# Low-Frequency Raman Spectroscopy of Oxyethylene/Oxybutylene/Oxyethylene Triblock Copolymers

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#### Introduction

In recent work we have used low-frequency Raman spectroscopy to determine the frequency of the singlenode longitudinal acoustic mode (LAM-1) of semicrystalline diblock  $E_m B_n$  copolymers<sup>1,2</sup> and triblock  $B_n E_m B_n$ copolymers<sup>3</sup> of ethylene oxide and 1,2-butylene oxide. [E denotes an oxyethylene chain unit, OCH<sub>2</sub>CH<sub>2</sub>, B denotes an oxybutylene chain unit,  $OCH_2CH(C_2H_5)$ , and *m* and *n* denote number-average block lengths in chain units.] In these copolymers only the E-blocks crystallize, the B-block being atactic. We have shown that the LAM-1 frequency is a sensitive indicator of E-block folding in systems for which small-angle X-ray scattering (SAXS) alone gives results that are not readily interpreted.<sup>3</sup> At the block lengths investigated it was found that semicrystalline  $B_n E_m B_n$  copolymers (m =37–90, n = 4-25) were more highly folded than  $E_m B_n$ diblock copolymers with comparable lengths crystallized under comparable conditions. Evidence for lengthy block copolymers obtained using SAXS and differential scanning calorimetry (DSC) has indicated that chain folding in  $E_m B_n E_m$  copolymers is similar to that in  $E_m B_n$  diblock copolymers rather than that in  $B_n E_m B_n$  triblock copolymers.<sup>4</sup> The purpose of this Note is to report results from Raman spectroscopy which confirm this difference between the two types of triblock copolymer.

Experimentally, comparison of the properties of short  $E_m B_n E_m$  and  $B_n E_m B_n$  copolymers prepared by sequential polymerization is not straightforward. This is because the slow reaction of ethylene oxide with the secondary oxyanion of a first-formed B-block (compared to the relatively fast reaction with the primary oxyanion of an E end) results in a widened E-block distribution and a degree of diblock character in an  $E_m B_n E_m$  copolymer.<sup>5</sup> In the preparation of  $E_m B_n$  and  $B_n E_m B_n$  copolymers, the addition of butylene oxide to the primary oxyanion of a first-formed E-block is uncomplicated, as the first ad-

dition to the E-block is fast compared to subsequent additions.

### **Experimental Section**

**Copolymers.** The method of preparation of the  $E_m B_n E_m$ block copolymers by sequential polymerization of 1,2-butylene oxide followed by ethylene oxide has been described previously.6 The initiator was 1,2-butanediol, and ampule and vacuum line techniques were employed to avoid unwanted initiation by moisture. As determined by GPC using poly-(oxyethylene) standards for calibration, the chain length distributions of the resulting copolymers were narrow,  $M_w/M_n <$ 1.10. End-group analysis using <sup>13</sup>C NMR gave accurate values of the chain lengths of the precursor poly(oxybutylene)s and the overall compositions of the copolymer, and thus the average molecular formulas. Comparison of the intensities of the <sup>13</sup>C NMR signals from end and junction groups confirmed triblock architecture. Copolymers with short E-blocks (m <35) contained a proportion of chains with uncapped B-block ends. The average formulas were not corrected using this information, as noted in subsequent discussion.

Raman Spectroscopy. Dried samples were melted and drawn into thin-glass capillaries which were then sealed in air taking precautions to exclude moisture. The samples were again melted and cooled slowly to -20 °C over a period of ca. 1 h at a cooling rate of ca. -1 °C min<sup>-1</sup>. One sample was melted and cooled rapidly to -20 °C. All spectra were recorded with the samples at -20 °C. Raman scattering at 90° to the incident beam was recorded by means of a Spex Ramalog spectrometer fitted with a 1403 double monochromator and with a third (1442U) monochromator operated in scanning mode. The light source was a Coherent Innova 90 argon ion laser operated at 514.5 nm and 400 mW. Conditions for the low-frequency range were bandwidth  $BW=0.5\ \mathrm{cm^{-1}},$  scanning increment SI=0.1 $cm^{-1}$ , integration time IT = 10 s. The low-frequency scale was calibrated by reference to the 9.6 and 14.9  $cm^{-1}$  bands in the spectrum of L-cystine. High-frequency spectra (BW =  $3 \text{ cm}^{-1}$ ,  $SI = 1 \text{ cm}^{-1}$ , IT = 2 s) were taken before and after recording the low-frequency spectra.

