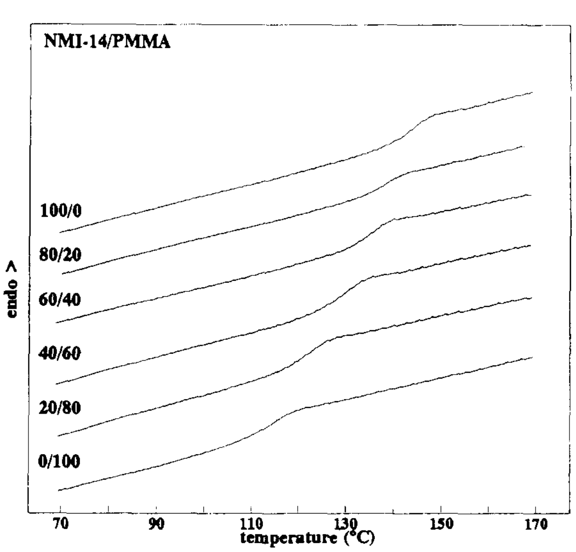

Figure 2 D.s.c. scans of NMI-14/PMMA blends

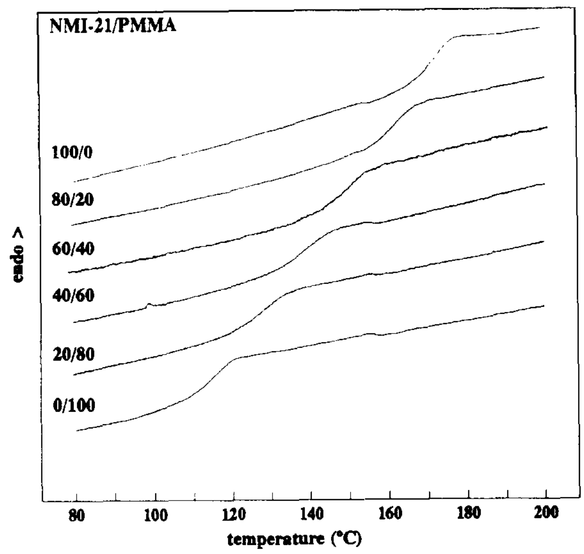

Figure 3 D.s.c. scans of NMI-21/PMMA blends

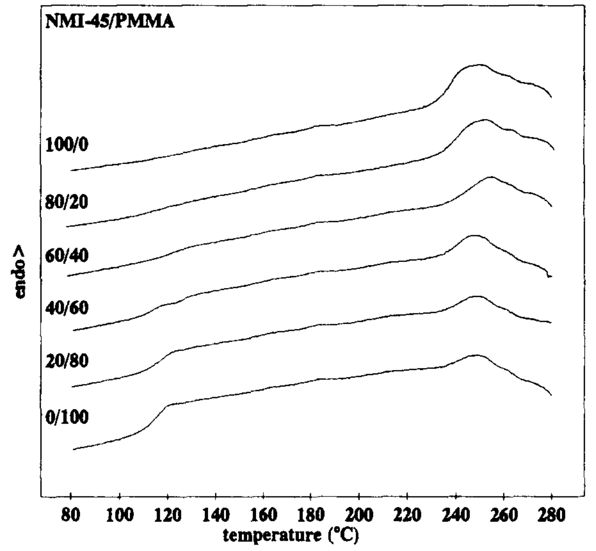

Figure 4 D.s.c. scans of NMI-45/PMMA blends

ones based on the Fox equation, a positive deviation has been observed, indicating specific interactions to be present in the blends; this positive deviation decreased with increasing maleimide content.

In terms of specific interactions, the above-mentioned phase behaviour can be explained using information obtained from *FT*i.r. measurements performed on the polymer blend of NMI-14 and PMMA and on model compounds of these polymers. The miscibility of the NMI-14/PMMA blend can be considered as resulting from a change in distribution of self-associated maleimide groups in favour of NH···O=C methyl methacrylate inter-association. In the NH stretching region, a shift of the *FT*i.r. absorption peaks to higher wavenumbers is observed with increasing fraction of PMMA in the blends (*Figure 6*). In the spectrum of the 50/50 NMI-14/PMMA blend, a distinct and broad multimer band is observed at 3275 cm^{-1}, whereas the dimer and multimer hydrogen bonded NH groups at 3352 and 3249 cm^{-1}, attributed to the self-associated maleimide groups, are no longer predominant[12]. The slight upward shift (25 cm^{-1}) of the inter-associated NH groups compared with the self-associated multimer NH groups is an indication of the

