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Lower critical solution temperature and upper critical solution temperature phase behaviour in random copolymer blends: poly(styrene-*co*-acrylonitrile)/poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile)/poly(ε-caprolactone)

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The phase behaviour of blends of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) is calculated as a function of copolymer composition from the data of the temperature dependence of all three segmental interaction parameters, $\chi_{i/j}(T)$ of the system SAN/PMMA, i.e. $\chi_{S/MMA}(T)$, $\chi_{AN/MMA}(T)$ and $\chi_{S/AN}(T)$. Using blends with different copolymer compositions might change the temperature dependence of the polymer–polymer interaction parameter $\chi_{AB}(T)$ dramatically, from increasing to decreasing with temperature. In the copolymer composition range from ~ 11 to 55 mol% of acrylonitrile in SAN the $\chi_{AB}(T)$ parameter is increasing with temperature, leading to lower critical solution temperature behaviour, and in the copolymer composition range up to ~ 10 mol% and > 56 mol% of AN in SAN the $\chi_{AB}(T)$ parameter is decreasing with increasing temperature, predicting upper critical solution temperature behaviour when one or two components have relatively low molecular weight, i.e. for oligomers. Similar conclusions can be obtained for blends of SAN with poly (ε-caprolactone).

(Keywords: phase behaviour; interaction parameter; blends)

INTRODUCTION

Many miscible or partially miscible blends of dissimilar polymers have been reported in the literature[1,2]. Only a few of them are blends consisting entirely of homopolymers, as the standard examples of polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and PS/poly(vinyl methyl ether) (PVME). Most of the miscible blends reported in the literature contain at least one random copolymer, i.e. homopolymer/copolymer or copolymer/copolymer blends. In the case of homopolymer/copolymer systems, the blends might be miscible in a certain range of copolymer composition and temperature even though none of the three homopolymers derived from the respective monomers are mutually miscible. Such miscibility behavour is called 'miscibility window' and may occur when the interaction parameter $\chi_{2/3}$ for pairs of different monomer segments in the copolymer itself is significantly larger compared to the other segmental interaction parameters caused by the 'repulsion effect'[3,4]. The first experimental results for such behaviour were found for blends of poly(styrene-*co*-acrylonitrile) (SAN)/poly(methyl methacrylate) (PMMA)[5], SAN/poly(ε-caprolactone) (PCL)[6] and PPO with random copolymers of *para*- and *ortho*-chlorostyrene[7].

Here we want to focus on blends of PMMA and SAN. Although PMMA is immiscible with PS and polyacrylonitrile (PAN), respectively, and also PS is immiscible with PAN, PMMA/SAN blends have been reported to be miscible as a function of the temperature and copolymer composition in the range from 9.4 up to 34.4 wt% of AN in SAN[8–10]. According to a mean field theory, this behaviour arises from the large segmental interaction parameter between styrene (S) and acrylonitrile (AN). Furthermore, it has been known that the phase separation in this system proceeds during temperature elevation, i.e. a lower critical solution temperature (*LCST*) behaviour can be observed.

In our previous paper we reported the equilibrium interfacial thickness of blends of PMMA with two different SANs containing 5.7 and 38.7 wt% AN, respectively, and with PS in the temperature range from 140 to 170°C[11]. The temperature dependence of polymer–polymer interaction parameters $\chi_{AB}(T)$ for the systems PS/PMMA, PMMA/SAN-5.7 and PMMA/SAN-38.7 was calculated from their interfacial thickness data using the theory of Broseta *et al.*[12] Furthermore, the temperature dependence of three segmental interaction parameters $\chi_{i/j}(T)$, i.e. $\chi_{S/MMA}(T)$, $\chi_{AN/MMA}(T)$ and $\chi_{S/AN}(T)$, was calculated from three $\chi_{AB}(T)$ parameters in terms of a mean field theory. All $\chi_{i/j}(T)$ parameters

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were decreasing with increasing temperature, but as mentioned above the polymer–polymer interaction parameter between PMMA and SAN might increase with temperature in a certain copolymer composition range, leading to *LCST* behaviour. This implies the possibility that the different temperature dependence of the segmental interaction parameters $\chi_{i/j}(T)$ leads to *LCST* behaviour without any obvious influence of free volume contributions. Furthermore, it is known that oligomers of styrene and methyl methacrylate show upper critical solution temperature (*UCST*) behaviour[13,14]. The same pattern occurs in the system SAN/PCL. Here the polymers also show *LCST* behaviour, whereas oligomers of styrene and ε-caprolactone show *UCST* behaviour[15,16].