#### **Results and Discussion**

Previous investigations<sup>1–4</sup> gave wide-angle X-ray scattering patterns (WAXS) from related copolymers which, apart from the amorphous halo originating from noncrystalline B-blocks, were indicative of the usual crystal structure of poly(oxyethylene) chains with 7/2 helices of alternating handedness in a monoclinic subcell.<sup>7</sup> The high-frequency Raman spectra of the present crystalline copolymers were consistent with this structure, e.g., bands at 291, 936, and 1231 cm<sup>-1.8</sup> A second indicator was the band in the region of 80 cm<sup>-1</sup>, which is assigned to the poly(oxyethylene) helix plus a lattice mode of the poly(oxyethylene) crystal.<sup>9,10</sup> These results indicate the same crystal structure for the E-blocks irrespective of block architecture.

Examples of low-frequency Raman spectra obtained for the crystallized  $E_m B_n E_m$  copolymers are shown in Figure 1. The LAM-1 frequencies ( $\nu_1$ ) obtained are listed in Table 1. Corrections were made for the effect of baseline slope on peak frequency, particularly needed when the signal overlapped the tail of the Rayleigh scattering. A further correction of the intensity for frequency and temperature was applied using  $I/I_{obs} \propto$  $\nu[1 - \exp(-h\nu/kT)]$ .<sup>11</sup> As described previously for related samples,<sup>10</sup> the resulting change in peak position was very small, a maximum of +0.3 cm<sup>-1</sup>. The values listed are averaged quantities from five or more spectra. Also



**Figure 1.** Uncorrected Raman spectra of semicrystalline  $E_m B_n E_m$  copolymers.

Table 1. LAM-1 Frequencies  $(v_1)$  of Semicrystalline  $E_m B_n E_m$  Copolymers<sup>a</sup>

	<i>I</i> <sub>E</sub> ∕Å	<i>I</i> /Å	$        \nu_1/\mathrm{cm}^{-1}      (slow cooled)$	E-block folds
$E_{12}B_{11}E_{12}$	34.2	108.3	9.1	1
$E_{13}B_{10}E_{13}$	37.1	110.4	10.1	1
$E_{21}B_{11}E_{21}$	59.9	159.6	8.3	1
$E_{31}B_{11}E_{31}$	88.4	216.6	6.2	1
$E_{35}B_{27}E_{35}$	99.8	297.5	6.8	1
$E_{39}B_{11}E_{39}$	111.2	262.2	6.6	1
$E_{45}B_{44}E_{45}$	128.3	416.2	5.5	1
(fast cooled)			9.5	2
$E_{50}B_{11}E_{50}$	142.5	324.9	6.0	1
$E_{51}B_{50}E_{51}$	145.4	472.2	5.3	1
$E_{72}B_{27}E_{72}$	205.2	508.4	6.5	2

<sup>*a*</sup>  $l_{\rm E}$  = E-block length and *l* = overall chain length. Estimated uncertainty in LAM-1 is ±0.5 cm<sup>-1</sup>.

listed in Table 1 are values of the average E-block length

$$l_{\rm F}/{\rm \AA} = 2.85 m$$

and the average overall length of the copolymer

$$l/Å = 2.85(2m) + 3.63n$$

where the coefficients in the equations are those reported by Craven et al.<sup>12</sup> and Flory.<sup>13</sup>

