

**Communication:** EBE and BEB triblock copolymers were prepared and characterized. Microphase separation in the melt state was studied, and the results combined with those for EB and BEB copolymers reported previously. The microphase separation temperature (MST) was determined from the temperature dependence of

SAXS. There was a large difference in MST between the diblock and triblock copolymers as expected from theory. The Flory-Huggins parameter ( $\chi$ ) was independent of block architecture for all three series provided that the E block lengths in the EBE copolymers exceeded 65.

## Microphase separation in oxyethylene/oxybutylene copolymers with diblock and triblock architectures

Chiriaphon Chaibundit,<sup>1</sup> Withawat Mingvanish,<sup>1</sup> Simon C. Turner,<sup>2</sup> Shao-Min Mai,<sup>\*2</sup> J. Patrick A. Fairclough,<sup>2</sup> Anthony J. Ryan,<sup>2</sup> Mark W. Matsen,<sup>3</sup> Colin Booth<sup>1</sup>

<sup>1</sup> Department of Chemistry, University of Manchester, Manchester M13 9PL, UK

<sup>2</sup> Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

<sup>3</sup> Department of Physics, University of Reading, Reading RG6 6AF, UK

### Introduction

Differences in molecular architecture at constant chain length and composition dramatically influence microphase separation in block copolymer melts. The need to locate the two block-junctions of a triblock copolymer at a domain boundary significantly reduces the conformational entropy of its ordered state relative to that of a diblock copolymer of comparable composition and chain length. As a consequence, the disordered phase of a triblock copolymer melt is more stable than that of a diblock copolymer of the same length and composition.

A useful summary of the theory of microphase-separation for diblock copolymers has been published by Matsen and Bates,<sup>[1]</sup> and full accounts of related work on triblock copolymers can be found in the papers of Mayes and Olvera de la Cruz<sup>[2,3]</sup> and those of Matsen and co-workers.<sup>[4–6]</sup> The quantity of major importance in determining the microphase separation temperature (MST) is the product ( $\chi r_v$ ) of the Flory-Huggins parameter ( $\chi$ ) and the length ( $r_v$ ) of the copolymer chain defined by the number of segments of given reference volume. Mayes and Olvera de la Cruz showed<sup>[2]</sup> a critical value for microphase separation of  $(\chi r_v)_c \approx 18$  for the melt of a symmetrical triblock copolymer compared to a value of  $(\chi r_v)_c \approx 10.5$  for the melt of a diblock copolymer of the same length and composition.<sup>[7]</sup> The effects of concentration fluctuations in the two systems have also been considered.<sup>[3]</sup> As for diblock copolymers, fluctuations in the disordered melt were found to cause an increase in  $(\chi r_v)_c$ , i.e. a decrease in the MST. In a recent report<sup>[8]</sup> we have

argued that the fluctuation correction of Fredrickson and Helfand<sup>[9]</sup> holds equally well for diblock and triblock copolymers.

In comparing results for different copolymers it is taken for granted that  $\chi$  has the same value for all architectures.<sup>[10]</sup> The matter has been addressed specifically by Adams et al.,<sup>[11]</sup> who found that microphase separation in a range of diblock and triblock polystyrene/polyisoprene block copolymers of constant composition, 13 wt.-% polystyrene, could be described by single  $\chi(T)$  relation. Our own study of symmetrical diblock and triblock polyoxyethylene/polyoxybutylene copolymers, types  $E_m B_n$  and  $B_{n/2} E_m B_{n/2}$ , gave a similar result.<sup>[8]</sup> Here we use the notation E = oxyethylene unit,  $OCH_2CH_2$ , and B = oxybutylene unit,  $OCH_2CH(C_2H_5)$ , with subscripts  $m$  and  $n$  denoting respectively the number of E and B repeat units in the copolymer.

The purpose of this note is to report an extension of that work to include the inverse series of triblock copolymers, type EBE. Specifically, we report new results for two  $B_{n/2} E_m B_{n/2}$  and eight  $E_{m/2} B_n E_{m/2}$  triblock copolymers. Together with previous results<sup>[8]</sup> for diblock and  $B_{n/2} E_m B_{n/2}$  copolymers, these new data provide a basis for a full comparison of  $\chi$  for the three architectures within the EB system.

