

Melting point depression in poly(ϵ -caprolactone) / poly(styrene-co-acrylonitrile) blends

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Summary

The melting point depression of poly(ϵ -caprolactone)/poly(styrene-co-acrylonitrile) (PCL/SAN) blends with changes in acrylonitrile content of SAN and in blend ratio was investigated by differential scanning calorimetry. For the melting points at a constant blend ratio occur a minimum in dependence on the copolymer composition for blends containing about 20 wt% acrylonitrile in SAN. From melting point depression data a negative, binary interaction parameter was obtained for PCL/SAN blends containing a SAN with 19.2 wt% AN. By optical microscopy it can be shown that the shape of the spherulites changes with copolymer composition of SAN and blend ratio.

Introduction

In miscible polymer-polymer melts in which one component is able to crystallize melting point depression can be observed. This phenomenon has been frequently used to obtain the polymer-polymer interaction parameter χ_{12} (1-5). The thermodynamic background is that at equilibrium the chemical potentials of the crystalline component are equal in both the solid phase and the liquid phase. Applying the well-known FLORY-HUGGINS formula for the GIBBS free energy (1) the melting point depression can be expressed by:

$$(1/V_1) [(1/T_m) - (1/T_m^0)] = -(BV_{2u} / \Delta H_{2u})(V_1 / T_m) \quad /1/$$

where the subscripts 1 and 2 refer to the amorphous polymer and the crystalline polymer, respectively. B is the interaction energy density, ΔH_{2u} the enthalpy of fusion per mole of repeating units of the pure polymer, V_{2u} the specific volume, V_1 the volume fraction of component 1. T_m and T_m^0 are the melting points of the mixture and the pure crystalline polymer, respectively. The interaction parameter is assumed to be of the form (1):

$$\chi_{12} = (BV_{1u} / RT) \quad /2/$$

As can be seen, Eq.s /1/ and /2/ allow the interaction parameter to calculate from the slope of a plot of $(1/V_1) [(1/T_m) - (1/T_m^0)]$ versus (V_1/T_m) (2).

The system PCL/SAN is suitable for studies on the melting point depression since miscible and immiscible blends

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can be prepared in dependence on the copolymer composition. Chiu and Smith (6) found a miscibility window in blends of SAN and PCL. For blends containing SAN with AN contents from 8 up to 28 wt% one glass transition was recorded. Immiscible blends were found if the AN content of SAN is less than 6 wt% or more than 30 wt%. At the edges of the miscibility window the typical LCST-behavior was observed. For the same system Rim and Runt (7) showed that the blend preparation is very important for thermodynamic considerations. They obtained different results for blends prepared in the melt or by solution casting. Due to the small differences in the melting points of the pure PCL and the blends they were not able to estimate the χ_{12} parameter.

Experimental

Materials

The PCL used in this work was PCL-700 produced by the Union Carbide Corporation. Molecular weight data are $M_n=15500$ g/mol and $M_w=40400$ g/mol (8). The polymerization of SAN and the molecular weights are reported elsewhere (9).

Blend preparation

The polymers were dissolved in 1,2-dichloroethane and cast onto a glass plate. The solvent was slowly evaporated at room temperature and then the thin films were dried in a vacuum oven at 40 °C for several days. Afterwards, small samples were taken into d.s.c. pans and heated with 64 K/min to 150 °C in a DSC-1B. The samples were isothermally annealed at 150 °C for two minutes and then cooled with 8 °C/min to room temperature. Furthermore, all samples were aged for about one month.

D.s.c. measurements

The d.s.c. measurements were carried out with a Perkin Elmer DSC-4 equipped with a data station. The heating rate was 10 K/min. It was measured under nitrogen and the sample weight was usually between 2 and 3 mg. The maxima in the endothermic peaks were taken as the melting points. All T_m data reported are the average of at least five runs.

Optical microscopy

The shape of the spherulites was observed by an optical phase contrast microscope (Carl Zeiss Jena) with crossed polarizer and analyser.

Results and Discussion

Fig.1 shows the melting point depression for different PCL/SAN blends. The melting points were measured in dependence on the blend ratio and the copolymer composition of SAN. One can see that the most significant melting point depression is measured for blends of PCL and SAN-19.2. SAN-19.2 means a SAN with 19.2 wt% of AN. These blends are situated in the center of the miscibility window, which is reported in ref.6. This is in agreement with the fact that in this case the interaction parameter χ_{12} must be highly negative. If one takes a SAN at the edges of the miscibility window it can be seen that the melting point depression is smaller.

