Blends

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

J. Kressler, H. W. Kammer*, and K. Klostermann

University of Technology, Department of Chemistry, Mommsenstraße 13, DDR-8027 Dresden, German Democratic Republic

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.

* To whom offprint requests should be sent
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 (\(M_w = 225000; \frac{M_w}{M_n} = 1.82\)) containing 31.5 wt% acrylonitrile came from VEB Chemisches Kombinat BUNA. The PMMA (\(M_w = 43000; \frac{M_w}{M_n} = 1.72\)) 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.