Notes

A High-Resolution Calorimetry Study of the Order−Disorder Transition in a Diblock Copolymer Melt

V. P. Voronov, V. M. Buleiko, and V. E. Podneks

Oil and Gas Research Institute of the Russian Academy of Sciences, Moscow 117917, Russia

I. W. Hamley*

School of Chemistry, University of Leeds,
Leeds LS2 9JT, U.K.

J. P. A. Fairclough† and A. J. Ryan†

Materials Science Centre, UMIST,
Manchester M1 7HS, U.K.

S.-M. Mai, B.-X. Liao, and C. Booth

Department of Chemistry,
University of Manchester, Manchester, M13 9PL, U.K.

Received May 27, 1997
Revised Manuscript Received August 11, 1997

Introduction

The order−disorder transition (ODT) in block copolymers can be located via a number of methods. Scattering techniques such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) provide an accurate method. The peak intensity, width, and shape all show a discontinuity at the transition, although most work indicates that the peak position, q^*, varies continuously through the transition.[1−5] From rheological measurements, the ODT is identified by a sharp decrease in the low frequency isochronal dynamic elastic moduli obtained during a heating ramp,[3,6,7] although this method may not provide a well-defined temperature for the ordered bcc−disordered phase transition.[8,9]

In the present paper we report a new method for locating the ODT in a diblock copolymer, namely high-resolution calorimetry, and compare the result with determinations by SAXS and rheology. Although calorimetry, in the form of differential scanning calorimetry (DSC), is commonly used to locate the melting point of semicrystalline copolymers, the method has not, to our knowledge, been used to locate the ODT. Because of the small enthalpy jump associated with the weakly first order ODT, it would be necessary to use a micro-DSC capable of measuring to millijoule resolution, such as the Setaram Micro DSC employed succesfully to locate the related transitions in aqueous micellar solutions of block copolymers.[10] In fact the instrument employed in this work was an adiabatic scanning calorimeter with an order of magnitude better precision, i.e., approaching 0.1 mJ.[11]

The copolymer used in the experiments was $E_{60}B_{29}$, where E denotes poly(oxyethylene) and B denotes poly(oxybutylene), and the subscripts are the number of repeat units. Because of the larger volume of a B unit, this copolymer is symmetrical in volume composition. Accordingly, on melting it forms a lamellar mesophase, as previously verified by SAXS.[3]

Experimental Section

The preparation of diblock copolymer $E_{60}B_{29}$ by sequential anionic copolymerisation has been described in an earlier publication.[3] Characterization of the polymer, also detailed elsewhere,[3] yielded a number-average molar mass $M_n = 4700$ g mol^{-1} and a volume fraction of E, $f_E = 0.52$. This sample contains 5% of a high molecular weight impurity, attributed to triblock $B_{29}E_{120}B_{29}$.[3]

The adiabatic scanning calorimeter has been described previously.[11] The calorimeter cell with a volume of 0.29 cm^3 was filled with 0.0969 g of block copolymer. The temperature was measured by a 100 Ω platinum resistance thermometer placed on the internal shield. The temperature difference between the calorimeter cell and the internal shield was controlled by a chromel−copper thermocouple.

Heating and cooling runs at different scanning rates were carried out. A fixed heating (cooling) power P was applied to the calorimeter cell during a run. As the conditions of the experiment were only quasi-adiabatic, the small thermal exchange q between the cell and internal shield was taken into account. For this purpose, the exchange q was measured just before (q_s) and just after (q_f) an experiment. The enthalpy relative to that at the start of the experiment [denoted $H(T)$] was determined as

$$H(T) = P(t - t_s) + (t - t_s)[(q_f - q_s)(T - T_s)/(T_f - T_s) + q_s] \tag{1}$$

where T is the temperature at time t. The heat capacity $C_p(T)$ of sample was obtained by numerical differentiation of the $H(T)$ data

$$C_p(T) = \frac{dH(T)}{dT} - C_{cell} \tag{2}$$

where C_{cell} is the heat capacity of the empty calorimeter cell.