Outside the miscibility window significant melting point depression did not occur.

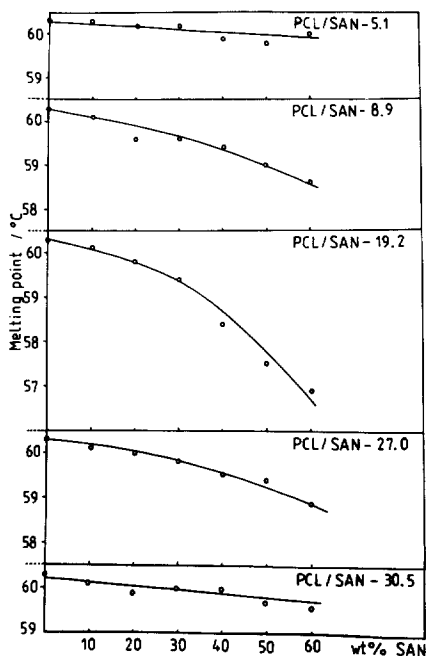


Fig.1: Melting points of PCL/SAN blends in dependence on the blend ratio and copolymer composition

This is also demonstrated in Fig.2. It is a plot of the melting points versus copolymer composition for 50/50 blends.

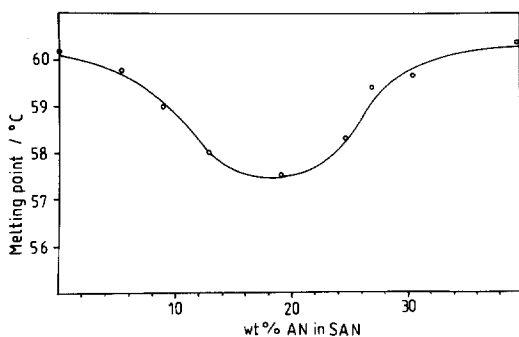


Fig.2: Melting points of PCL/SAN 50/50 blends in dependence on the copolymer composition

The reported miscibility window occurs between 8 and 28 wt% AN in SAN. In this region we can find a significant melting point depression. Outside this window the melting point is similar to the melting point of the pure PCL also for PCL/polystyrene 50:50 blends (0 wt% AN). This analysis indicates that a melting point depression of a crystalline polymer in a polymer blend implies miscibility. Therefore, mel-

ting point depression allows for the estimation of the interaction parameter χ_{12} for PCL/SAN-19.2 blends. Fig.3 shows a plot of $(1/T_m - 1/T_m^0)/V_1$ versus V_1/T_m .

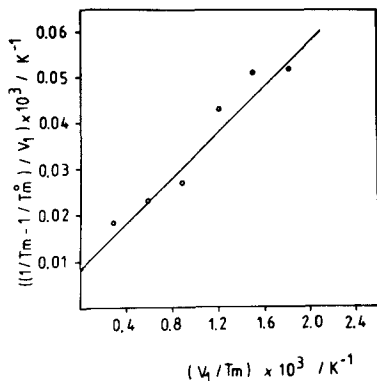


Fig.3: $(1/T_m - 1/T_m^0)/V_1$ versus V_1/T_m plot for PCL/SAN-19.2 blends

The slope of the least square line is 0.026 and the intercept is 8.7×10^{-6} . Using the constants $\Delta H_{2u} = 3880$ cal/mol (10), $V_{2u} = 105$ cm³/mol (10) and $V_{1u} = 121$ cm³/mol (11) one obtains $\chi_{12} = -0.18$. In using melting point depression to calculate the parameter χ_{12} it must be recognized that a polymeric diluent in a miscible blend containing a crystalline polymer may alter the spherulite size which in turn influences the melting point. This effect has been neglected. However, corrections for this effect should be made to obtain more accurate χ_{12} values.

Another interesting phenomenon is presented in Fig.4.

