The influence of the microstructure of some chlorine containing polymers on their miscibility with poly(butadiene-*stat*-acrylonitrile)

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A range of poly(butadiene-*stat*-acrylonitrile), BAN, copolymers with compositions ranging between 17.8 wt% and 66.9 wt% acrylonitrile, have been mixed with three chlorine containing ($\sim$56 wt% Cl) polymers: conventional poly(vinyl chloride), PVC, chlorinated poly(1,4-butadiene) and chlorinated polyethylene, CPE. The polybutadiene which has been chlorinated at the double bonds can be regarded as head-to-head PVC, (H-H) PVC, whereas the CPE is a random copolymer of head-to-tail PVC, (H-T) PVC, and (H-H) PVC. Thus the samples which contain the same amount of chlorine will vary only in its sequence distribution along the chain. When these were blended with BAN samples, the extent of the miscibility ranges established were found to increase in the order: (H-T) PVC < CPE < (H-H) PVC. This gives a qualitative demonstration of the influence of sequence distribution on the miscibility of some polymer blends. Substitution of bromine for chlorine in the halogenated poly(1,4-butadiene) resulted in immiscible blends and highlighted the sensitivity of many polymer blend systems to small changes in the chemical structure of the polymers.

(Keywords: copolymer miscibility; chlorine microstructure; chlorinated polymers; poly(butadiene-*stat*-acrylonitrile))

INTRODUCTION

It is now well established that miscible blends can be obtained when certain copolymers are mixed with other homopolymers or copolymers, even when apparently there are no strong intermolecular interactions present that would encourage such intimate mixing. These miscibility regions are strongly dependent on the copolymer compositions and give rise to the so called 'miscibility windows'. Less well documented are systems in which the microstructure of the polymer or copolymer can affect the miscibility, although such a possibility has been discussed by Balazs *et al.*[1–4] and by Cantow and Schulz[5,6]. The former considered that the sequence distribution in copolymer components of a blend could be a factor controlling the miscibility and considered that the interaction parameter, derived from the mean field approach to describe the blend[7,8] could be divided into a composition dependent component and a copolymer sequence distribution component. The latter factor arises from the various possible arrangements of the comonomer units in a selected segmental triad in the copolymer chain which would lead to a variety of differing intrasegmental interaction energies. Hence the contribution from this feature would depend on the sequence distribution of comonomers along the chain. Some of the details of this treatment have been criticized and modified by Cantow *et al.*[5,6,9], who introduced the idea that the chain tacticity would also be a mediating factor. Their analysis starts by using a syndiotactic triad structure as a reference point and they then consider how the nature and position of the flanking groups in the triad influences the direction-specific interactions between the central groups of adjacent triads.

Such models are somewhat difficult to confirm experimentally with any precision because of the exacting nature of the structural information required, but general experimental observations can be made which lend support to the idea that sequence distributions and chain tacticities can be important factors.

Masse *et al.*[10] have demonstrated that, if chlorinated copolymers which differ mainly in their microstructure are mixed together, then the distribution of the chlorine in the chains is a controlling factor in determining the phase behaviour. They observed that fully chlorinated poly(1,4-butadiene) [the analogue head-to-head poly(vinyl chloride), (H-H) PVC] was immiscible with conventional head-to-tail PVC, (H-T) PVC. Similarly when chlorinated polyethylene, CPE, samples were mixed with (H-H) PVC, a two-phase blend was obtained at room temperature, although they found that a 'miscibility window' could be identified if the temperature was raised above 420 K.

Here we present further evidence to support the suggestion that the sequence distribution of chlorine atoms in such polymers exerts an influence on the miscibility of systems such as (H-T) PVC, (H-H) PVC and CPE when blended with poly(butadiene-*stat*-acrylonitrile), BAN.

