

Phase behaviour of ternary system styrene–maleic anhydride (SMA) and two styrene–acrylonitrile (SAN) copolymers having different compositions

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Abstract

The phase behaviour of the binary copolymer systems SMA–SAN and SAN–SAN can be described well using the copolymer repulsion model. However, the phase behaviour of the ternary system consisting of SMA–SAN(1)–SAN(2) with SAN(1) and SAN(2) having different chemical compositions is not known. In order to reveal this, the composition of the blends, the composition of the SMA (ranging from 22 to 34 wt% MA) at constant SAN compositions (26, 34 and 28, 32 wt% AN), the molar mass of the SMA ($M_w = 3.5$ and 110 kg/mol) as well as the temperature (25 and 230°C) were varied. The number of phases was studied using differential scanning calorimetry (DSC) and a critical evaluation of the predicted and observed glass transition temperatures based on the Fox equation. The binodals and spinodals were calculated using the Flory–Huggins approach. From a comparison of predicted and observed miscibility, it is concluded that this ternary system can be described using the aforementioned model. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Flory–Huggins model; Copolymer repulsion; Interaction parameters

1. Introduction

The miscibility behaviour of both binary systems styrene–maleic anhydride (SMA) and styrene–acrylonitrile (SAN) copolymers and SAN–SAN copolymers was investigated in several studies [1–9]. From these studies, it appeared that the miscibility behaviour can be predicted by the copolymer repulsion model [10] and that the SAN copolymers form miscible blends with other SAN copolymers provided that the composition of the copolymers deviates less than 4–5% AN. SAN copolymers form miscible blends with SMA copolymers provided that the AN and MA content in the copolymers do not differ much.

Ternary blends are gaining interest to optimize material properties. A number of investigations is reported where special attention is paid to the role of the third component. This third one can form a separate phase, distribute between the other phases or act as a miscibilizer resulting in a homogeneous system. Di-octylphthalate (DOP) was used in the systems polyvinylchloride (PVC)–chlorinated polyethylene (CPE) and in the system PVC–chlorinated polyvinylchloride (CPVC) [11]. In both cases, it appeared that considerable amounts of DOP were necessary when

both other components formed immiscible blends. In these cases, the entropy was the main driving force to obtain a homogeneous system. Polystyrene (PS) and polycarbonate (PC) form immiscible blends. Tetramethylpolycarbonate (TMPC) is miscible with both PS and PC. However, the ternary system shows no composition region in which a homogeneous system exists [12]. Similar behaviour is observed in the system polybutylene terephthalate (PBT)–PC–polyhydroxyether of bisphenol A (Phenoxy) [13], polycaprolactone (PCL)–Phenoxy–SAN [14] and polyethylenenaphthanate (PEN)–polyetherimide (PEI)–polyether–ether ketone (PEEK) [15]. Polycaprolactone was used as a miscibilizer in the system PCL–PVC–CPVC provided that the PCL concentration in the blend was sufficient (>35 wt%) [16]. Styrene acrylic acid (SAA) copolymers form homogeneous blends with polyethyleneoxide (PEO) and with polymethylmethacrylate (PMMA). However, PMMA and PEO are not miscible. Fortunately, very strong interactions due to the presence of acrylic acid group result in a miscible ternary system provided the acrylic acid content is high enough [17]. For this system, the enthalpy is the main driving force to obtain a homogeneous system.

However, only a limited number of studies is available where a systematic approach is applied to predict and to verify the phase behaviour of a ternary blend of copolymers

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experimentally [18–20]. In the case of styrene copolymers, Cowie [18] investigated the miscibility behaviour of some ternary systems. The prediction was based on an extended Flory–Huggins approach in which the χ_{blend} is calculated from the weighted binary segment interaction parameters. From these studies, it appeared that the experimentally determined miscibility behaviour of styrene copolymers in ternary systems was in agreement with the prediction.

For the system SMA–SAN(1)–SAN(2), such an approach has not been reported yet. Fortunately, much information concerning the binary segmental interaction parameters is known even at various temperatures [6,8,19]. By choosing the proper compositions of the copolymers, the number of miscible binaries (SMA–SAN(1), SMA–SAN(2) and SAN(1)–SAN(2)) can range from 0 to 3. Formation of a homogeneous ternary system depends on the composition differences between both SAN copolymers and the SMA–SAN copolymers. A prerequisite to obtain a homogeneous system consisting of high molar mass components is a proper balance of interactions (enthalpic contribution). If this contribution is not sufficient, the molar mass of, e.g. the miscibilizer can be reduced (entropic contribution).