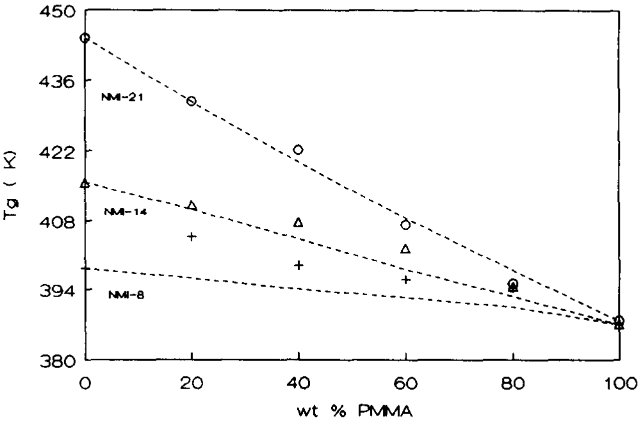

Figure 5 Comparison of experimental T_g values with calculated T_g values (Fox) for NMI-8/PMMA (+), NMI-14/PMMA (△) and NMI-21/PMMA (○)

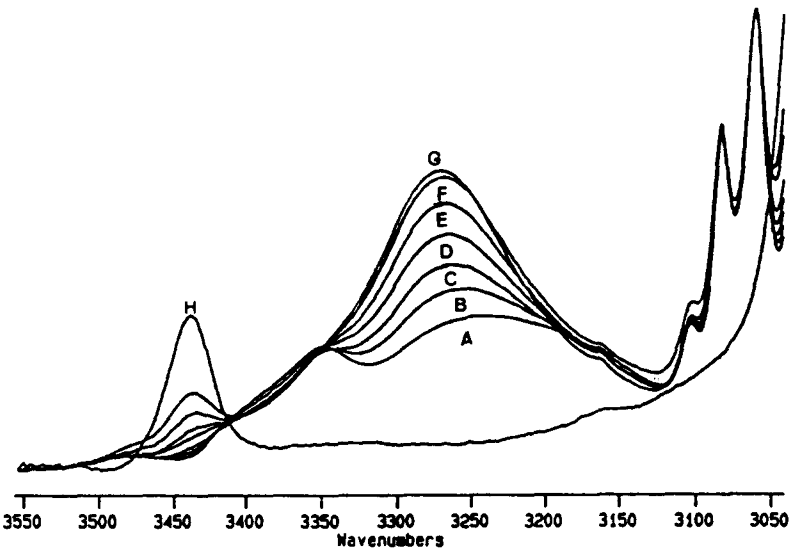

Figure 6 *FT*i.r. spectra in the NH stretching region of NMI-14/PMMA blends: 100/0 (A), 90/10 (B), 80/20 (C), 70/30 (D), 60/40 (E), 50/50 (F), 40/60 (G) and 0/100 (H)

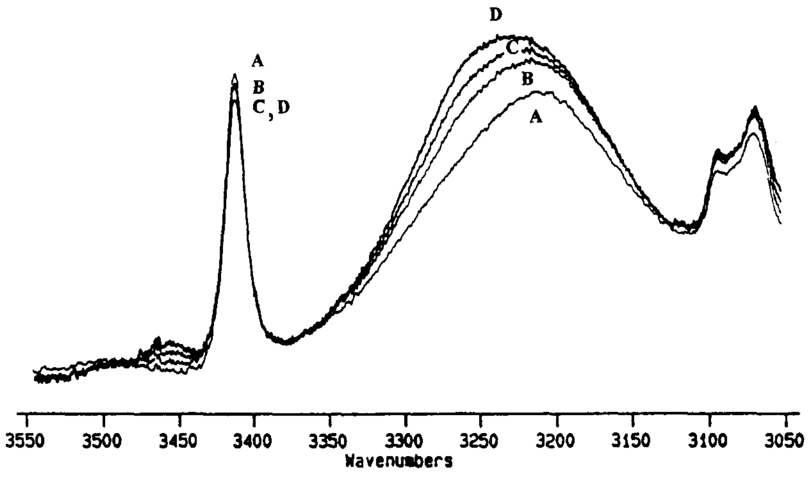

Figure 7 *FT*i.r. spectra in the NH stretching region of the model compounds α-methyl-α-phenylsuccinimide and methylisobutyrate at various concentrations: 0.05 M (A), 0.05 M/0.05 M (B), 0.05 M/0.10 M (C) and 0.05 M/0.15 M (D)

somewhat weaker strength of the maleimide–MMA interaction. However, miscible blends are obtained and this can be considered as the result of a concentration effect; there are more ester carbonyl groups than imide carbonyl groups present in the blends. It has to be noticed that all the *FT*i.r. spectra were autoscaled as the thickness of the films for the samples varied somewhat for the various compositions and that the absorption peak at 3440 cm^{-1} is attributed to the overtone of carbonyl groups in the PMMA. The carbonyl region of the NMI-14/PMMA blends has not been analysed because five or more carbonyl groups absorb in this region and partially or totally overlap each other.