### Experimental part

The EBE copolymers were prepared by sequential anionic polymerization of 1,2-butylene oxide followed by ethylene

Tab. 1. Molecular characteristics and microphase-separation temperatures of diblock and triblock oxyethylene/oxybutylene copolymer melts.

| Copolymer   | $\bar{M}_n/\text{g} \cdot \text{mol}^{-1}$<br>(NMR) | $\bar{M}_w/\bar{M}_n$<br>(GPC) | $r_v^{\text{a)}$ | $\phi_E^{\text{a)}$ | MST/ $^{\circ}\text{C}^{\text{b)}$<br>(SAXS) | $(\chi r_v)_c^{\text{d)}$ |
|---|---|--------------------------------|------------------|---------------------|--|---------------------------|
| E <sub>75</sub> B <sub>54</sub>                                 | 7200  | 1.03                           | 177              | 0.424               | 126  | 11.06                     |
| E <sub>85</sub> B <sub>45</sub>                                 | 7000  | 1.04                           | 170              | 0.500               | 140  | 10.53                     |
| E <sub>100</sub> B <sub>51</sub>                                | 8100  | 1.04                           | 196              | 0.509               | 165  | 10.53                     |
| E <sub>76</sub> B <sub>38</sub>                                 | 6100  | 1.03                           | 148              | 0.514               | 114  | 10.53                     |
| E <sub>96</sub> B <sub>47</sub>                                 | 7600  | 1.05                           | 185              | 0.519               | 163  | 10.53                     |
| E <sub>114</sub> B <sub>56</sub>                                | 9000  | 1.05                           | 220              | 0.519               | 210  | 10.53                     |
| E <sub>155</sub> B <sub>76</sub>                                | 12300   | 1.08                           | 299              | 0.519               | 270  | 10.53                     |
| E <sub>56</sub> B <sub>27</sub>                                 | 4400  | 1.04                           | 107              | 0.523               | 53 <sup>c)</sup>                             | 10.54                     |
| E <sub>60</sub> B <sub>29</sub>                                 | 4700  | 1.03                           | 115              | 0.523               | 60   | 10.54                     |
| B <sub>34</sub> E <sub>93</sub> B <sub>34</sub> <sup>e)</sup>   | 9000  | 1.04                           | 222              | 0.420               | 72   | 18.41                     |
| B <sub>44</sub> E <sub>127</sub> B <sub>44</sub> <sup>e)</sup>  | 11900   | 1.04                           | 293              | 0.433               | 129  | 18.26                     |
| B <sub>25</sub> E <sub>90</sub> B <sub>25</sub>                 | 7600  | 1.02                           | 184              | 0.488               | 50 <sup>c)</sup>                             | 18.02                     |
| B <sub>26</sub> E <sub>95</sub> B <sub>26</sub>                 | 7900  | 1.02                           | 193              | 0.492               | 68   | 18.03                     |
| B <sub>36</sub> E <sub>137</sub> B <sub>36</sub>                | 11200   | 1.04                           | 273              | 0.502               | 134  | 18.06                     |
| B <sub>29</sub> E <sub>111</sub> B <sub>29</sub>                | 9100  | 1.03                           | 221              | 0.503               | 90   | 18.07                     |
| B <sub>27</sub> E <sub>105</sub> B <sub>27</sub>                | 8500  | 1.03                           | 207              | 0.507               | 83   | 18.10                     |
| B <sub>37</sub> E <sub>150</sub> B <sub>37</sub>                | 11900   | 1.04                           | 290              | 0.517               | 143  | 18.17                     |
| B <sub>30</sub> E <sub>122</sub> B <sub>30</sub>                | 9700  | 1.03                           | 235              | 0.518               | 101  | 18.18                     |
| E <sub>71</sub> B <sub>79</sub> E <sub>71</sub> <sup>e)</sup>   | 11900   | 1.29                           | 291              | 0.487               | 153  | 18.27                     |
| E <sub>38</sub> B <sub>38</sub> E <sub>38</sub> <sup>e)</sup>   | 6100  | 1.14                           | 148              | 0.514               | 46 <sup>c)</sup>                             | 18.00                     |
| E <sub>51</sub> B <sub>50</sub> E <sub>51</sub> <sup>e)</sup>   | 7700  | 1.10                           | 197              | 0.519               | 90   | 17.97                     |
| E <sub>45</sub> B <sub>44</sub> E <sub>45</sub> <sup>e)</sup>   | 7000  | 1.16                           | 173              | 0.520               | 74   | 17.96                     |
| E <sub>72</sub> B <sub>68</sub> E <sub>72</sub> <sup>e)</sup>   | 11200   | 1.22                           | 273              | 0.528               | 141  | 17.93                     |
| E <sub>90</sub> B <sub>82</sub> E <sub>90</sub> <sup>e)</sup>   | 13800   | 1.13                           | 335              | 0.537               | 203  | 17.91                     |
| E <sub>65</sub> B <sub>59</sub> E <sub>65</sub> <sup>e)</sup>   | 10000   | 1.19                           | 242              | 0.538               | 124  | 17.90                     |
| E <sub>103</sub> B <sub>86</sub> E <sub>103</sub> <sup>e)</sup> | 15300   | 1.12                           | 369              | 0.559               | 219  | 17.93                     |

<sup>a)</sup>  $r_v = m + 1.89n$  and  $\phi_E = m/[m + 1.89n]$  (see ref.<sup>[13]</sup>, Tab. 2).