SMA is applied to increase the HDT of SAN copolymers. However, if two SAN copolymers having a large difference in chemical composition (binary SAN(1)–SAN(2) not miscible) is present, the proper composition of SMA copolymer must be applied to reach miscibility and hence heatboosting in the desired phase. The aim of this investigation is to predict the phase behaviour of the ternary copolymer system SMA–SAN(1)–SAN(2) using the model proposed by Cowie [18] and to verify this experimentally using differential scanning calorimetry (DSC).

2. Experimental

2.1. Materials

Both SMA and SAN copolymers are commercially available types. The characteristics of SMA and SAN copolymers are given in Table 1.

2.2. Preparation of blends using melt mixing

The copolymer materials were mixed using a mini-mixer

Table 1
Characteristics of materials used

Copolymer	AN/MA (wt%)	M_w (kg/mol)	T_g
SMA22	22	110	146
SMA28	28	110	164
SMA34	34	110	178
SMA33	33	3.5	134
SAN26	26	200	106
SAN28	28	152	105
SAN32	32	78	109
SAN34	34	106	108

operating at 230°C. The screw rotated at 400 rpm. After 5 min mixing, the samples were collected and quenched outside the machine. Using this equipment, small amounts of blend (only 1.5 g) can be prepared. The binary combination (50–50 wt%) SMA(18)–SAN(25) shows a LCST of 250°C [9,20]. For other copolymer and blend compositions, cloud points were found at even higher temperatures. Based on these observations, it was assumed that the LCST of the ternary blends would not be lower than the operation temperature. This assumption seems to be justified with an exception for the unstable region [20].

2.3. Preparation of blends using the solvent route

The materials were dissolved in methylethylketone (MEK) (<5 wt%) over a period of 3 h at 20°C. Subsequently the solution was precipitated in isopropanol. The polymer was filtrated using a Buchner funnel with a standard filter (MN 615 Macherey–Nagel). The blend obtained was dried for 24 h at 80°C in vacuum.

2.4. Molar masses of the copolymers

SMA in solution may partially hydrolyse resulting in carboxylic acid groups attached to the polymer chain. Unfortunately, these groups can interact with the packing of the SEC columns. To cope with these difficulties, Tacx et al. developed a method [21], which was also applied in this investigation.

2.5. Differential scanning calorimetry

The glass transition temperatures (T_g) were obtained using a Perkin–Elmer DSC-7 calorimeter at a scanning rate of 10°C/min. The scanned temperature interval ranged from 20 to 250°C. The T_g values were obtained from the second run and the criterion for one phase blend was the occurrence of a single T_g .

2.6. Prediction of phase behaviour

The model to predict the spinodals and binodals was described by Cowie [18]. It is based on the Flory–Huggins theory in which the interaction parameters are calculated from the corresponding binary segmental interaction parameters. The software was developed by Ferguson [18] and is based on the algorithm of Su et al. [22] and Hsu et al. [23].

3. Results

3.1. Ternary blends of SMA–SAN(26)–SAN(34) prepared at 230°C

Ternary blends of two SAN copolymers having 26 and 34 wt% AN were prepared with SMA copolymers having maleic anhydride content of 22, 28 and 34 wt%, respectively, using the melt route at 230°C. The difference

between the compositions of both SAN copolymers is larger than 4% AN. Hence the binary system SAN(26)–SAN(34) is not miscible. The phase diagrams are presented in Fig. 1a–c. In the phase diagrams, the blend composition is expressed in volume fractions using the molar volumes of the monomeric units. The filled and open circles in the phase diagram indicate miscible and immiscible systems, respectively. The binodals and spinodals are represented by dashed and full lines, respectively. The interaction parameters to predict the binodals and spinodals must be available at the temperature at which the blends were prepared. Unfortunately, the parameters are not available at 230°C. Suitable values were found at 25 [5] and 170°C [8] and are given in Table 2. As an approximation, the parameters determined at 170°C were applied. A comparison of the values of the interaction parameters determined at 25 and 170°C seems to indicate that the values are dependent on temperature. However, it should be realized that the parameters determined at 25°C were obtained using the number average molar mass while the other set of parameters was obtained using the weight average molar mass. Fortunately, both sets of parameters indicate that the S–MA and S–AN interactions are unfavourable, while the MA–AN interaction is favourable.