It is useful to compare the spectra of blends of NMI-14/PMMA with a model blend system that is less complicated. α-Methyl-α-phenylsuccinimide and methylisobutyrate are appropriate low-molecular weight analogues for NMI and PMMA, respectively.

*FT*i.r. spectra of the NH stretching region of mixtures of α-methyl-α-phenylsuccinimide with methylisobutyrate in CCl_4 are consistent with the above observations. Spectrum A in *Figure 7* corresponds to a 0.05 M solution of α-methyl-α-phenylsuccinimide in CCl_4. Two absorption bands are observed: one attributed to the 'free' NH groups at 3415 cm^{-1} and one attributed to the hydrogen-bonded NH groups (multimer) at 3210 cm^{-1}. Upon addition of methylisobutyrate and increasing the concentration from 0.05 M to 0.15 M, a small decrease is observed in intensity for the 'free' NH groups and a small shift for the multimer to higher wavenumber (20 cm^{-1}). From these spectra it can be derived that the strength of the NH···O=C (ester) hydrogen bond is comparable to, or even somewhat weaker than, that of the NH···O=C (imide) because of the small upward shift. A change in distribution of the NH···O=C (imide) in favour of the NH···O=C (ester) is observed and attributed to the higher concentration of the latter. This also explains the intensity decrease of the maleimide 'free' NH band.

In terms of specific interactions, it can be concluded that copolymers containing between 8 and 21 wt% maleimide groups are miscible with PMMA because the inter-association of the maleimide groups in NMI and the MMA groups in PMMA predominates over the self-association of the maleimide groups in NMI. At higher maleimide levels, as in NMI-45, the self-association of the maleimide groups appears to exceed the inter-association, and this is only the result of a concentration effect because both specific interactions are of somewhat equal strength. This also explains the decrease in positive deviation *versus* blend composition with increasing maleimide content.

Table 2 Cloud points (°C) for NMI/PMMA blends

Blend composition	NMI-8/PMMA	NMI-14/PMMA	NMI-21/PMMA
20/80	278	280	291
40/60	260	282	284
60/40	266	284	287
80/20	278	287	298

Liquid–liquid phase separation upon heating above a lower critical solution temperature (*LCST*) was observed for all miscible NMI/PMMA blends. The minima of the representative cloud point curves are 260°C for NMI-8/PMMA, 280°C for NMI-14/PMMA and 284°C for NMI-21/PMMA blends, as can be seen from *Table 2*. An increase in cloud point with increasing imide content was observed. An extrapolation of the miscibility window of NMI/PMMA blends would indicate that NMI polymers containing imide contents between 3 and 34 wt% are miscible with PMMA. However, one has to be careful with extrapolating.

Influence of MMA content in NMI/PMMA blends

Two NMI copolymers were blended with PMMA and studied for their miscibility behaviour. Blends of NMI-21/PMMA without MMA monomer units in NMI-21 were compared with NMI-21-MMA/PMMA blends, with the NMI-21-MMA tetrapolymer containing 40 wt% MMA monomer (same imide and anhydride level). The presence of MMA in the tetrapolymer seemed to influence the distribution of hydrogen bonds remarkably. Although miscibility was observed for NMI-21/PMMA blends (*Figure 3*) at all compositions, two distinct T_gs were observed for the NMI-21-MMA/PMMA blends. By introducing a high MMA level in the NMI, one would expect to lower the solubility parameter of the NMI polymer towards that of the PMMA and thus enhance the chance of finding a miscible system. However, this is