<sup>b)</sup> MST = microphase separation temperature; estimated error:  $\pm 1^{\circ}\text{C}$ .

<sup>c)</sup> Data for supercooled melt.

<sup>d)</sup> Calculated values of  $(\chi r_v)_c$ : ref.<sup>[6]</sup>.

<sup>e)</sup> Newly prepared samples.

oxide following the procedures described previously for EB copolymers,<sup>[12]</sup> but using 1,2-butane diol as initiator. Characterization of the products was by gel permeation chromatography (for distribution width) and by <sup>13</sup>C NMR spectroscopy (for absolute value of number-average molar mass and overall composition, plus confirmation of block structure). Together the two techniques give a complete molecular description of the copolymers. A summary including all the copolymers considered in this study is given in Tab. 1: the EB copolymers and the majority of the BEB copolymers have been described previously.<sup>[8,13]</sup> Copolymers newly synthesized for this work are distinguished by footnote e).

The relatively wide chain length distributions of the EBE copolymers ( $\bar{M}_w/\bar{M}_n > 1.1$ ) are a consequence of the slow addition of ethylene oxide to the secondary oxyanions of the first-formed central B block. This effect implies an asymmetry of E-block lengths in the copolymers, to the extent that a proportion of diblock copolymers may be present if the average E-block length is significantly less than 50.<sup>[14,15]</sup> Accordingly, copolymers E<sub>38</sub>B<sub>38</sub>E<sub>38</sub>, E<sub>45</sub>B<sub>44</sub>E<sub>45</sub>, and to a lesser extent E<sub>51</sub>B<sub>50</sub>E<sub>51</sub>, must be regarded as being part diblock in character, with consequent effect on the MST (see Section 3).

Included in Tab. 1 are the volume fractions of the oxyethylene blocks in the copolymers in their liquid state ( $\phi_E$ , essentially independent of temperature) and the overall length of the copolymer molecule in segments ( $r_v$ ), taking the segment reference volume to be that of an E unit. The calculations were based on specific volumes reported previously.<sup>[16]</sup>

Microphase-separation temperatures were determined by monitoring small-angle X-ray scattering (SAXS) patterns integrated over at 6 s intervals while the copolymer was heated at  $10^{\circ}\text{C} \text{ min}^{-1}$  from  $10^{\circ}\text{C}$  to  $\approx 20^{\circ}\text{C}$  above MST and then cooled at the same rate back to  $10^{\circ}\text{C}$ . The measurements were made on a beamline 8.2 of the SRS at the CCLRC Daresbury Laboratory, Warrington, UK. Details of the equipment and methodology have been reported previously: see for example<sup>[8]</sup> and<sup>[12]</sup> and references therein. Data were presented as intensity versus scattering vector  $q = 4\pi \sin \theta / \lambda$ , where  $\lambda = 1.54 \text{ \AA}$  is the wavelength and  $2\theta$  the scattering angle. An example is illustrated in Fig. 1 which shows a three-dimensional relief diagram of time-resolved SAXS data obtained for copolymer E<sub>65</sub>B<sub>59</sub>E<sub>65</sub> during heating and cooling the copolymer; similar patterns have been reported for E<sub>m</sub>B<sub>n</sub> diblock and B<sub>n/2</sub>E<sub>m</sub>B<sub>n/2</sub> triblock copolymers.<sup>[8,13]</sup> The SAXS pattern at low temperature is consistent with the expected semicrystalline lamellar phase. At intermediate temperature ( $54 \leq T \leq 124^{\circ}\text{C}$ ), the sharp narrow peak indicates an ordered melt with a totally different periodicity from the semicrystalline structure. The broad scattering peak at higher temperatures ( $T > 124^{\circ}\text{C}$ ) indicates a disordered melt with composition fluctuations. The phase sequence is reversed on cooling.