The ternary system prepared with SMA(22) includes one miscible binary blend (SMA(22)–SAN(26)) and two immiscible binary blends (SAN(26)–SAN(34)) and (SMA(22)–SAN(34)). The predictions indicate only a very small area representing the blend composition region where a homogeneous system exists. All ternary blends investigated appeared to be immiscible as is shown in Fig. 1a with one exception for the blend having the highest SAN26 concentration. The binary system (SMA(22)–SAN(26)) appeared to be miscible as expected. Even the ternary system SMA(22)–SAN(26)–SAN(34) with blend composition 90/5/5 wt% showed two glass transition temperatures.

The ternary system with SMA(28) has two binary combinations which are miscible (SMA(28)–SAN(26) and SMA(28)–SAN(34)) and one immiscible binary (SAN(26)–SAN(34)). The predictions and experimental data are presented in Fig. 1b. From the results, it is clear that both are in agreement. Also here one exception is observed. One ternary blend having the highest SAN26 concentration is miscible. The data point is just on the spinodal. Two binary combinations were investigated and appeared to be miscible as expected. Only a small area of

blend compositions where a homogeneous system exists can be observed.

The phase diagram of the ternary system of SMA(34)–SAN(26)–SAN(34) is presented in Fig. 1c. Also in this case only one binary (SAN(26)–SAN(34)) is immiscible. Also here only a small blend composition region where a homogeneous system exists is observed. From these results, it can be concluded that the predicted phase behaviour is in agreement with the observed phase behaviour.

3.2. Ternary blends of SMA–SAN(26)–SAN(34) prepared at 25°C

The same components were used to prepare ternary blends at 25°C. The experimental results and the predictions of the phase behaviour are presented in Fig. 2a–c. In this case the interaction parameters calculated by Cowie [5] were used since these parameters were obtained at room temperature. In case of SMA(22)–SAN(26)–SAN(34) only one miscible binary (SMA(22)–SAN(26)) is present. In addition, here a large blend composition region where no miscible system exists is calculated. This is in agreement with the limited number of experimental data. In case of SMA(28)–SAN(26)–SAN(34) only one binary is immiscible (SAN(26)–SAN(34)). At this temperature, this leads to a relatively large blend composition region where a homogeneous ternary system exists. Again in case of SMA(34)–SAN(26)–SAN(34) one binary is miscible (SMA(34)–SAN(34)). This leads to the appearance of a large area of immiscibility.

A comparison of the results obtained at 230 and 25°C indicates that in case of SMA(28)–SAN(26)–SAN(34) significant differences appear. At 25°C, the area of miscibility is larger. This is observed from the experimental data as well as from the predictions indicating that the χ parameters are sufficiently accurate to describe the behaviour. Moreover this behaviour is expected for systems showing LCST.

3.3. Ternary blends of SMA–SAN(28)–SAN(32) prepared at 230°C

Ternary blends of SMA–SAN(28)–SAN(32) were prepared using the melt route. Also in this case three SMA copolymers were used having 22, 28 and 32% MA. In this case the difference between the compositions of the SAN copolymers is smaller, i.e. 4%. In the binary case, the two SAN copolymers are miscible. Hence a significantly different phase behaviour is expected. This indeed is observed. The results are presented in Fig. 3a–c. The system SMA(22)–SAN(28)–SAN(34) has two miscible and one immiscible binary (SMA(22)–SAN(32)) which results in the expected phase diagram presented in Fig. 3a. In case of the systems SMA(28)–SAN(28)–SAN(32) and SMA(34)–SAN(28)–SAN(32) all binaries are miscible. The ternary systems are completely miscible which is shown in Fig. 3b and c. Also from this set of results, it is

Table 2
Values of the interaction energy densities at 25 [5] and 170°C [8]

Segments	25°C (J/cm ³)	170°C (J/cm ³)
S–MA	40.0	44.8
S–AN	22.8	28.5
MA–AN	1.0	– 1.3