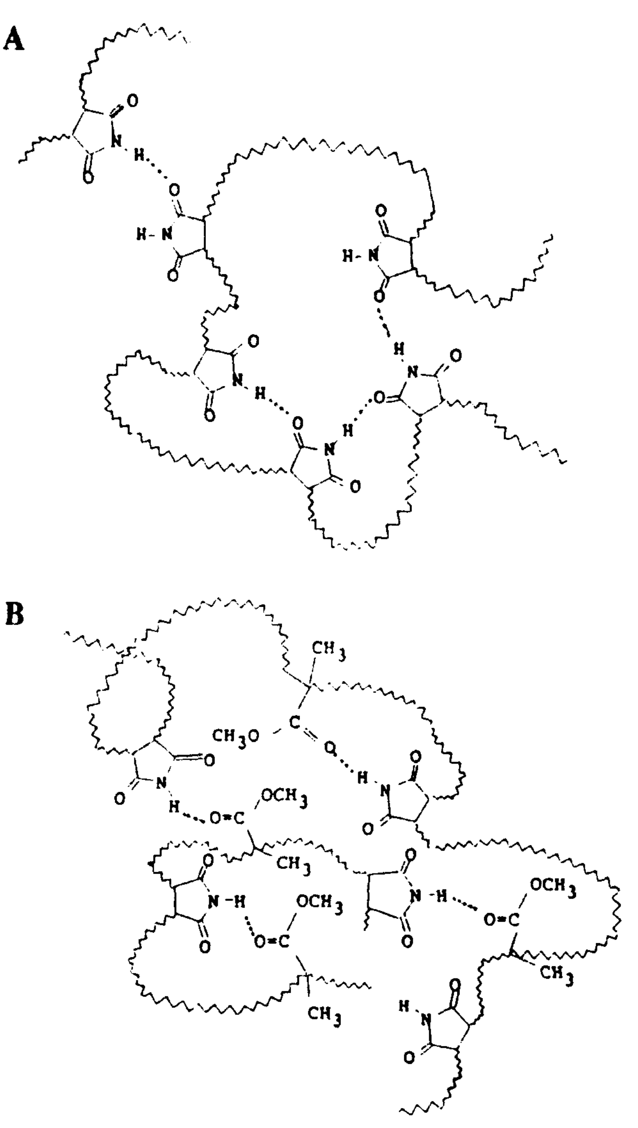

Figure 8 Schematic representation of hydrogen bonding in NMI-21 (A) compared with hydrogen bonding in NMI-21-MMA (B)

not the case, and from the *FT*i.r. spectra of the blends one can deduce that the tetrapolymer NMI-21-MMA is a more self-associating polymer than the tetrapolymer NMI-21, although both copolymers contain 21 wt% maleimide. In the NMI-21-MMA, hydrogen bonding is thought to occur predominantly between the imide proton and the MMA carbonyl (self-association) and not between the imide proton and the imide carbonyl (self-association) (*Figure 8*). If this statement is correct, the amount of hydrogen bonds present in NMI-21-MMA should be about twice that found in NMI-21. As this polymer is more self-associated, most of the imide protons are hydrogen-bonded with its own MMA carbonyl groups; this means that blending of NMI-21-MMA with PMMA will not change any hydrogen bond distribution into more favourable ones and thus blends with PMMA will not be miscible.

CONCLUSIONS

Blends of PMMA with NMI polymers having a maleimide content between 8 and 45 wt% were studied. NMI polymers with 8 to 21 wt% maleimide were miscible with PMMA over the whole composition range, whereas NMI-45/PMMA blends were immiscible. This behaviour has been explained in terms of the competing equilibria of self-association and inter-association. Upon increasing the maleimide content in the NMI copolymer, the self-association increases as more maleimide groups are present. In blends of PMMA with NMI, a competition for hydrogen bonding exists between the maleimide groups mutually (self-association) and between maleimide and methyl methacrylate groups (inter-association). This competition is dependent upon the equilibrium constant and the concentration at a given temperature. At low maleimide content in the copolymer (8–21 wt%), the inter-association exceeds the self-association, whereas at high maleimide content (45–100 wt%), the self-association exceeds the inter-association. *LCST* curves were established for the miscible blends. Minima of the cloud point curves were found at 260°C for NMI-8/PMMA, 280°C for NMI-14/PMMA and 284°C for NMI-21/PMMA blends. That the miscibility behaviour indeed is dependent upon the competition between the self- and inter-association is illustrated once more in the miscibility behaviour of NMI-21/PMMA and NMI-21-MMA/PMMA blends. The first blend appeared to be miscible while the latter was not miscible at all, as was determined by d.s.c. The self-association in NMI-21-MMA is higher than in NMI-21, and blending with PMMA will not change the hydrogen bonding distribution into more favourable ones than in NMI-21-MMA.

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