In order to explain the inversion of phase diagrams from *UCST* to *LCST* behaviour we calculated the temperature dependence of polymer–polymer interaction parameters $\chi_{AB}(T)$ as a function of the copolymer composition from the $\chi_{i/j}(T)$ parameters in the framework of a mean field theory. Furthermore, the miscibility windows of blends of PMMA/SAN with PCL/SAN are predicted with changing molecular weights.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of all three segmental interaction parameters $\chi_{i/j}(T)$ in the SAN/PMMA system reported in a previous paper[11]. All

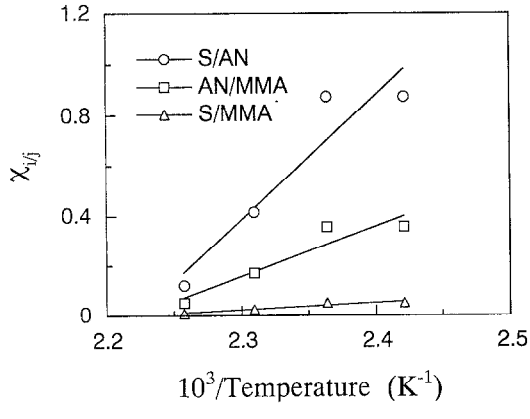

Figure 1 Plot of the segmental interaction parameters $\chi_{i/j}$ of the PMMA/SAN systems *versus* the reciprocal temperature taken from ref. 1

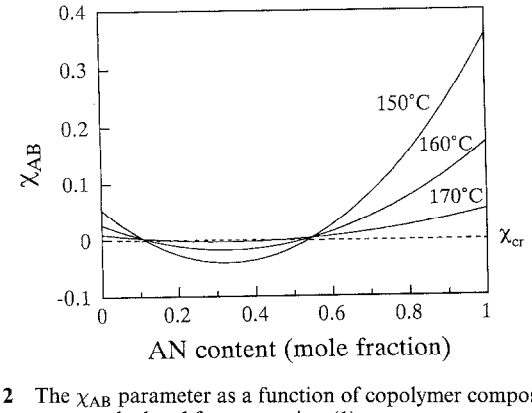

Figure 2 The χ_{AB} parameter as a function of copolymer composition and temperature calculated from equation (1)

$\chi_{i/j}(T)$ parameters are decreasing with increasing temperature. Their temperature dependence can be considered as an approximately linear relationship of χ *versus* the reciprocal temperature in the temperature range from 140 to 170°C.

Using these three $\chi_{i/j}(T)$ parameters at various temperatures, it is possible to calculate the polymer–polymer interaction parameter χ_{AB} as a function of the copolymer composition by[3]:

$$\chi_{AB} = \beta\chi_{1/2} + (1-\beta)\chi_{1/3} - \beta(1-\beta)\chi_{2/3} \quad (1)$$

where β represents the mole fraction of component 2 (AN) in the random copolymer (it should be noted that different authors are using different definitions of β, which of course can be easily converted). These results are shown in *Figure 2*. The χ_{AB} parameter is identical at 140°C and 150°C. The copolymer composition dependence of χ_{AB} parameters for every temperature is of parabolic shape. In the copolymer composition range from ~ 11 to 55 mol% of AN in SAN the χ_{AB} parameter is increasing with increasing temperature. This is in good agreement with the experimentally observed *LCST* behaviour[8–10], i.e. the blend should be miscible in the range where the χ_{AB} parameter is smaller than the critical χ_{cr} value which is given by the Flory–Huggins theory:

$$\chi_{cr} = (1/2)(N_A^{-0.5} + N_B^{-0.5})^2 \quad (2)$$

where N_A and N_B are the numbers of segments for polymers A and B, respectively, with the segment is taken to be of equal volume between the two polymers. Equation (2) is of course only an approximation for a concentration independent χ parameter and for incompressible liquids[17]. *LCST* behaviour occurs in the case that the χ_{AB} parameter increases further with temperature