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EXPERIMENTAL

Polymer samples. Samples of BAN were used which had been prepared and characterized previously[11]; details are summarized in *Table 1*. Solution CPE was prepared as described by Walsh *et al.*[12] and BP grade HD 6007 polyethylene was used as a starting material. A sample containing 56.0 wt% chlorine was selected for this study, as it was the closest to PVC. A head-to-head sample of PVC was prepared by chlorinating *cis*-poly(1,4-butadiene) according to the method of Tarshiani and Dreyfuss[13], and by adjusting the reaction time it was possible to prepare a sample containing 56.3 wt% chlorine. I.r. analysis of the parent sample of polybutadiene showed 93% *cis*-1,4, 5% *trans*-1,4 and 2% 1,2 placements in the chain so the final chlorinated polymer should be a reasonably accurate analogue of (H-H) PVC. A fully brominated sample was prepared using the same method.

Conventional (H-T) PVC, a commercial sample, was purified by repeated dissolution and reprecipitation before use. The sample characteristics of these chlorine containing polymers are listed in *Table 2*.

Characterization. Molecular weights were measured in polystyrene equivalents using a Waters GPC, which were then corrected using the appropriate Mark–Houwink coefficients when available. The glass transition temperatures (T_gs) were measured using a Perkin-Elmer differential scanning calorimeter (DSC 4) and T_g was taken as the temperature of the onset of the baseline shift characterizing this transition in the d.s.c. scan. Scanning rates of 20 K min^{-1} were used.

Blend preparation. All blends were prepared by first dissolving both components in a common solvent, dichloromethane. The main studies used blend samples prepared by coprecipitation into a 10-fold excess of methanol, but films were also cast for comparison purposes. As will be seen (*Table 3*), the clear films did not always represent one-phase systems as adjudged from T_g measurements nor did opaque films always represent immiscible blends. Samples were rigorously dried in a vacuum oven before use.

The criterion used to establish miscibility in the coprecipitated blends was the presence of a single T_g. If two T_g values, corresponding to those of the components, were observed the blend was adjudged to be immiscible. Occasionally the component T_g values were very close together and the blend was then subjected to an ageing procedure, as suggested by Bosma *et al.*[14]. In this way it was possible to resolve two enthalpy relaxation peaks if the blend was immiscible but only one if the blend was miscible. D.s.c. measurements were run several times to ensure that they were truly representative of the blend under examination.

Table 1 Characteristic parameters of BAN samples used in blends with chlorinated polymers

Wt% AN in sample	$10^4 M_n$	M_w/M_n	T_g(K)
17.8	2.25	1.58	219
23.5	10.90	6.46	228
29.1	6.87	5.15	239
33.0	6.57	4.28	245
37.2	8.56	5.15	249
40.0	7.48	4.08	256
46.6	5.90	–	265
50.0	5.49	3.73	268
56.6	3.98	2.91	284
62.3	6.58	1.54	296
66.9	6.45	1.53	312

Table 2 Characteristics of chlorine containing polymers

Sample	Wt% Cl[a]	$10^4 M_n$	$(M_w/M_n)^b$	T_g(K)
PVC	56.0	6.93	2.08	361
(H-H) PVC	56.3	19.60	3.54	345
CPE	56.0	8.54	5.14	322

[a] Microanalysis

[b] G.p.c. polystyrene equivalents

Table 3 Glass transition temperatures and film clarity in blends of BAN with (H-T) PVC, CPE and (H-H) PVC

	(H-T) PVC		CPE		(H-H) PVC	
Wt% AN in BAN	T_g(K)	Cast film[a]	T_g(K)	Cast film	T_g(K)	Cast film
17.8	228+356	T	239+324	T	221+323	T
23.5	234+319	T	264	T	273	T
29.1	282	T	279	T	289	T
33.0	277	T	278	T	287	T
37.2	278	T	280	T	282	T
40.0	284	T	283	T	275	T
45.0	284	SO	–	–	–	–
46.6	277+299	O	278+302	O	296	T
50.0	278+365	O	276+303	O	307	SO
56.6	278+365	O	288+336	O	315	O
62.3	–	–	–	–	303+336	O
66.9	–	–	–	–	316+349	O

