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## Blends

# Phase Behavior of Poly(Methylmethacrylate) and Poly(Styrene-Co-Acrylonitrile) Blends

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## Summary

Laser light scattering was used to study the miscibility behavior of PMMA/SAN blends. These systems tend to phase separation at elevated temperatures. Above the lower critical solution temperature (LCST) a regular highly interconnected two-phase morphology is displayed. The region of stability of this structure is determined. Finally, the binary interactional parameter is estimated. It is negative due to the sufficiently repulsive intramolecular interactions relative to the repulsive intermolecular interactions.

## Introduction

Most pairs of high molar mass polymers are immiscible due to their low combinatorial entropy of mixing. Miscibility of polymers is expected in three cases:

1. Polymers of low molar mass which have a sufficiently high combinatorial entropy of mixing;
2. polymers capable of specific interactions leading to favorable (exothermic) heats of mixing (1).
3. systems of a random copolymer and a homopolymer which have a sufficiently strong "repulsion effect" (2,3,4).

Miscible polymers tend to phase separation at elevated temperatures. This lower critical solution temperature (LCST) behavior is typical for miscible polymer blends.

PMMA/SAN blends are classic examples of miscible blends displaying LCST behavior (5-8). STEIN et al. (5) observed miscibility of the two components varying the copolymer composition from 9 to 26.5 wt% of AN. For systems in the composition range from 26 to 30 wt% of AN there is some evidence that also an upper critical solution temperature occurs (9). In contrast to thermodynamic requirements, however, BERNSTEIN et al. (8) could not prove the reversibility of the phase transition near a LCST.

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Furthermore, they reported the cloud point curve to be independent of the heating rate in the range from 5 to 15 K/min. Therefore, a study of PMMA/SAN blends was carried out over the whole composition range using laser light scattering. Another interesting feature is the following: These systems display just above the LCST a regular highly interconnected two-phase morphology, as also observed in the system polystyrene/poly(vinyl methyl ether) (10). Results are presented concerning the area of stability of those regular structures.

## Experimental

The SAN ($\overline{M_w}$ = 225000; $\overline{M_w}/\overline{M_n}$ = 1.82) containing 31.5 wt% acrylonitrile came from VEB Chemisches Kombinat BUNA. The PMMA ($\overline{M_w}$ = 43000; $\overline{M_w}/\overline{M_n}$ = 1.72) sample was prepared at 60°C in butanone-2 using 0.02 mol/l AIBN as initiator and a monomer concentration of 8 mol/l. The molecular weights were estimated by g.p.c. calibrated with polystyrene standards. The SAN and PMMA samples were dissolved at 5 wt% of total polymer in 1,2-dichloroethane. The solution was cast onto a cover glass and the solvent evaporated at room temperature. The cast films were transparent and showed a single glass transition between the glass transition temperatures of the pure components. (The difference in the glass transition temperatures of SAN and PMMA was observed to be 14 K)

The cover glass was inserted into a high temperature cell under $N_2$. The $Kr^+/Ar^+$ ion laser beam (150 mW) of 647 nm wavelength was applied vertically to the film specimen. The scattered light (measured at 90°) was focused onto the slit of a Raman spectrometer (11). Experiments were carried out at different heating rates. At the cloud point phase separation occurs resulting in a drastic increase in the Tyndall scattering. The light microscopy observations of the films were carried out with a hot-stage plate under a Zeiss microscope.

## Results and Discussion

Elevating the temperature the light scattering intensity stayed constant up to a certain temperature $T_A$ (cloud point). Above $T_A$ the scattering intensity increased with temperature (Fig.1). The $T_A$ corresponds to an onset temperature of phase separation and varied with the heating rate. Selected results of $T_A$ vs. heating rate plots are shown in Fig.2. The intercept of $T_A$ at which the heating rate is zero may correspond to the binodal temperature. Similar experiments were carried out with various compositions. Obviously, due to the temperature dependence of the viscosity the slope of the $T_A$-heating rate curve decreases with increasing temperature. The binodal points thus estimated are indicated by dots in Fig.3.

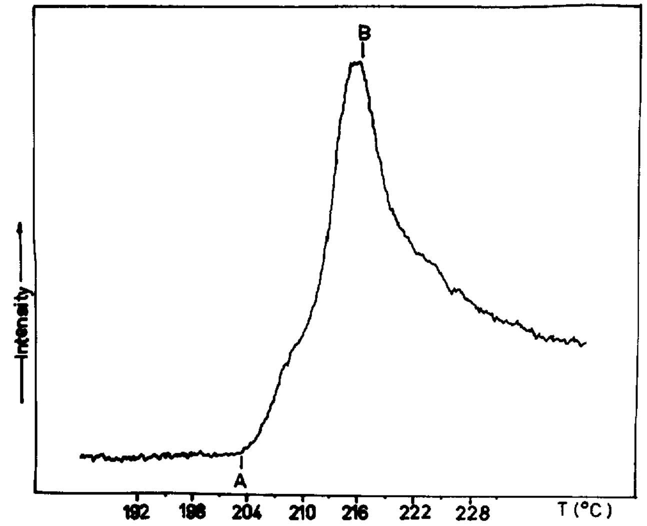

**Fig. 1.** Scattering intensity vs. temperature. The temperatures $T_A$ and $T_B$ correspond to the cloud point and the dissolution of the regular two phase structure, respectively.