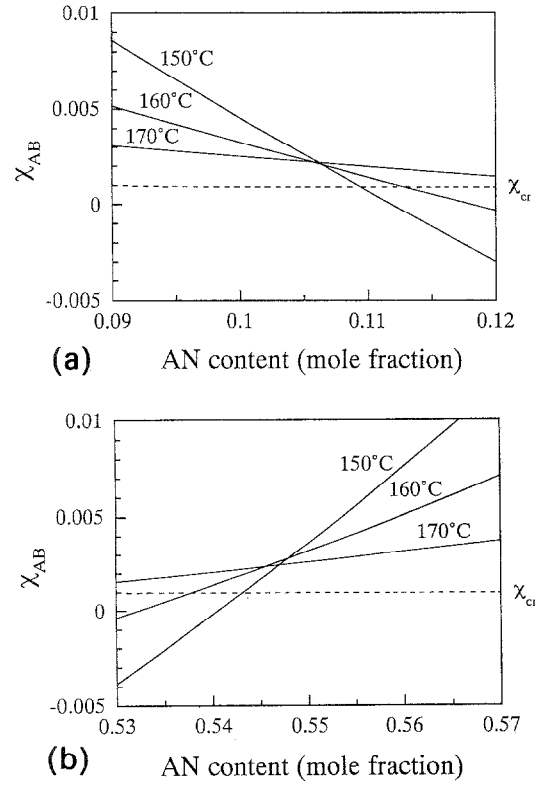

Figure 3 Enlarged view of *Figure 2*: (a) at ~ 10 mol%; (b) at ~ 55 mol%

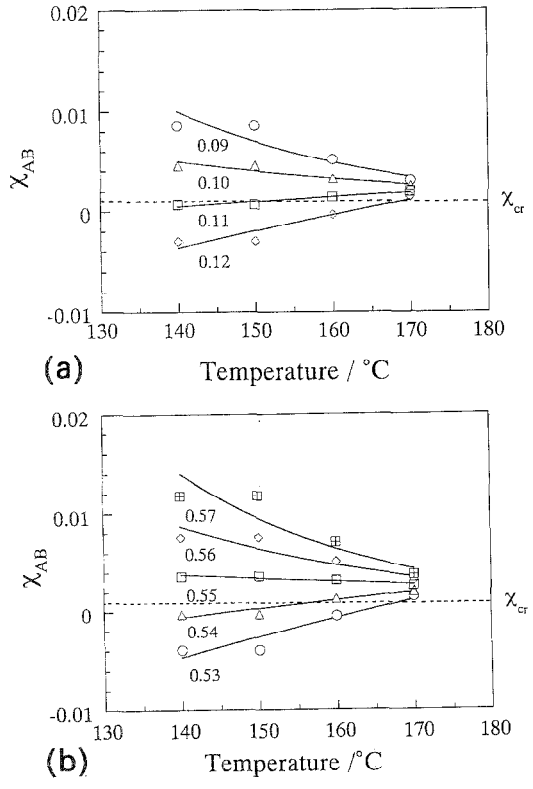

Figure 4 Temperature dependence of the χ_{AB} parameter for certain copolymer compositions: (a) low AN content range; (b) high AN content range