[a] T, transparent; SO, slightly opaque; O, opaque

RESULTS AND DISCUSSION

Blends of BAN with conventional (H-T) PVC

The 'miscibility window' for blends of (H-T) PVC) with various BAN samples is illustrated in *Figure 1*, where the miscible and immiscible blend behaviour is plotted against the weight per cent acrylonitrile (AN) in BAN. The 'window' is found to lie between 25 wt% and 45 wt% AN, although there are ambiguous areas around those limits where there is a suggestion of partial miscibility in some of the blends. This is reflected in an inward movement of the two T_g values measured for the phase separated blends, and this makes the definition of the miscibility boundaries rather imprecise. However, when the data are compared with results from other workers[15–17], the observed miscibility ranges are generally comparable, although our results do suggest a slight extension of the 'window', especially at high weight per cent AN values, when compared with previous work. Some of the differences at the boundaries may be due to sample variation and differing thermal histories.

In several of our coprecipitated blends, the initial d.s.c. scan suggested that the system was of two phases, but subsequent thermal scans on the same sample indicated only one T_g, which was always observed on the second scan. This was reproducible and suggests that an element of melt blending had taken place which was required to stabilize the mixture. Huh and Karasz[17] also reported similar behaviour and found that high temperature

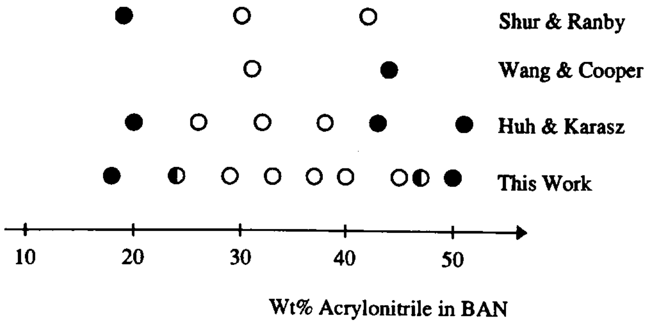

Figure 1 Room temperature 'miscibility windows' for the system PVC/BAN: (○) miscible blend; (●) immiscible blend. The data obtained in this study are compared with those from previous workers[15–17]

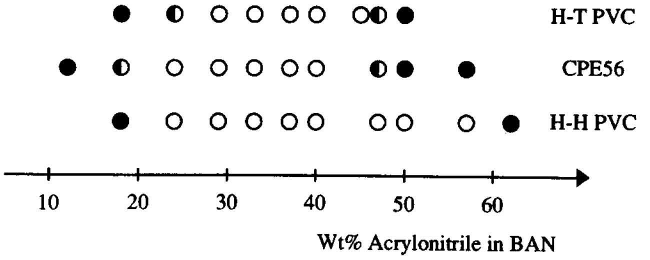

Figure 2 Comparison of the room temperature miscibility of blends of BAN with conventional poly(vinyl chloride), (H-T) PVC, chlorinated polyethylene, CPE 56, and chlorinated poly(1,4-butadiene), (H-H) PVC: (○) miscible blends; (●) immiscible blends

annealing was a necessary prerequisite for obtaining miscible blends of their chlorinated samples. They used a more severe heating cycle by raising the temperature to 423–443 K for ~15 min, whereas our samples were heated only briefly to just below 420 K. These authors also observed lower critical phase separation in their blends. This phenomenon was not detected in the blends studied here but Huh and Karasz used a PVC sample with a molecular weight of 1.36×10^5 and this may have influenced both the miscibility limits and the phase stability.

Blends of BAN with (H-H) PVC and CPE

The miscibility ranges for blends of BAN with (H-H) PVC and CPE are shown in *Figure 2*, where they are compared with the range measured for (H-T) PVC.

For BAN/CPE blends there is an improvement in miscibility when compared with (H-T) PVC, and the range has become slightly wider at the low weight per cent AN end while retaining much the same upper limit. Examination of the BAN/(H-H) PVC blends shows that the miscibility range is now markedly larger and the limits now lie at 20 and 60 wt% AN.