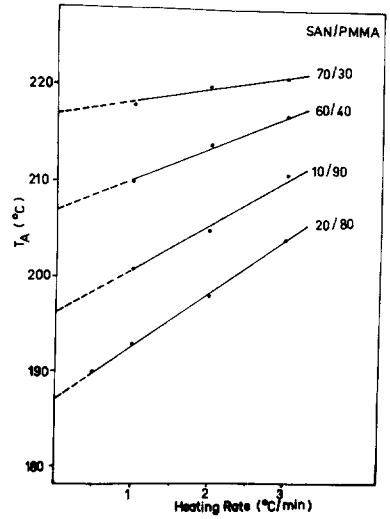

Fig.2 $T_A$ vs. heating rate
The intercepts with the ordinate represent the binodal temperatures

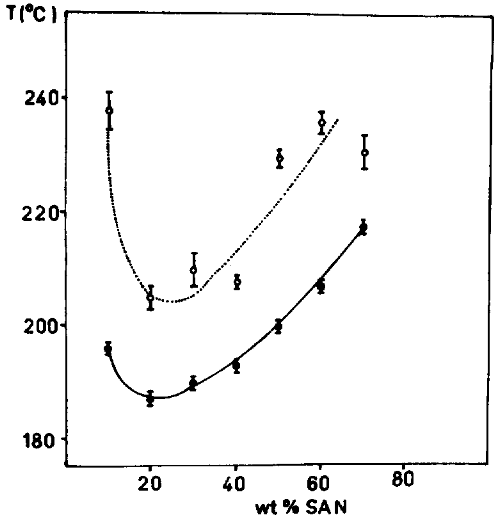

Fig.3 Phase diagramm
Binodal-full curve
Stability limit of the regular structure-dotted curve (see text)

The binodal displays a minimum at 187 °C for a blend containing 20 % SAN by weight. For blends with less than 10 and more than 70 wt%, respectively, no phase separation could be observed.

In order to confirm the reversibility of the phase transition we carried out experiments as follows (cf. Fig.4). The homogeneous film specimen of the 50/50 blend was heated until phase separation occured. This was followed by cooling of the sample below the binodal temperature. Below this temperature appreciable change in the scattering intensity with time could be detected. The intensity decay of isothermal annealing (at 190°C) in Fig.4, leading after a certain time to the original intensity, corresponds to phase dissolution. Starting again heating the cloud point occured at the same temperature as before.

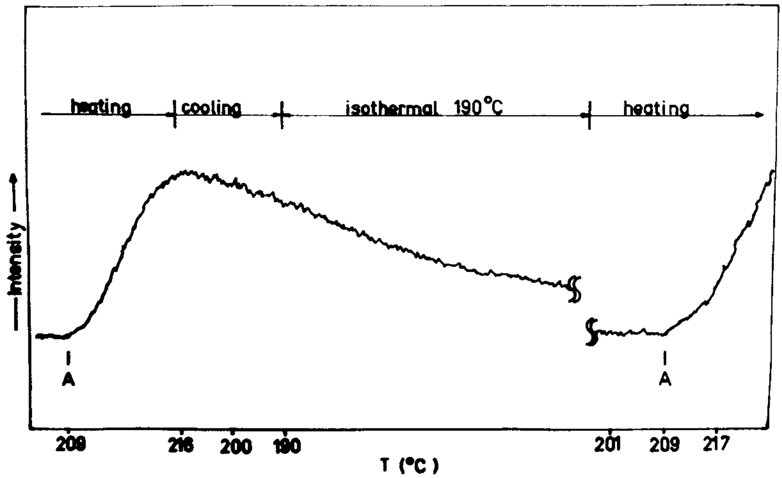

Fig. 4 Light scattering intensity vs. temperature to prove the reversibility of the phase transition (see text)

Just above the LCST the blend displays a very regular highly interconnected two-phase morphology. Fig.5 shows a typical example.

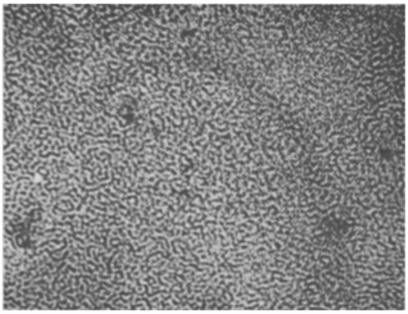

Fig. 5 Light micrograph of the regular two-phase morphology above the binodal. PMMA/SAN 60/40

The increase of the scattering intensity in the temperature range between $T_A$ and $T_B$ as plotted in Fig.1 reflects this microdomain structure. Obviously, the intensity decay above $T_B$ corresponds to a transition of the regular two-phase structure in an irregular two-phase structure. This is shown in Fig.6.