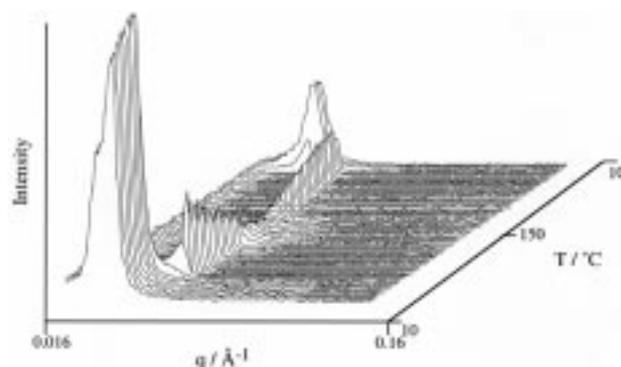


Fig. 1. Three-dimensional relief diagram of time-resolved SAXS obtained with a time resolution of 6 s while heating and cooling copolymer E<sub>65</sub>B<sub>59</sub>E<sub>65</sub>. The plot shows intensity versus scattering vector,  $q$ , versus temperature,  $T$ . The thermal cycle was  $10^{\circ}\text{C} \rightarrow 150^{\circ}\text{C} \rightarrow 10^{\circ}\text{C}$  at a ramp rate of  $10^{\circ}\text{C} \text{ min}^{-1}$ .

## Results and discussion

Microphase separation temperatures were obtained from the step change in peak-maximum intensity and also from the related changes in peak width and shape: see Fig. 1 and, for details, ref.<sup>[12]</sup> The values listed in Tab. 1 are corrected for a small thermal lag.

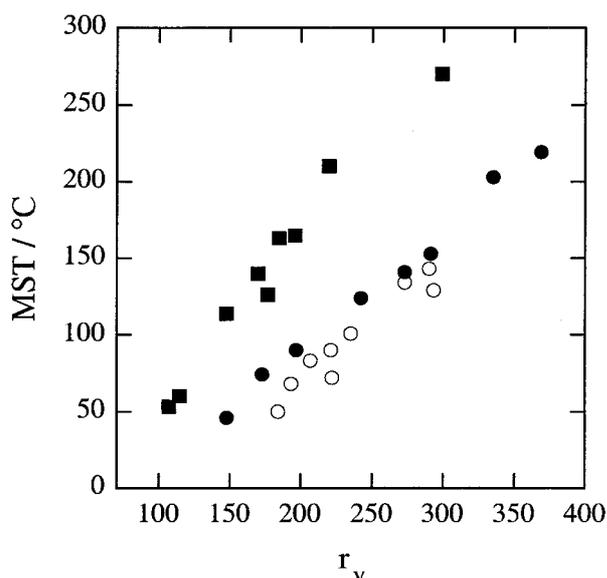


Fig. 2. Values of MST for triblock BEB (○), EBE (●) and diblock EB (■) copolymers plotted against chain length  $r_v$ .

Values of the MST are plotted against copolymer chain length ( $r_v$  in segments) in Fig. 2. Smooth curves are not expected: the samples cover a range of composition as well as overall chain length. Fig. 2 emphasizes the large difference in MST between the diblock copolymers on the one hand and the triblock copolymers on the other, an effect already referred to in the Introduction. The systematic difference between the results for the two types of triblock reflects three features of the system. One feature is the overall asymmetry of the microphase diagram for triblock copolymers with respect to copolymer composition. This occurs because the stretching energy of middle block domains tends to be slightly lower than that of end blocks.<sup>[6]</sup> The second feature is the asymmetry of the E and B segments defined by a reference volume, which is conveniently represented<sup>[17]</sup> by the segment asymmetry factor,

$$\varepsilon = (v_E b_E^2 / v_B b_B^2)$$

where  $v_E$ ,  $v_B$ ,  $b_E$  and  $b_B$  represent the volumes and statistical lengths of the E and B units. The third feature is the diblock character of the EBE copolymers with short E blocks.

The microphase-separation boundaries predicted by self-consistent mean-field theory for diblock and triblock copolymers with asymmetry factor  $\varepsilon = 0.6$  have been reported previously.<sup>[8,13]</sup> In fact the actual value for the E/B system is 0.65,<sup>[12,13]</sup> but calculations indicate that such a small difference is quantitatively unimportant.<sup>[6]</sup> These boundaries are reproduced in Fig. 3 for the volume fraction range  $\phi_E = 0.4$  to 0.6, and values of  $\chi r_v$  at values of  $\phi_E$  corresponding to those of the present samples are