Analysis of the CPE sample used in this study by *FT*i.r. showed that there were no detectable quantities of CCl_2 units in the chain. This is in agreement with the findings of other workers[10,18] who concluded the fraction of CCl_2 units in CPE samples with chlorine contents of <60% was so small that it could be neglected. The CPE sample will then contain both (H-T) and (H-H) chlorine placements along the chain as the CH_2 and CHCl units will be distributed randomly. Consequently it is quite consistent to observe that the 'miscibility window' for solution CPE, containing 56 wt% Cl, and blended with BAN, is intermediate in size between the conventional PVC and chlorinated polybutadiene, as it is in effect a random copolymer of (H-T) PVC and (H-H) PVC.

Having established these different miscibility boundaries it is possible to analyse the systems in terms of the segment interaction energy densities B_{ij} for the two extreme cases, (H-T) PVC and (H-H) PVC. These interaction parameters can be calculated using the mean field treatment for a homopolymer/copolymer blend, i.e. A_x and (C_yD_{1-y}), as detailed elsewhere[19], where $x = 1.0$ and y is the volume fraction of C in the copolymer. The relevant equation for the interaction parameter describing the blend is:

$$B_{\text{blend}} = yB_{\text{VC-AN}} + (1-y)B_{\text{VC-B}} - y(1-y)B_{\text{B-AN}} \qquad (1)$$

where the segment chosen is the vinyl chloride unit in both the (H-T) and (H-H) structural variations.

The criterion for miscibility is $B_{\text{blend}} < B_{\text{crit}}$ where

$$B_{\text{crit}} = \frac{RT}{2}(V_1^{-0.5} + V_2^{-0.5})^2 \qquad (2)$$

and V_i is the molar volume of the ith component. A value of B_{crit} was calculated using the polymer pairs nearest the phase boundaries. Mean values of B_{crit} were obtained for both systems in this way and if used in conjunction with the previously established[20] average value of $B_{\text{B-AN}} = 36\ \text{J cm}^{-3}$, then the unknown B_{ij} values can be calculated. These are summarized in *Table 4*. The values suggest that the interaction between the vinyl chloride, VC, segment and the butadiene unit is the same, irrespective of the PVC microstructure, and that the major reason for the differences in miscibility lies in the AN–VC interaction which is more favourable in the case of the head-to-head structure.

The interpretation of these interaction parameters should be exercised with certain reservations, as the T_g values for the chlorinated samples differ by up to 40 K. This means that the flexibility of these chains and hence their relative abilities to pack with other polymers in the blends will differ. The effect of such variations may be that segment–segment interactions will not be equivalent in the blends and hence the phase equilibria will be altered. While this implies that the consequences of these differences in structure are mainly responsible for variable blending characteristics, other possibilities such as specific intermolecular interactions should be considered (e.g. weak hydrogen bonding or dipolar interactions) before coming to a final conclusion.

The existence of a weak specific interaction between PVC and AN containing copolymers, which could be either a weak hydrogen bond involving the methine protons or a dipole–dipole interaction, has been postulated by Coleman *et al.*[20]. These authors found it necessary to have some such interaction present, if the phase behaviour was to be described accurately using their analytical approach. If hydrogen bonding is present in these blends, the differences in the strengths of

Table 4 Segmental interaction parameters derived from equation (1)

Interacting segments (i,j)	(H-H) PVC (J cm^{-3})	(H-T) PVC (J cm^{-3})
VC–AN	14.3	17.8
VC–B	3.2	2.9