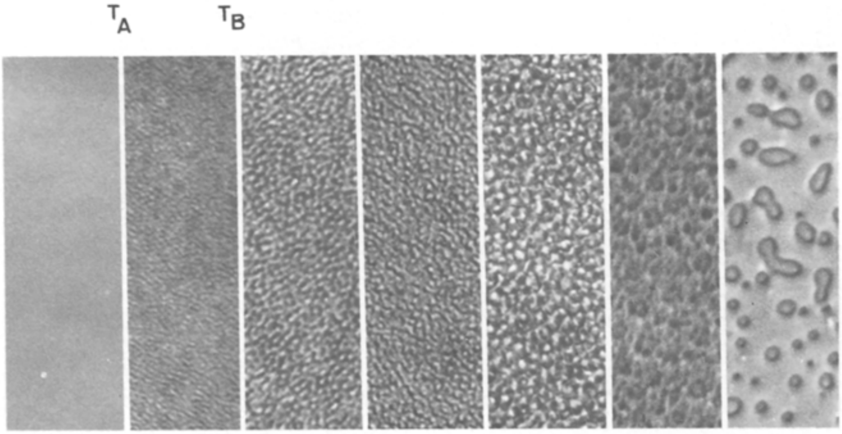

Fig. 6 The morphology of the 60/40 PMMA/SAN blend as a function of temperature. ⊢——⊣ 5 µm

The temperature $T_B$ was determined in the same way as the temperature $T_A$ representing the binodal. The points thus estimated are indicated by open circles in Fig.3. So, a second curve can be drawn in Fig.3. The area between the two curves reflects the region of stability of the regular two-phase morphology. For a blend containing 20 wt% SAN the regular structure could be observed at 195°C over a period of 8h. Appreciable structural change did not take place.

According to the thermodynamic theory the condition on the free energy of mixing for miscibility is only satisfied when the interactional parameter $X_{AB}$ is negative (4,12). In the case of a mixture consisting of a homopolymer (A) and a random copolymer (B) the parameter $X_{AB}$ is given by (2,3,4)

$$X_{AB} = \beta\chi_{12} + (1-\beta)\chi_{13} - \beta(1-\beta)\chi_{23} \qquad /1/$$

where $\beta$ represents the mole fraction of component 2 in the random copolymer and $\chi_{ij}$ are the respective segmental interactional parameters. Considering blends of PMMA and SAN we let 1 = MMA, 2 = S, and 3 = AN. Here, we employ the solubility parameter approach to estimate the parameters $\chi_{ij}$ :

$$\chi_{ij} = \frac{V}{RT}\,(\delta_i - \delta_j)^2 \qquad /2/$$

where $\delta_i$ are the solubility parameters of the respective components and V is a reference volume. For V it has been taken the geometric mean of the molar volumes of the involved polymer repeat units. Following the route of KRAUSE (13) and employing group molar constants according to (14) we obtain for the solubility parameters (densities: $\rho_1 = 1.16$, $\rho_2 = 1.05$, $\rho_3 = 1.20$ g/cm$^3$) at 20°C: $\delta_1 = 9.3$, $\delta_2' = 9.1$, and $\delta_3' = 13.0$ (cal/cm$^3$)$^{1/2}$. The parameters $\delta_2'$ and $\delta_3'$ refer to the pure homopolymers 2 and 3, respectively. However, this is not the reference state to be used in calculating the parameter $X_{AB}$ for a homopolymer A and a copolymer B formed from monomers 2 and 3. Using the above solubility parameters we get

$$\delta'_{SAN} = \beta\delta'_2 + (1 - \beta)\,\delta'_3 = 10.9 .$$

On the other hand, we can consider the copolymer as a "homopolymer" with the weighted repeat unit 2 + 3 and again calculate $\delta_{SAN}$ applying the above procedure ($\rho_{SAN} = 1.07$ g/cm$^3$). As a result we get

$$\delta_{SAN} = \beta\delta_2 + (1 - \beta)\,\delta_3 = 9.7$$

in excellent agreement with results submitted in (15). The parameter $_{SAN}$ refers to the appropriate reference state.

Assuming that the difference ($\delta'_{SAN} - \delta_{SAN}$) reflects corresponding shifts of the respective solubility parameters one can calculate the "true" solubility parameters of the components comprising the copolymer: $\delta_2 = 7.9$ and $\delta_3 = 11.8$.

Inserting these values in Eq./2/ we get for the parameters $\chi_{ij}$: $\chi_{12} = 0.31$, $\chi_{13} = 0.66$, $\chi_{23} = 2.13$. Therefrom, the interactional parameter /1/ results to be $X_{AB} = -0.06$. This result confirms that the so-called repulsion effect can lead to exothermic mixing in the absence of specific interactions.

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