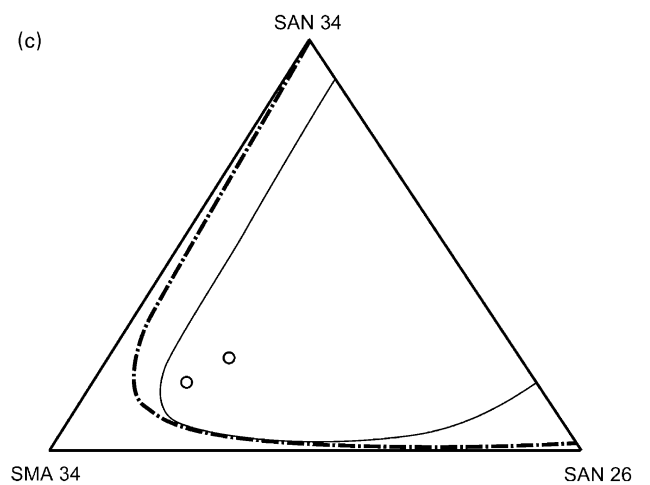
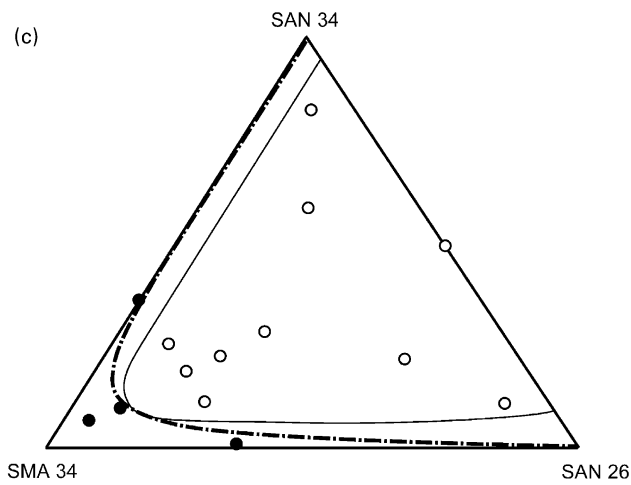
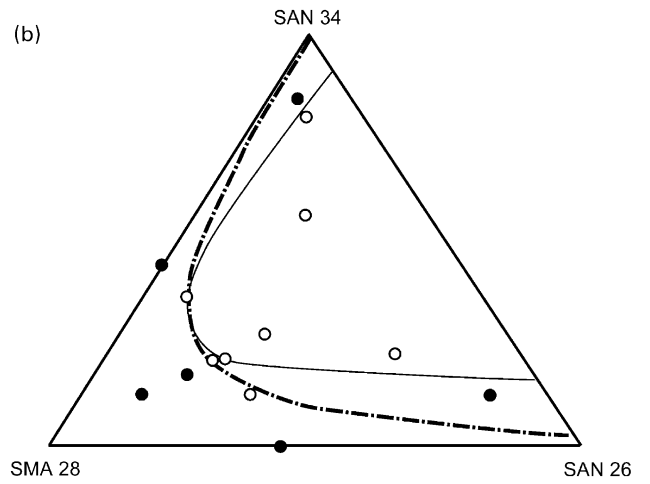
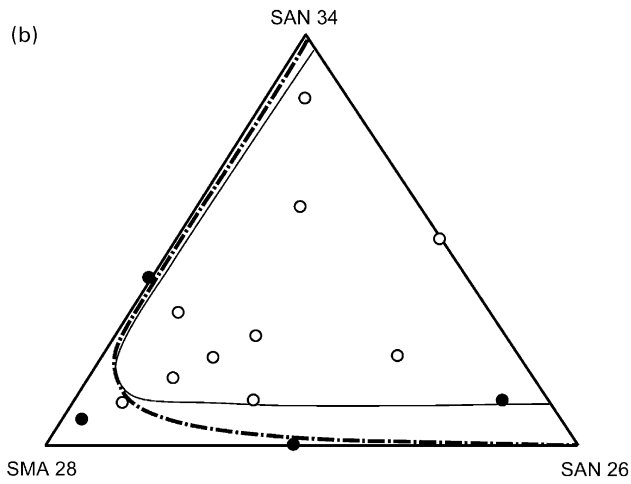
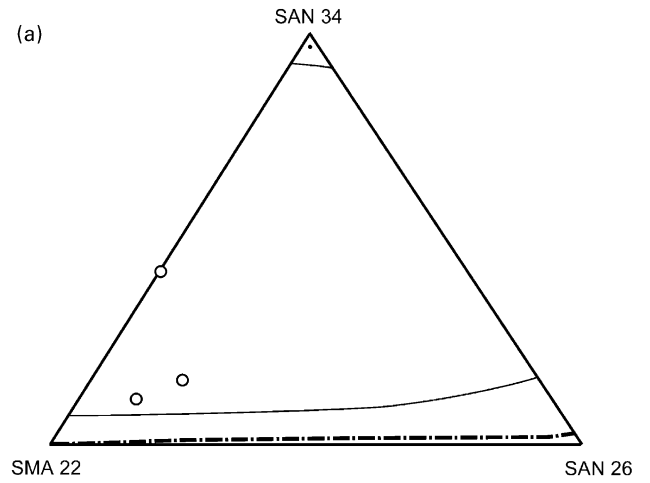
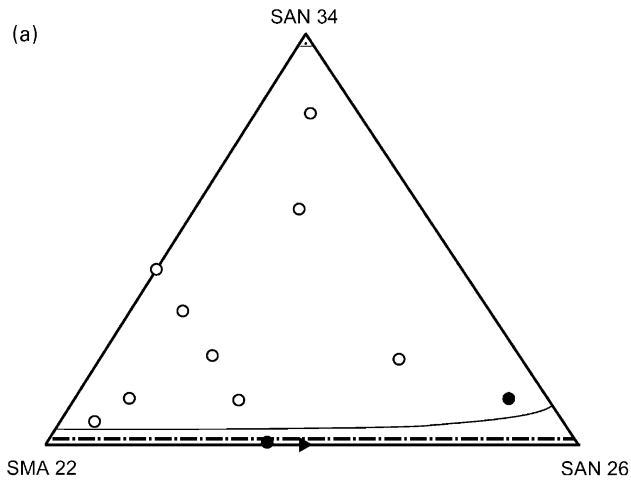