interaction between (H-T) PVC and (H-H) PVC, when each are mixed with BAN, could be caused by an enhancement of the hydrogen bond strength in the (H-H) PVC arising from the vicinal chlorine atoms, i.e. a reinforcement of hydrogen bonding caused by a co-operative effect due to the close placement of the chlorine atoms in the chain. If, however, the relative values of B_{ij} in *Table 4* are meaningful, then the (VC-AN) interaction parameter would be expected to reflect the effect of these favourable attractive forces. The values calculated from the experimental phase boundary measurements are actually quite large and unfavourable, particularly when compared with those calculated for the (VC-B) interactions where no major specific attractive forces are expected. Indeed the magnitudes of these parameters are more in line with differences between the relative values of the homopolymer solubility parameters, which are reported[20] (in units of $J^{1/2} cm^{-3/2}$), as $\delta = 16.5$ (polybutadiene), 20.2 (PVC) and 28.2 (polyacrylonitrile), e.g. using this comparison the (VC-B) interaction should be more favourable ($\Delta\delta = 3.7$), than the (VC-AN) interaction ($\Delta\delta = 8.0$), in agreement with the values of B_{ij} shown in *Table 4*. This suggests that hydrogen bonding is not a major factor in determining the miscibility in these BAN-chlorinated polymer blends.

The other possible reason for the differences could be dipolar interactions, but although these may be present, this seems a less likely explanation for a widening of the miscibility range with (H-H) PVC. The dipole moments of small model compounds show no significant changes when the chlorine atoms are varied from a 1,2-position to a 1,3-position, e.g. the dipole moment for *cis*-1,2-dichloroethylene is 1.9 D whereas it is 2.08 D for 1,3-dichloropropane. There is no apparent co-operative effect operating here.

One must then conclude that the extension of the 'miscibility windows' in these blends is caused by differences in chain packing which affect the local environment of the segments and hence the phase equilibria. The suggestion, that the differences in behaviour are essentially structural in origin, is in general agreement with work reported on other blends where the effects of structural variations could be compared. The effect of polymer tacticity on the miscibility of blends comprising chlorinated polymers and poly(methyl methacrylate), PMMA, has been reported by several groups. Schurer *et al.*[21] observed that PVC was more miscible with syndiotactic PMMA than with the isotactic form. This was confirmed by Vorenkamp *et al.*[22], who concluded that the major reason for this distinguishable behaviour lay in the fact that the syndiotactic PMMA chains are more rigid than the isotactic chains. This leads to differences in free volume that are reflected in the temperatures recorded for the lower critical cloud points, which are higher for blends of PVC with syndiotactic PMMA. Lemieux *et al.*[23] also examined blends of PMMA samples of differing tacticity with PVC, but extended their study to include chlorinated PVC and poly(vinyl chloride-*stat*-vinylidene chloride). They found that the temperature ranges of the lower critical cloud point curves were dependent on both the PMMA microstructure and the chlorine content, and concluded that the differences in miscibility arose from the variation in environment of the carbonyl unit, offered by the tactic forms of PMMA which altered the balance of specific interactions with the chlorinated polymers.

The dependence of segmental interaction parameters on the local environment has been observed in other systems. It was found necessary to distinguish between inter- and intramolecular interactions and to assign different values for segmental interactions, such as AN–methyl methacrylate[24], and AN with both butadiene and styrene[25]. Only by making this distinction could a satisfactory description of the miscibility regions be obtained in some blends involving these monomers. The influence of the microstructure of these chlorine containing polymers on blend miscibility is then not too surprising.

Brominated polybutadiene

Head-to-head poly(vinyl bromide), (H-H) PVBr, prepared in the same way as (H-H) PVC, was blended with BAN by co-dissolution in tetrahydrofuran followed by coprecipitation in methanol. No miscible blends were obtained and clearly the introduction of bromine into the system changed the miscibility quite markedly. It should be stated, however, that the thermal treatment of the blends was, out of necessity, different. PVBr tends to degrade rapidly if heated at elevated temperatures and all blends had to be kept below 390 K. Bearing in mind the observation that some of the BAN/PVC blends were only fully miscible after heating to 420 K, there is the possibility that the PVBr/BAN blends required a similar treatment. As the thermal approach was ruled out because of degradation, a better solvent for blend preparation was tried. Cyclohexanone proved to be the best for co-dissolution, but the coprecipitated blends remained two phase.