Measurements of the dynamic elastic moduli were made using a Rheometrics RMS-800 dynamic mechanical spectrometer operated in the parallel plate geometry. Specimens were prepared by melt pressing films 1 mm thick in the 25 mm parallel-plate fixture of the rheometer. The furnace was heated at 2 °C min^{-1} between measurement temperatures and held for 1 min at the set temperature prior to testing at 100 rad s^{-1}. The furnace was flushed with dry nitrogen throughout the experiments and the samples were checked for degradation by GPC after heating. Experiments were performed with a strain amplitude of 1%, well within the linear viscoelastic regime.

SAXS experiments were performed on beamline 8.2 of the Synchrotron Radiation Source (SRS) at the Daresbury Laboratory, Warrington, U.K. Details of the storage ring, radiation, camera geometry and data collection electronics, and the design and operation of the X-ray DSC have been described elsewhere.[12,13] White radiation from the source was monochromated using a cylindrically bent Ge(111) crystal to give an intense beam of $\lambda = 1.50 \pm 0.01$ Å X-rays. A multiwire quadrant detector was located 3 m from the sample position, with a vacuum chamber between the sample and detector to reduce air scattering and absorption. The samples were

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* To whom correspondence should be addressed.

† Current address: Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K.

S0024-9297(97)00727-4 CCC: $14.00

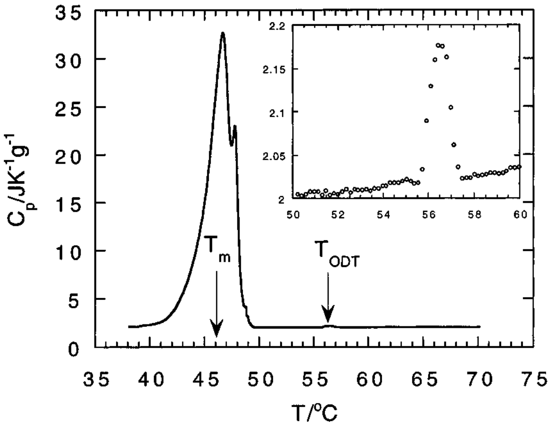

Figure 1. Specific heat of $E_{60}B_{29}$ measured at a heating rate of 5 °C h^{-1}. The melting temperature (T_m) and order–disorder transition (T_{ODT}) are indicated. Inset: heat capacity in the vicinity of the ODT on an expanded scale.

prepared by putting polymer (in powder form) into a cell comprising a TA Instruments DSC pan containing a 0.75 mm brass spacer ring fitted with windows made from 25 μm thick mica. The loaded pans were placed in the cell of a Linkam DSC of single-pan design. A more complete description of the DSC and sample pans can be found elsewhere.[13]

Heating and cooling rates of 1 °C min^{-1} were used. A scattering pattern from an oriented specimen of wet collagen (rat-tail tendon) was used to calibrate the SAXS detector. A parallel plate ionization detector placed before the sample cell recorded the incident intensities. The experimental data were corrected for background scattering (from the camera, hot stage and empty cell), sample absorption, and any positional alinearity of the detectors.

Results and Discussion

Figure 1 shows the specific heat capacity of $E_{60}B_{29}$ over the temperature region from the crystal to the isotropic phase measured at a heating rate of 5 °C h^{-1}. The large peak in the heat capacity data at 46.5 °C corresponds to the melting transition from the crystal to the lamellar mesophase. The latent heat of this phase transition is 90.2 ± 2 J g^{-1}. The endotherm near 48 °C is due to melting of the triblock impurity. This was confirmed by separate experiments using a Perkin-Elmer DSC4 on the closely-related triblock $B_{32}E_{120}B_{32}$. This yielded a melting temperature (corrected for thermal lag) of 49 ± 1 °C, being an average value for crystallization of stored, quenched, and slow-cooled samples.

As the specific enthalpy change associated with the lamellar–isotropic phase transition is much smaller than that with melting, we present it on an enlarged scale in the inset of Figure 1. For more precise determination of the latent heat of the ODT, we used a heating rate of 0.2 °C h^{-1}. An enthalpy jump $\Delta H_{ODT} = 0.171 \pm 0.003$ J g^{-1} was obtained as a difference between values of left and right branches of $H(T)$ extrapolated to the middle of the transition (T_{ODT} = 56.25 °C) (see Figure 2).