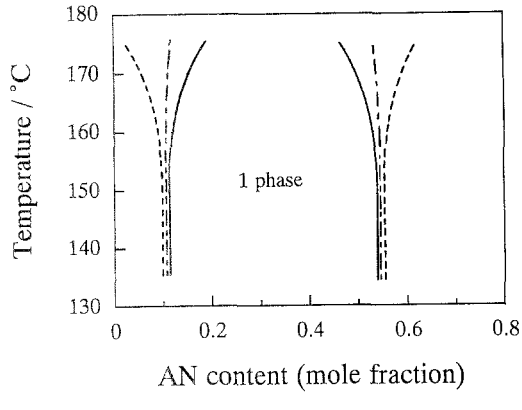

Figure 5 Miscibility window of PMMA/SAN blends calculated from the segmental interaction parameters for the various χ_{cr} values: (——) 0; (— — —) 0.002; (– – –) 0.005

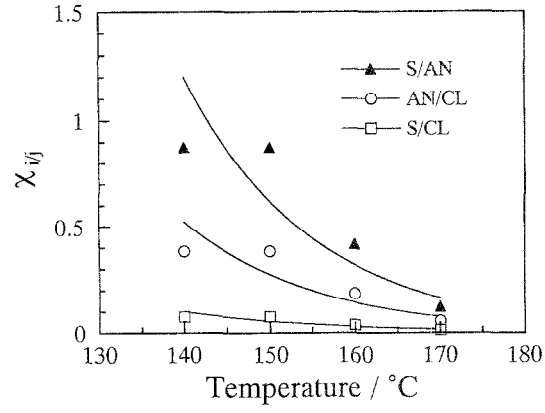

Figure 6 Segmental interaction parameters $\chi_{i/j}$ of the PCL/SAN as a function of the temperature

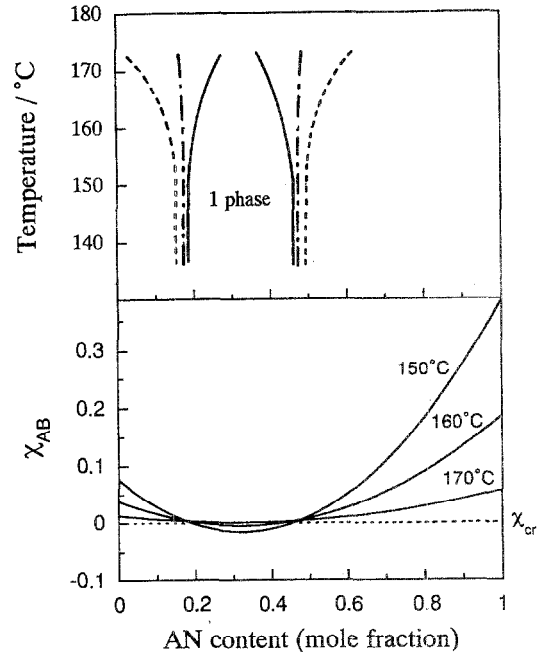

Figure 7 Calculated χ_{AB} parameters as a function of copolymer composition and calculated miscibility windows for various χ_{cr} values: (——) 0.001; (— — —) 0.004; (– – –) 0.01

and becomes larger than the χ_{cr} value. In contrast, in the copolymer composition range up to ~ 10 mol% and > 56 mol% of AN in SAN, the χ_{AB} parameter is decreasing with increasing temperature which might finally result in *UCST* behaviour in the case that χ_{AB} becomes smaller than χ_{cr}. *Figure 3* shows the details of the temperature dependence of the χ_{AB} parameter of ~ 10 and 55 mol% of AN in SAN. In the case that both polymers have 2000 segments ($\chi_{cr} = 0.001$) only *LCST* behaviour can be seen in a certain copolymer composition range. For instance, the polymer blend of PMMA with SAN which contains 11 mol% AN has a *LCST* between 150°C and 160°C. However, the oligomer blend of PMMA and SAN with a certain copolymer composition could show *UCST* behaviour.

