

## **Pulse Induced Critical Scattering from Solutions of Randomly Crosslinked Polystyrene in Cyclohexane**

**K. Kajiwara<sup>1</sup>, W. Burchard<sup>1</sup>, L.A. Kleintjens<sup>2</sup> and R. Koningsveld<sup>2</sup>**

<sup>1</sup> Institut für makromolekulare Chemie der Universität Freiburg, Stefan-Meier-Str. 31, D-7800 Freiburg i. Br., Federal Republic of Germany

<sup>2</sup> DSM Research and Patents, NL-6160 MD Geleen, Netherlands

### Summary

The spinodal decomposition was observed by the Pulse Induced Critical Scattering technique for the three branched polystyrenes in cyclohexane. Branched polystyrenes were prepared by  $\gamma$ -irradiation on linear polystyrene of narrow molar-mass distribution for various periods. The location of the spinodals was hardly affected with regard to temperature though the crosslinking has increased the molar mass by a factor 10.

### Introduction

The spinodal decomposition range in a polymer/solvent system can be located by light-scattering measurements. The forward scattering intensity  $I(0)$  by a binary homogeneous solution is related to  $\Delta G_{\text{mix}}$ , the free enthalpy (Gibbs free energy) of mixing per unit volume, by (Debye, 1959)

$$I^{-1}(0) \propto (\partial^2 \Delta G_{\text{mix}} / \partial \phi^2)_{p,T} \quad (1)$$

The spinodal condition reads

$$(\partial^2 \Delta G_{\text{mix}} / \partial \phi^2)_{p,T} = 0 \quad (2)$$

where  $\phi$  is the volume fraction of polymer. Hence, extrapolation of  $I^{-1}(0)$  to zero as a function of temperature  $T$  yields the spinodal temperature for the  $\phi$  value considered. Chu et al. (1969) and Scholte (1970, 1971), i.a., have so determined spinodals with conventional photometers measuring the intensity of light scattered at various angles at several temperatures, well above phase separation. This method is rather time-consuming and does not infrequently involve long extrapolations.

To improve matters on this point Gordon et al. (1972, 1973, 1974) developed the Pulse Induced Critical Scattering technique (PICS) which allows measurement of the scattered light intensity at temperatures within the meta-stable region of the miscibility gap. The solution is kept there for a few seconds only and readings are taken before phase separation sets in. Thus the experimental data are brought considerably closer to the spinodal temperature than is possible with the conventional method, and the extrapolation improves.

As useful expression for the concentration and molar-mass (distribution) dependence of  $\Delta G_{\text{mix}}$  is supplied by the Flory-Huggins theory (Flory, 1942, 1944; Huggins, 1942). Using it to derive the spinodal condition with the multicomponent analogue of eq. 2 we find (Stockmayer, 1949; Koningsveld & Staverman, 1968)

$$1/(1-\phi) + 1/\phi m_w - 2\chi - \phi(\partial\chi/\partial\phi) = 0 \quad (3)$$

where we allow the Flory-Huggins interaction parameter  $\chi$  to depend on the overall polymer concentration  $\phi$  as well as on temperature:

$$\chi = \chi(T, \phi)$$

Within this framework the spinodal further depends on  $m_w$ , the mass-average relative chain length which is proportional to the mass-average molar mass.

Effects of chain branching have been introduced in the model, i.a. by Kleintjens (1979, 1980) whose expression for  $\Delta G_{\text{mix}}$  provided a correct description of the thermodynamic behaviour of diphenylether solutions of low-density polyethylene. This polymer contains a large number of short side chains in addition to long branches.

The present note is a preliminary report on spinodals by PICS of cyclohexane solutions of polystyrene, randomly crosslinked by radiation at doses below that of the gel point. These samples represent a type of branching different from that in low-density polyethylene. PICS spinodals on branched polystyrene in cyclohexane have been reported previously by Derham and Gordon (1974).

### Experimental

Commercial polystyrene of narrow molar-mass distribution (Pressure Chemical Co) was crosslinked by  $\gamma$ -irradiation in vacuo for various periods. The number- and mass-average molar masses ( $M_n$ ,  $M_w$ ) were determined with the usual techniques of high-speed membrane osmometry and static light scattering. Chain scission during irradiation was negligible (Gordon et al., 1975).

TABLE I

sample	dose (Mrads)	$M_n$ $10^{-5}$ (g.mole $^{-1}$ )	$M_w$ $10^{-5}$ (g.mole $^{-1}$ )	$\alpha/\alpha_c^*$
S2R0 (primary chain)	0	1.81	1.88	0
S2R3	55	2.65	6.18	0.695
S2R4	67	2.85	7.70	0.756
S2R5	78	3.06	18.80	0.900

\* The reduced extend of crosslinking;  $\alpha/\alpha_c = 1$  at the gel point

Characteristics of the samples are listed in Table I. The molar-mass distribution widens considerably when the gel point is approached. However, no change in the number of free chain ends occurs by crosslinking.

