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# The miscibility and phase separation in binary blends of poly(ethyl methacrylate) with styrene/acrylonitrile copolymers

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## SUMMARY

The miscibility and lower critical solution behaviour of pol(ethyl methacrylate) with poly(styrene-stat-acrylonitrile) have been studied. Poly(ethyl methacrylate) is miscible with styrene/acrylonitrile copolymers having acrylonitrile contents between 9 and 34 wt %. By increasing the size of the pendant group from methyl to ethyl, the repulsive interaction between the methacrylate and acrylonitrile increases, but that between the methacrylate and styrene decreases.

## INTRODUCTION

Because the combinatorial entropy on mixing is very small the miscibility of polymer pairs is most often the result of an exothermic heat of mixing and specific interactions are the most obvious source of favourable interaction.

It has been shown recently (1-4) that blends of a random copolymer and homopolymer exhibit miscibility in the absence of specific interactions and that miscibility in these mixtures may be enhanced by the interaction of dissimilar segments in the random copolymer chain. The interaction parameter $\chi_{blend}$ for a blend of a homopolymer A with copolymer BC is expressed by the equation

$$\chi_{blend} = y\,\chi_{AC} + (1-y)\,\chi_{AB} - y(1-y)\,\chi_{BC} \qquad (1)$$

where y is the volume fraction of C in the copolymer and $\chi_{AB}$, $\chi_{AC}$ and $\chi_{BC}$ are the segmental interaction parameters. If the interaction between segments B and C is sufficiently strong (i.e. sufficiently positive), a negative $\chi_{blend}$ can result even when $\chi_{AB}$ and $\chi_{AC}$ are positive. These miscible blends tend to phase separate at elevated temperatures and a lower critical solution temperature (LCST) is often observed.

Statistical styrene/acrylonitrile (SAN) copolymers (the most commonly studied being the industrial sample containing 28-30 wt % acrylonitrile) are miscible with a variety of different polymers (5-27). The miscibility of SAN copolymers with the poly(n-alkyl methacrylates) is limited to the first three members of the series (11). While the system SAN-poly(methyl methacrylate) has been studied in detail (5-10), the data for the system SAN-poly(ethyl methacrylate) are limited.

The aim of our contribution is to calculate the binary segmental interaction parameters from the phase separation of poly(ethyl methacrylate) with SAN copolymers and to compare the results obtained with the system poly(methyl methacrylate) - SAN copolymers.

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## EXPERIMENTAL SECTION

### Materials

The SAN copolymers used were prepared by photo-initiated copolymerization in the presence of naphthalene (26) as low conversion materials, thereby keeping the chemical heterogeneity very low. Molecular characteristics of the SAN copolymers used are summarized in Table 1. Poly(ethyl methacrylate) (PEMA) was an unfractionated sample from Röhm and Haas Co., Darmstadt, FRG, having $M_n = 7.43 \times 10^4$, $M_w = 1.52 \times 10^5$ and $T_g = 337$ K.

Table 1: Molecular characteristics of the copolymers

| Sample No. | Wt. % acrylonitrile | $M_n \times 10^5$ | Conversion |
|---|---|---|---|
| 12 | 6.4 | 0.61 [a] | - |
| 11 | 8.5 | 0.64 | - |
| 10 | 12.9 | 3.49 | 7.5 |
| 1 | 15.5 | 4.00 | 4.5 |
| 2 | 20.4 | - | 5.0 |
| 3 | 23.4 | 4.97 | 7.1 |
| 4 | 29.4 | 6.26 | 7.8 |
| 5 | 31.1 | 4.33 | 7.0 |
| 6 | 33.8 | 5.32 | 6.8 |
| 7 | 37.0 | 9.08 | 6.7 |
| 8 | 39.3 | 3.59 | 6.1 |

[a] Intrinsic viscosity in butanone at 298 K.

### Blend Characterization

Films of 50/50 composition were cast from butanone solutions (4-5 wt %) in a closed box under a dry nitrogen atmosphere at room temperature. The films obtained were then dried under an infrared lamp and finally in a vacuum oven at 350 K for 3 days.