By using all three segmental interaction parameters $\chi_{i/j}$ of various temperature and equation (1), the χ_{AB} parameters can be calculated as a function of temperature for various copolymer compositions. These calculated χ_{AB} parameters are shown in *Figure 4*. It can be seen in *Figure 4a* that between 10 mol% and 11 mol% of AN in SAN a change of the temperature dependence of the χ_{AB} parameters occurs, i.e. it changes from decreasing to increasing with temperature. As can be seen in *Figure 4b* the same change occurs at ~ 55 mol%. Again, *UCST* behaviour can only be observed when both components have relatively low molecular weights, i.e. for oligomers. This suggestion is proved by experimental findings in blends of low molecular weight PS and PMMA[13,14].

Taking three $\chi_{i/j}(T)$ parameters and equation (1) for various χ_{cr}, one can calculate the critical copolymer composition, β_{cr} (the copolymer composition separating domains of miscibility and immiscibility in the copolymer composition *versus* temperature plot) for every χ_{cr} as shown in *Figure 5*. For the infinite or high molecular weight components the calculated miscibility window

Table 1 Temperature dependence of segmental interaction parameters: $\chi_{i/j} = A + B/T$ (values of A and B were obtained by best fitting for *Figures 1* and *6*)

i/j	*A*	*B*
S/MMA	−0.635	2.87×10^2
AN/MMA	−4.44	2.00×10^3
S/AN	−11.0	4.94×10^3
AN/CL	−4.76	2.14×10^3
S/CL	−0.913	4.12×10^2

S, styrene; MMA, methyl methacrylate; AN, acrylonitrile; CL, caprolactone

shows the well-known shape (solid line) and is in fairly good agreement with the experimentally determined miscibility window. However, for lower molecular weights of the components, i.e. for larger χ_{cr} system, the calculated miscibility window becomes at first temperature independent (dash-dot line). There are many cases of reported miscibility windows which show hardly any temperature dependence or the transition from miscibility to immiscibility occurs within an extremely small copolymer composition range. For blends where at least one component has a low molecular weight the behaviour changes dramatically and only *UCST* can be observed (dash line). A similar behaviour was reported for blends of polybutadienes with various vinyl contents and a hydrogenated terpene of low molecular weight[18]. Here a so-called 'miscibility valley' occurred, i.e. the miscibility changes from immiscible to miscible to a certain copolymer composition range via *UCST* behaviour. But in this case the reported temperature dependence of the χ_{AB} parameter is different. The two crossing points, as shown in *Figure 3*, do not exist.

Having the temperature dependence of the parameter $\chi_{S/AN}$, it is possible to extend the analysis for different systems. For instance, the miscibility window of the SAN/PCL blend system is known, i.e. also the critical β-value is given[6]. Taking the temperature dependence of the $\chi_{S/AN}$ parameter and the values of β_{cr} in the miscibility window, it is possible to calculate the parameters $\chi_{S/CL}$ and $\chi_{AN/CL}$. The result is shown in *Figure 6*. The $\chi_{S/CL}$ and $\chi_{AN/CL}$ parameters are both decreasing with increasing temperature. Again it can be expected that oligomers of styrene and ε-caprolactone show *UCST* behaviour. This is in good agreement with experimental findings[15,16]. With this set of $\chi_{i/j}$ parameters as a function of temperature, it is possible to calculate the polymer–polymer interaction parameters χ_{AB} as a function of the copolymer composition and β_{cr} for various χ_{cr} values, i.e. the miscibility area can be calculated. This result is shown in *Figure 7*. It can be seen that the behaviour of this system is the same as reported for blends of SAN/PMMA.

CONCLUSIONS

The phase behaviour of random copolymer and oligomer blends can be explained by means of a simple mean field model taking into account the temperature dependence of the segmental interaction parameter (*Table 1*). The classical assumption of the Flory–Huggins theory, i.e. $\chi = A + B/T$, is sufficient to explain *LCST* behaviour in polymer blends and *UCST* behaviour in low molecular weight blends. The description for the systems SAN/PMMA and SAN/PCL is nearly quantitative. Also, the *UCST* behaviour in oligomer blends of styrene with methyl methacrylate and ε-caprolactone, respectively, is in agreement with the calculations.

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