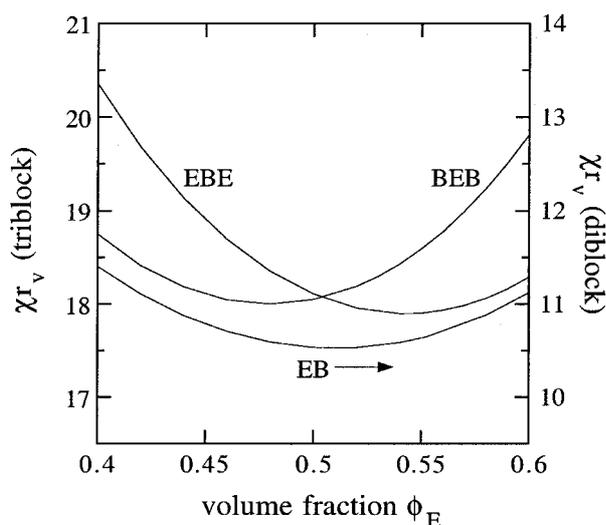


Fig. 3. The microphase-separation boundaries predicted by self-consistent mean-field theory for diblock and triblock copolymers with asymmetry factor  $\varepsilon = 0.6$ .

listed in Tab. 1. The slight asymmetry in the diblock boundary results from the segment asymmetry factor. The marked asymmetry in the triblock boundaries is modified by the ' $\varepsilon$  effect', which reduces the asymmetry for the BEB copolymers but reinforces it for the EBE copolymers.

In calculating values of  $\chi$  (from  $r_v$  and  $\chi r_v$  as listed in Tab. 1) it was borne in mind that  $\chi$  might well be dependent on composition. For example, this is known to be so for the related EP system [P denotes oxypropylene,  $\text{OCH}_2\text{CH}(\text{CH}_3)$ ].<sup>[18]</sup> Accordingly, to minimize any possible effect on the present work, samples were chosen within a narrow composition range,  $\phi_E = 0.42$  to 0.56. The values so obtained are plotted against reciprocal temperature in Fig. 4. Results for the diblocks and the BEB triblocks fall on a single straight line. The data points for the EBE copolymers with long E blocks ( $m/2 \geq 65$ ) fit reasonably well to the same line. The deviation of the data points for the EBE copolymers with short E blocks ( $m/2 \leq 51$ ) is understandable in the light of the discussion in Section 2. The diblock character of these copolymers (i.e. the asymmetric length of the end blocks), which becomes increasingly important as  $m$  decreases, means that the MST will be higher than expected for a true triblock copolymer, so causing deviation towards lower values of  $1/T$ .

The straight line through the data points in Fig. 4 is based on the data points for the EB and BEB copolymers only, i.e. those copolymers with narrow block length distributions (see Tab. 1). The equation for the temperature dependence of  $\chi$  is:

$$\chi = 51.6/T - 0.0617$$

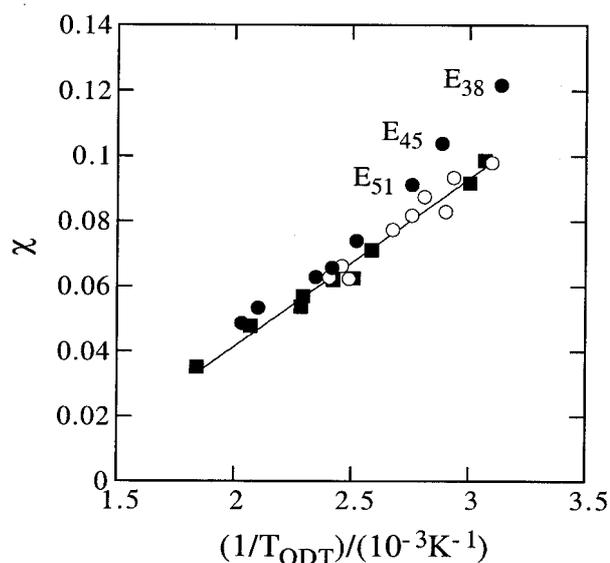


Fig. 4. Values of the Flory-Huggins interaction parameter  $\chi$  versus reciprocal microphase separation temperature (MST) calculated for triblock BEB (○), EBE (●) and diblock EB (■) copolymers with  $\phi_B \approx 0.5$ . The line is the least squares fit to the data points for the EB and BEB copolymers.

Not surprisingly, values of  $\chi$  calculated from this equation differ insignificantly from those calculated from the equation reported previously,<sup>[8]</sup> which was based on the same data set less the two newly-synthesized BEB copolymers, i.e.

$$\chi = 52.6/T - 0.0632$$

Previously<sup>[8]</sup> we have considered the effect of fluctuations on  $\chi$  and its temperature dependence for the EB and BEB copolymers. In view of the small difference in present and previous results, this calculation is not repeated here.

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