The glass transition temperatures, $T_g$, of the samples and blends were determined using a Perkin-Elmer DSC-2 differential scanning calorimeter, scanning at 20 K $min^{-1}$ or a Polymer Laboratories dynamic mechanical thermal analyzer at 10 Hz and at a heating rate of 5 K $min^{-1}$.

The blend miscibility was monitored using the criteria that a miscible blend exhibited one $T_g$ and was prepared as a transparent film (determined visually) whereas a phase-separated blend showed the $T_g$ for both components and the film was opaque.

The LCST data were detected visually on the microscope hot stage using a heating rate of 10 K $min^{-1}$ as the temperature, where the first milky turbidity of the original transparent film occurred (cloud point temperature).

## RESULTS AND DISCUSSION

### SAN-Poly(ethyl methacrylate) Blends

It has been reported recently that SAN co-polymers are miscible with poly(ethyl methacrylate) (10,11), The experimental results reported here extend this study to include a wider range of compositions for the SAN copolymers. From these measurements a miscibility window was constructed and the phase boundary compositions were established. The results are presented in Fig. 1 and the corresponding data are listed in Table 2. Fig. 1 shows that poly(ethyl methacrylate) forms one phase blends with SAN copolymers in the copolymer composition range of 9 to 34 wt % acrylonitrile; the copolymer composition range in the binary blend SAN-poly(methyl methacrylate) is only slightly broader (7,8).

The shape of the miscibility window is similar to the window of SAN-poly (methyl methacrylate) (7,8) including the existence of a range where no LCST can be detected up to the decomposition of the blends. In the case of SAN-poly(ethyl methacrylate) blends the LCST values are about 30 K lower and also the miscibility "chimney" is narrower, confirming that poly(ethyl methacrylate) interacts less strongly with SAN copolymers than does poly(methyl methacrylate).

Table 2: Cloud points used for the determination of the miscibility window

| wt % AN in SAN | $T_g$ (K) | cloud point (K) |
|---|---|---|
| 6.4 | 378 + 340 | opaque |
| 8.5 | 358.5 | 468 |
| 12.5 | 362 | clear up to decomposition |
| 15.5 | 358.5 | clear up to decomposition |
| 20.4 | 362 | 523 |
| 23.4 | 361 | 481 |
| 29.4 | 362.5 | 464 |
| 31.1 | 361.5 | 457 |
| 33.8 | 361 | 455 |
| 37.0 | 360.5 | 449 |
| 39.3 | 377 + 337 | opaque |

The comparison with the results of the SAN-poly(ethyl methacrylate) blends (11) shows, that the width of both miscibility windows is practically the same, the differences in boundary compositions are probably due to the differences in chemical polydispersity (low acrylonitrile content SAN copolymers) and the use of tetrahydrofuran, which is a thermodynamically less favourable solvent than butanone especially for high acrylonitrile content SAN copolymers, due to its hygroscopicity (27). The reason for the differences, in miscibility window shape is unknown.