Results obtained from rheological experiments are presented in Figure 3. This shows the temperature dependence of the dynamic shear moduli at a fixed frequency of 100 rad s^{-1} on heating. On the basis of the precipitous drop which is particularly noticeable for G', the ODT is determined to be 54 ± 2 °C, in good agreement with the value obtained from calorimetry.

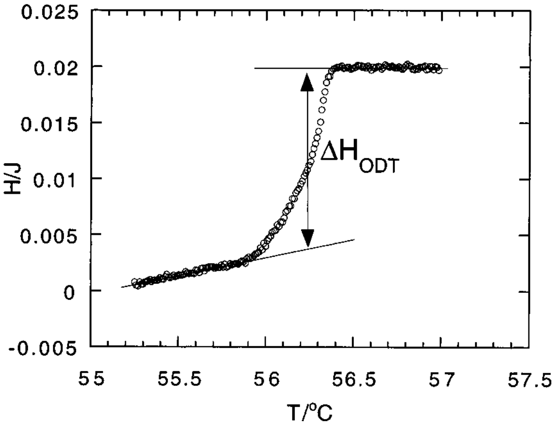

Figure 2. Enthalpy as a function of temperature in the vicinity of the ODT, obtained at a heating rate of 0.2 °C h^{-1}.

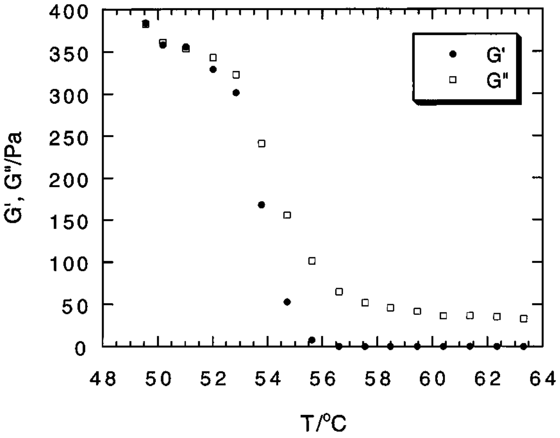

Figure 3. Temperature dependence of the isochronal (ω = 100 rad s^{-1}) dynamic shear moduli obtained with a strain amplitude of 1% on heating the polymer.

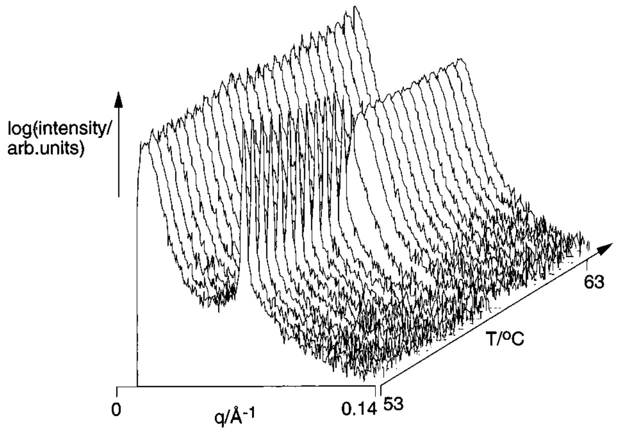

Figure 4. Small-angle X-ray scattering profiles obtained on heating $E_{60}B_{29}$ at 1 °C min^{-1}. The ODT is located at 58 ± 1 °C.

The SAXS data obtained during a heating ramp at 1 °C/min (Figure 4), show a change from a narrow Gaussian peak to a broad Lorentzian peak at the ODT,[3] determined to be 58 ± 1 °C. This value differs slightly from the previously published value[3] (60 °C), because we repeated the SAXS experiment with a slower heating rate, and using a recalibrated DSC.

In summary, we have demonstrated the utility of high-resolution calorimetry for determining the order–disorder transition in a nearly symmetric block copolymer. The ODT obtained by this method was in good agreement with that determined from rheology and SAXS.

Acknowledgment. I.W.H. and A.J.R. are grateful to the EPSRC (U.K.) for the research grant that supported J.P.A.F. (GR/K03982), and for their support of the synthetic work. Dr. B. U. Komanschek is acknowledged for configuring the SAXS experiments at Daresbury.

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MA970727G