Fig. 1. (a) Phase diagrams of ternary systems SMA(22)–SAN(26)–SAN(34) obtained using the melt mixing route at 230°C; (b) Phase diagrams of ternary systems SMA(28)–SAN(26)–SAN(34) obtained using the melt mixing route at 230°C; (c) Phase diagrams of ternary systems SMA(34)–SAN(26)–SAN(34) obtained using the melt mixing route at 230°C.

Fig. 2. (a) Phase diagrams of ternary systems SMA(22)–SAN(26)–SAN(34) obtained using the solvent route at 25°C; (b) Phase diagrams of ternary systems SMA(28)–SAN(26)–SAN(34) obtained using the solvent route at 25°C; (c) Phase diagrams of ternary systems SMA(34)–SAN(26)–SAN(34) obtained using the solvent route at 25°C.

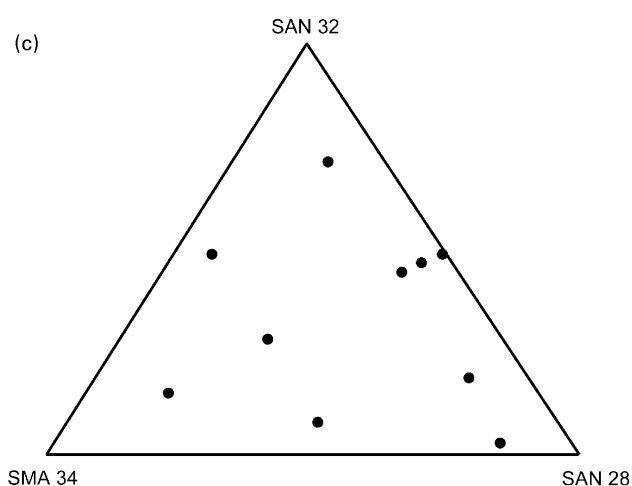
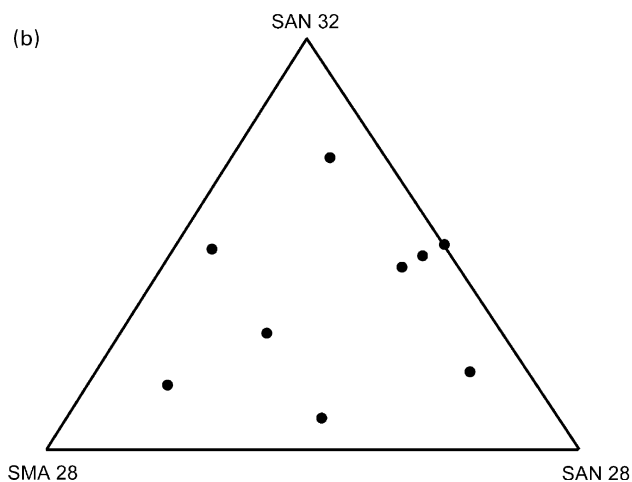
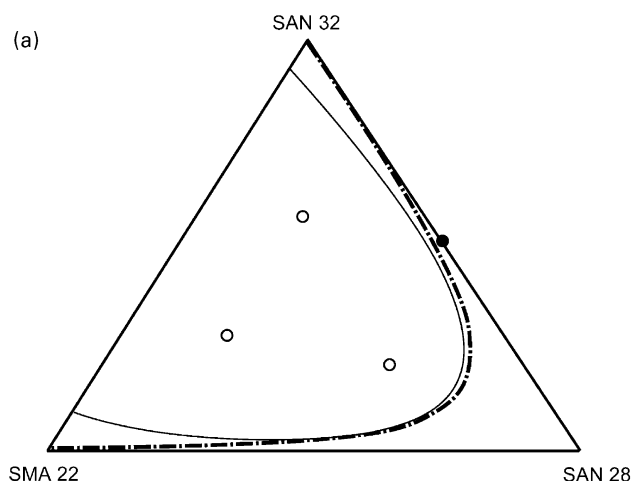