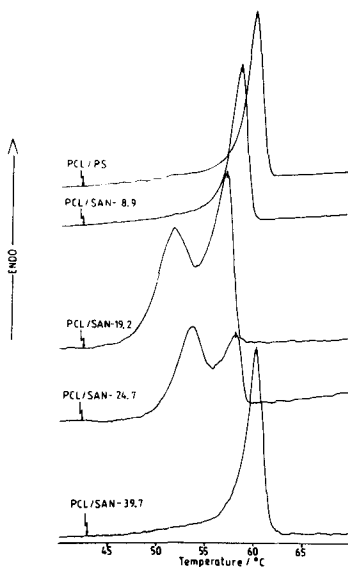
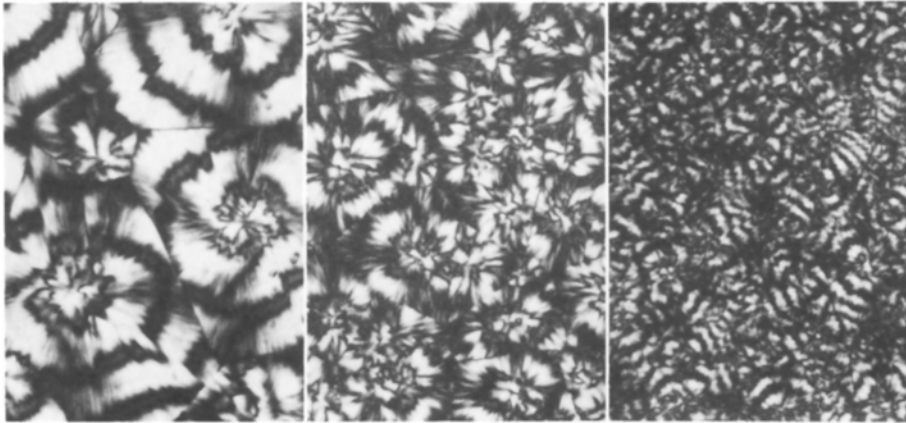


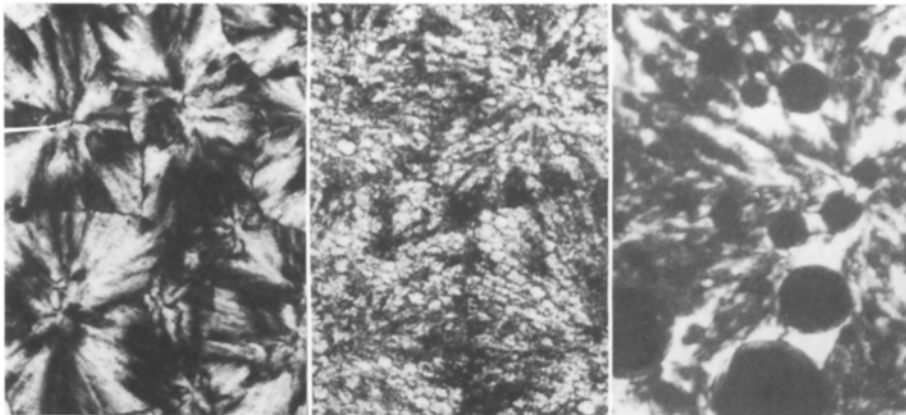
Fig.4: D.s.c. traces of different PCL/SAN 50:50 blends and PCL/poly-styrene (PS) blend

There are shown d.s.c. traces of PCL/SAN 50:50 blends with different SAN copolymers. For miscible blends two endothermic peaks can be found and for immiscible blends only one. The melting point depression of Fig.1 is always related to the endothermic peak at higher temperatures. The endothermic peak at lower temperatures is relatively independent of the blend ratio. The occurrence of two endothermic peaks of blends prepared in the melt is not completely clear. All blends prepared from solution show only one endothermic peak. For blends prepared in melt it seems possible that the melting behavior is influenced by recrystallization of the original lamellae and melting of the recrystallized PCL. Some evidence is given by a small exothermic peak between the two endothermic peaks of miscible SAN/PCL blends at very low heating rates (7).

Using optical microscopy one can observe different spherulitic shapes (Fig.5).



a) PCL/SAN-19.2 90:10 b) PCL/SAN-19.2 70:30 c) PCL/SAN-19.2 50:50



d) PCL/SAN-5.4 90:10 e) PCL/SAN-5.4 70:30 f) PCL/SAN-5.4 50:50

Fig.5: Light micrographs of the spherulites of a miscible blend (with SAN-19.2) and an immiscible blend (with SAN-5.4)

Fig.s 5a-c show the spherulites of a miscible blend at different blend ratios and Fig.s d-f depict spherulites of immiscible blends. As mentioned above the size of the spherulites decreases with increasing SAN content. Obviously, in miscible blends the amorphous SAN/PCL phase interweaves the spherulites and finally separates the crystalline regions whereas in immiscible blends the amorphous phases are dominantly pushed back into the interspherulitic regions.

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