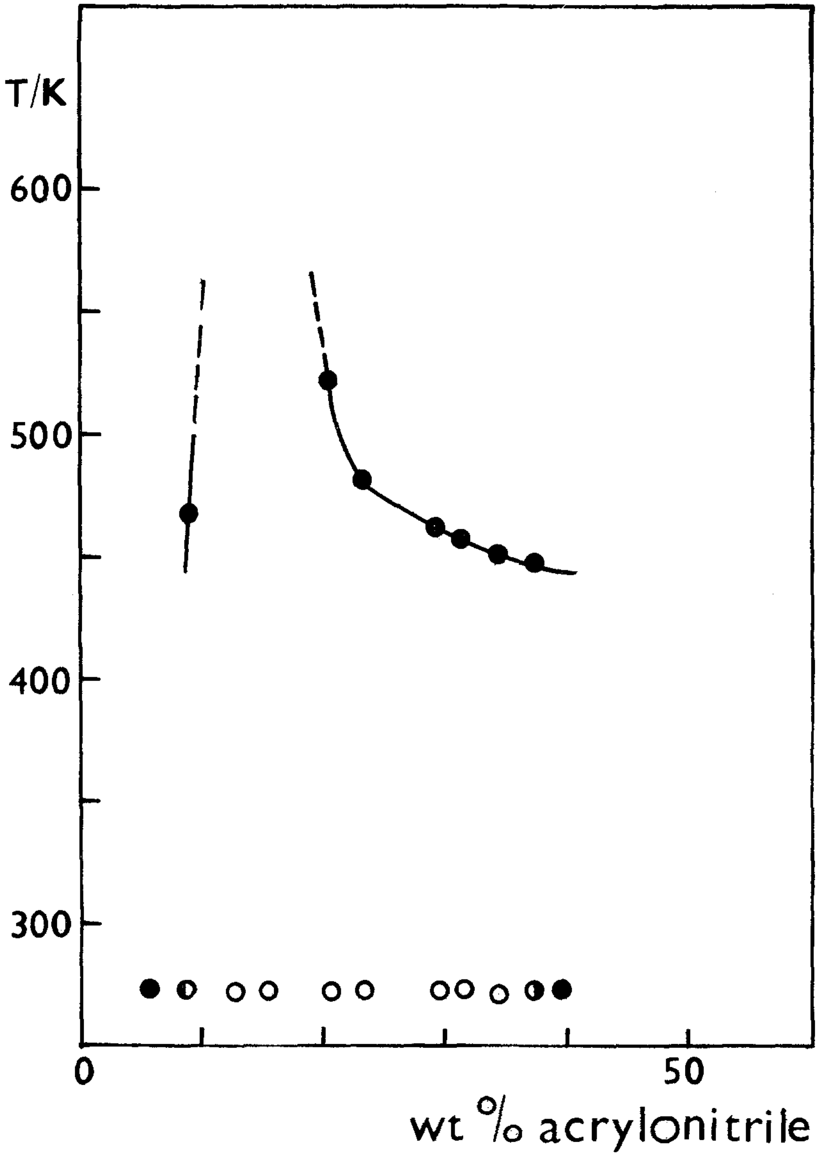

FIG. 1 Location of the room temperature miscibility and LCSTs for blends of poly(ethyl methacrylate) with a range of SAN copolymers of varying acrylonitrile content. Open circles represent miscible blends, closed circles the immiscible ones.

## Segmental Interaction Parameters

Based on the binary interaction model, the interaction parameter $\chi_{blend}$ for the present system is given by equation (1). The criterion for miscibility is that $\chi_{blend} < \chi_{crit}$ where

$$\chi_{crit} = 1/2\,(N_1^{-1/2} + N_2^{-1/2})^2 \qquad (2)$$

with $N_1$ and $N_2$ being the degrees of polymerization of poly(ethyl methacrylate) and the copolymer. For the binary blends studied $\chi_{crit} = 0.00075$ and since $\chi_{S\text{-}AN}$ is 0.829 (8), other $\chi$ values can be evaluated. For the SAN-poly(ethyl methacrylate) system, the miscibility limits are considered located at 9.0 and 34 wt % acrylonitrile and the values of $\chi_{S\text{-}EMA}$ and $\chi_{EMA\text{-}AN}$ are then 0.026 and 0.5 respectively.

For pairs of homopolymers, equation (1) reduces to $\chi_{blend} = \chi_{ij}$, the miscibility being governed simply by pair interaction parameters. The high molecular weight homopolymers based on styrene, ethyl methacrylate, and acrylonitrile are not miscible with each other and this is reinforced by the values of the interaction parameters determined, as the mixing is endothermic in each case. The comparison with the corresponding interaction parameters of the binary blend SAN-poly(methyl methacrylate), i.e. $\chi_{S\text{-}MMA} = 0.003$ and $\chi_{MMA\text{-}AN} = 0.46$, shows that the introduction of an ethyl group instead of methyl leads to a small increase in the repulsive interaction between the methacrylate and acrylonitrile whereas that between the methacrylate and styrene is slightly decreased. Both changes are relatively small, so the appearance of a miscibility window for SAN copolymers with poly(ethyl methacrylate), as with the system SAN-poly(methyl methacrylate) is favoured by strong repulsion within the copolymer coupled with the weak interactions with the homopolymer.

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