This difference in miscibility between chlorine and bromine containing polymers has been reported in other systems. Cousin and Prud'homme[26] found PVC to be miscible with a range of six polyesters but only two of these formed miscible blends with PVBr, whereas ten Brinke *et al.*[8] pointed out that copolymers of *o*- and *p*-chlorostyrene were miscible with poly(phenylene oxide) whereas the corresponding bromostyrene polymers were not. These authors concluded that associations between the blend components were weaker when bromine replaced chlorine and this was sufficient to alter the miscibility. This is certainly a possible explanation, but the larger bromine atoms may also exacerbate free volume differences between the blend components and this too could contribute to the observed immiscibility in the blends studied here.

CONCLUSIONS

The miscibility of BAN with polymers, containing equivalent amounts of chlorine, increases in the order (H-T) PVC < CPE < (H-H) PVC and is clearly related to the sequence distribution of the chlorine in the chains.

Replacement of chlorine by bromine eliminates all evidence of miscibility in (H-H) PVBr/BAN blends.

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REFERENCES

1 Balazs, A. C., Sanchez, I. C., Epstein, I. R., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1985, **18**, 2188

2 Balazs, A. C., Karasz, F. E., MacKnight, W. J., Ueda, H. and Sanchez, I. C. *Macromolecules* 1985, **18**, 2784

3 Van Hunsel, J., Balazs, A. C., MacKnight, W. J. and Koningsveld, R. *Macromolecules* 1988, **21**, 1528

4 Balasz, A. C. and De Meuse, M. T. *Macromolecules* 1989, **22**, 4260

5 Cantow, H.-J. and Schulz, O. *Polym. Bull.* 1986, **15**, 449

6 Cantow, H.-J. and Schulz, O. *Polym. Bull.* 1986, **15**, 539

7 Paul, D. R. and Barlow, J. W. *Polymer* 1984, **25**, 487

8 ten Brinke, G., Karasz, F. E. and MacKnight, W. J. *Macromolecules* 1983, **16**, 1827

9 Licht, U. and Cantow, H.-J. *Polym. Bull.* 1988, **20**, 387

10 Masse, M. A., Ueda, H. and Karasz, F. E. *Macromolecules* 1988, **21**, 3438

11 Cowie, J. M. G., Elexpuru, E. M., Harris, J. H. and McEwen, I. J. *Makromol. Chem. Rapid Commun.* 1989, **10**, 691

12 Walsh, D. J., Higgins, J. S. and Rostami, S. *Macromolecules* 1983, **16**, 388

13 Tarshiani, Y. and Dreyfuss, M. P. *J. Polym. Sci., Polym. Chem. Edn* 1990, **28**, 205

14 Bosma, M., ten Brinke, G. and Ellis, T. *Macromolecules* 1988, **21**, 1465

15 Shur, Y. J. and Ranby, B. *J. Appl. Polym. Sci* 1975, **19**, 2143

16 Wang, C. B. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn* 1983, **21**, 11

17 Huh, W. and Karasz, F. E. *Polym. Mater. Sci. Eng.* 1989, **60**, 792

18 Chai, Z., Shi, L. and Sheppard, R. N. *Polymer* 1984, **25**, 369

19 Cowie, J. M. G., Harris, J. H. and McEwen, I. J. *Macromolecules* in press

20 Coleman, M. H., Graf, J. E. and Painter, P. C. 'Specific Interactions and the Miscibility of Polymer Blends', Technomic Publ. Co. Inc., Lancaster, PA, 1991

21 Schurer, J. W., de Boer, A. and Challa, G. *Polymer* 1975, **16**, 201

22 Vorenkamp, E. J., ten Brinke, G., Meijer, J. G., Jager, H. and Challa, G. *Polymer* 1985, **26**, 1725

23 Lemieux, E., Prud'homme, R. E., Forte, R., Jérôme, R. and Teyssié, P. *Macromolecules* 1988, **21**, 2148

24 Cowie, J. M. G., McEwen, I. J. and Reid, V. M. C. *Polymer* 1990, **31**, 905

25 Cowie, J. M. G., Elexpuru, E. M. and McEwen, I. J. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 407

26 Cousin, P. and Prud'homme, R. E. *Am. Chem. Soc. Adv. Chem. Ser.* 1986, **211**, 87