Previously,<sup>3</sup> we found it useful to determine the extent of chain folding in crystallized  $B_n E_m B_n$  copolymers by plotting the product  $v_1 l_E$  against *l*. Because  $E_m B_n E_m$ copolymers have two crystallizable E-blocks, and thus two vibrating stems, it is advantageous in comparing present and previous data to plot against *l*\*, where *l*\* = 1/2 for  $E_m B_n E_m$  copolymers and  $I^* = I$  for  $B_n E_m B_n$  and  $E_m B_n$  copolymers. This plot is shown in Figure 2. Given that data points for the  $E_m B_n$  copolymers are known to correspond to unfolded E-blocks and that those for the  $B_n E_m \hat{B}_n$  copolymers correspond to once- or twice-folded E-blocks, the  $E_m B_n E_n$  copolymers with lengthy E-blocks  $(m \ge 35)$  are readily identified as having either unfolded or once-folded E-blocks, the latter for the slowly cooled sample of copolymer  $(E_{72}B_{27}E_{72})$  and the rapidly cooled sample of  $E_{45}B_{44}E_{45}$ . The lines drawn in Figure 2 indicate values of  $v_1 l_E$  that best represent the data points for unfolded and once-folded E-blocks of the  $E_m B_n E_n$  copolymers.

The data points for the  $E_m B_n E_m$  copolymers with short E-blocks fall below the line expected for unfolded E-blocks. This is a consequence of their E-block-length distributions, which contain a proportion of uncapped B-block ends and a larger proportion of very short



**Figure 2.** LAM-1 frequencies ( $\nu_1$ ) from Raman spectroscopy for E/B copolymers plotted as  $\nu_1 I_E$  vs  $I^*$ , where  $I_E$  is the length of the E-block, (2.85 *m* Å) and  $I^*$  is either the half-length of a  $E_m B_n E_m$  copolymer or the full length of a  $B_n E_m B_n$  or  $E_m B_n$ copolymer: ( $\bullet$ ) slowly cooled  $E_m B_n E_m$ ,  $m \le 51$ ; ( $\bullet$ ) rapidly cooled  $E_{45} B_{44} E_{45}$  and slowly cooled  $E_{72} B_{27} E_{72}$ ; ( $\Box$ ) slowly cooled  $B_n E_m B_n$  (ref 3); ( $\bigtriangledown$ ) slowly cooled  $E_m B_n$  (refs 1 and 2). The lines show  $\nu_1 I_E = 0.75$  and  $\nu_1 I_E = 1.27$ .

E-blocks.<sup>5</sup> Obviously, the missing E-blocks do not contribute to the LAM-1 frequency measured in our experiments, and nor will the very short E-blocks. For example, the low value of  $v_1 l_E$  plotted in Figure 2 for copolymer  $E_{12}B_{11}E_{12}$  would approach the level of the "unfolded" line if  $l_E$  were doubled, which is entirely reasonable considering that approximately 20 mol % of the B-blocks are uncapped at this average E-block length.<sup>5</sup> The results confirm that all the EBE copolymers with  $m \leq 51$  crystallize with unfolded E-blocks on slowly cooling to -20 °C.

We speculate that the difference between the results for  $E_m B_n E_m$  and  $B_n E_m B_n$  triblock copolymers evident in Figure 2 lies not in state of chain folding at the point of crystallization of a chain, which is determined kinetically and depends on overall chain length, but in the subsequent perfecting of the lamellar crystals at the crystallization temperature through a process of chain unfolding. Unfolding a once-folded chain in a crystalline layer at or below its crystallization temperature, i.e., without heating to initiate melting and recrystallization, is a slow process involving the chain end passing through the crystal. This kinetic pathway will be open to  $E_m B_n E_m$  copolymers but effectively closed if both E-block ends carry B-blocks.

However, the equilibrium state of a semicrystalline copolymer is not necessarily its unfolded state. In the EB system, chain conformations in equilibrium structures are potentially complicated by the mismatch in area of cross section of the E- and B-blocks (21 Å<sup>2</sup> for E compared with 34 Å<sup>2</sup> for B) and the consequent need to reconcile possible conformations with the requirement of maintaining approximately normal densities of the two components of the lamellae. In practice, the chain conformation adopted is a three-way compromise between opposing equilibrium requirements of normal density, maximum lamellar thickness, and the kinetic requirement of a lamellar thickness which optimizes the crystallization rate. This complication has been discussed by others.<sup>14</sup> The results reported for  $E_m B_n E_m$ copolymers show that the unfolded equilibrium conformation is accessible for triblock copolymers of the EB system, which reinforces the argument<sup>3,4</sup> that the oncefolded conformation of  $B_n E_m B_n$  copolymers is not the equilibrium state but is determined kinetically.

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