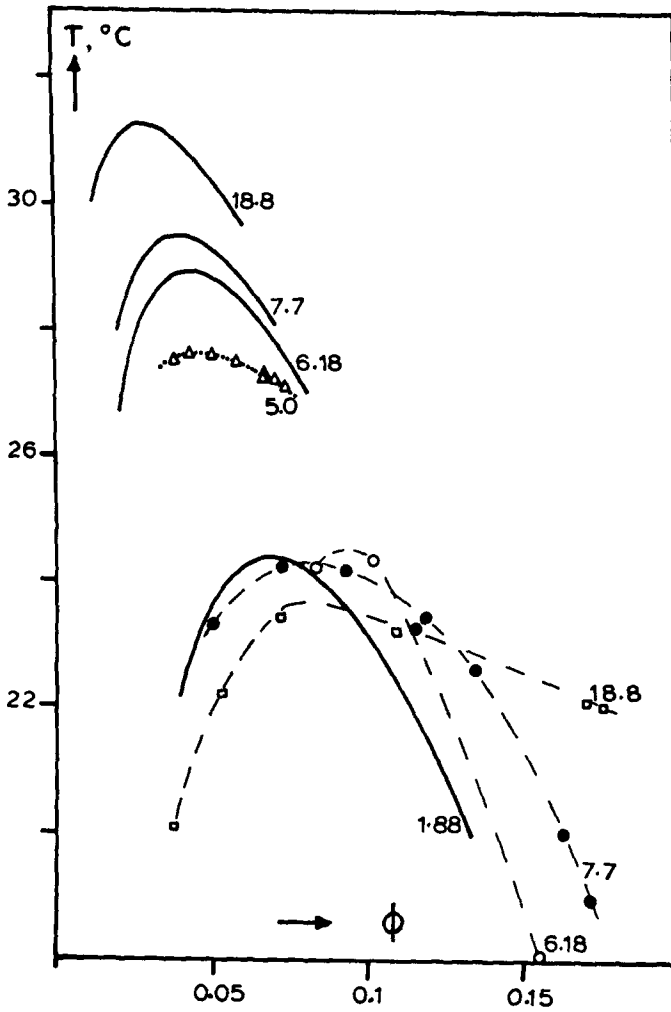


Figure 1

Spinodal points by Pulse Induced Critical Scattering (PICS) for branched polystyrene samples S2R3 (o), S2R4 (●) and S2R5 (□) (see Table I) in cyclohexane. Mass-average molar masses ( $M_w$ , in  $10^2$  kg/mole) are indicated. Dashed curves drawn by hand, drawn curves: spinodals calculated for linear polystyrenes at the same  $M_w$  values. PICS data for linear polystyrene at  $M_w = 5 \cdot 10^2$  kg/mole:  $\Delta$  (from Irvine, 1980)

### Results and Discussion

Figure 1 shows spinodal temperatures by PICS for the three branched polystyrenes S2R3, S2R4 and S2R5 in cyclohexane. Although the crosslinking has increased the molar masses by a factor 10 the location of the spinodals is hardly affected with regard to temperature. This is demonstrated by the location of the spinodals for linear polystyrenes with similar molar masses, including that of S2R0 (primary chains). The latter spinodals were calculated with eq. 3 in which the  $\chi(T, \phi)$  function, suggested by Kurata (1975) for linear polystyrene in cyclohexane, was used to estimate  $\chi$ .

$$\chi = (0.3015 + 61.0/T) + (-0.300 + 190/T)\phi \quad (4)$$

Some experimental PICS data by Irvine and Gordon (1980) are also shown and prove that the location of the calculated spinodals is essentially correct.

The system on hand shows a remarkable and unexpected feature in that the increase in molar mass by crosslinking appears to be roughly compensated by branching with regard to the spinodal temperature range. In fact, the spinodals do not deviate much from that of the linear primary chains. In another respect, however, the spinodal shows direct sensitivity to branching, an increase of which tends to shift the right-hand-side of the curve to higher temperatures. This is in qualitative agreement with previous findings of Derham and Gordon (1974) who report larger shifts, however. Leaving the cause of this difference undiscussed at this moment, we may still conclude that the levelling effect branching has on the rhs of the spinodal must be very strong because the molar-mass distribution of the samples widens simultaneously. For linear polystyrene it is well documented (Scholte, 1972; Derham et al. 1975; Irvine et al. (1980) that widening of the distribution has quite the opposite effect of steepening the rhs of the spinodal.

Obviously, the influence of branching on  $\Delta G_{\text{mix}}$  must in this respect be overwhelming in order to outweigh the distribution effect to such an extent.

Kleintjens' analysis of low-density polyethylene in diphenylether indicates that the lowering of the  $\theta$ -point by branching is related to the concentrations of end groups and branch points on the chains, to the extent that the short side chains mainly determine the cloud-point depression. Thus the  $\theta$ -point is hardly or not affected by the long branches present.

It is too early to say whether this may also be true for the present system. In the first place we probably have larger concentrations of long branches on the polystyrene chains than there are in low-density polyethylene, the system is much closer to its critically branched state (Gordon, (1972), Kajiwara, (1975, 1982). Secondly, it is interesting to note the tendency of the left-hand sides of the spinodals to cluster. Any attempt at describing the system must start disentangling branching and molar mass effects. This calls for a considerable extension of the experimental information which is currently being collected. Spinodals and critical points are being measured on samples based on primary chains varying in length.

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