Fig. 3. (a) Phase diagrams of ternary systems SMA(22)–SAN(28)–SAN(32) obtained using the melt mixing route at 230°C; (b) Phase diagrams of ternary systems SMA(28)–SAN(28)–SAN(32) obtained using the melt mixing route at 230°C; (c) Phase diagrams of ternary systems SMA(34)–SAN(28)–SAN(32) obtained using the melt mixing route at 230°C.

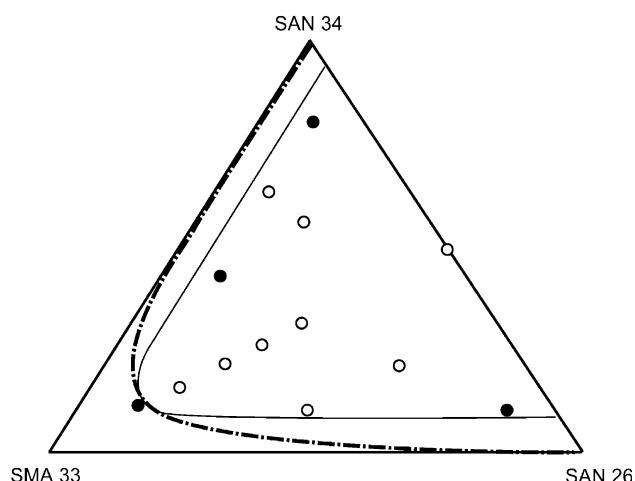


Fig. 4. Phase diagrams of ternary systems SMA(33)–SAN(26)–SAN(34) obtained using the melt mixing route at 230°C.

concluded that the predictions are in agreement with the experimental results.

3.4. Ternary blends of SMA(33)–SAN(26)–SAN(34) prepared at 230°C

Decreasing the molar mass of the SMA copolymer is a route to increase the tendency to form miscible systems due to the increase of the entropy of mixing. A SMA having 33 wt% MA and a molar mass of only 3500 g/mol was applied. Ternary blends of SMA(33)–SAN(26)–SAN(34) appeared to have a small area of blend compositions where a miscible system is obtained. The phase diagram is presented in Fig. 4. From the results, it is observed that there is a small discrepancy between observed and predicted phase behaviour. This bias might be caused by application of a set of interaction parameters outside the region of determination. From a comparison of the results obtained in Figs. 1c and 4, it is concluded that despite the significant decrease in molar mass only slight changes, both in predicted and experimentally determined phase behaviour, is obtained. This clearly indicates that the repulsion between the SAN copolymers having such a large composition difference is hard to overcome by the gain in entropy, even in systems having a relatively large concentration of low molar mass SMA.

4. Conclusions

Ternary blends of SMA–SAN(1)–SAN(2) can consist of 0–3 miscible binaries depending on the composition of the copolymers. Predictions of the spinodals and binodals of ternary systems were performed based on a model proposed by Cowie [18]. This approach is based on the Flory–Huggins theory. The predictions are in good agreement with the experimental data obtained from DSC provided that the proper segment interaction parameters are applied.

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