Crystal transformation of styrene–butadiene block copolymer

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The crystal transformation of styrene–butadiene block copolymer, which has the attribute of shape-memory, has been studied. It is demonstrated from differential scanning calorimetry and wide-angle X-ray diffraction measurements that reversible crystal transformation takes place with temperature; two distinct crystal forms exist above and below the crystal transformation temperature of ~45°C.

(Keywords: crystal transformation; styrene-butadiene; block copolymer)

Introduction

Some special elastomers, with the quality of shape-memory, have recently been developed. Shape recovery is related to a transition temperature, such as a glass transition temperature, in an amorphous polymer and to melting and/or crystal transformation transition temperatures in a crystalline polymer. The styrene–butadiene block copolymer used here corresponds to the latter case. Crystal structure and crystal modification have not yet been studied in this polymer, although two crystal modifications are known to appear in *trans*-1,4-polybutadiene homopolymer[1–3]. In this study, crystal transformation is discussed on the basis of X-ray diffraction and differential scanning calorimetry (d.s.c.) measurements.

Experimental

Styrene–butadiene block copolymer ($M_w = 7 \times 10^4$; weight ratio of composition, St/Bu = 34/66; characterization of polybutadiene portion, *trans* 86%, *cis* 9%, vinyl type 5%) was kindly supplied by Asahi Kasei Kogyo Ltd. The copolymer was moulded at 130°C and $90\,\mathrm{kg\,cm^{-2}}$ for 15 min to make a sheet with a thickness of about 0.4 mm. A strip of the sheet was drawn five-fold in a water bath at 97°C and quenched in an ice–water mixture at constant length.

D.s.c. measurement was performed on a Seiko Denshi Kogyo DSC 200 differential scanning calorimeter at a constant heating and cooling rate of $10\,\mathrm{K\,min^{-1}}$.

Wide-angle X-ray diffractograms were obtained with a Rigaku Denki Model D-IA X-ray diffractometer equipped with a scintillation counter, utilizing nickel-filtered CuKα radiation. The temperature of the sample was controlled with a heating device.

Results and discussion

The undrawn and drawn samples show the same d.s.c. curves in the heating and cooling cycle, as depicted in *Figure 1* for the former sample. The heating run gives two endothermic peaks. Taking into account the results from X-ray diffraction measurements discussed below, the thermal behaviour can be interpreted as follows. The first endotherm corresponds to crystal transformation from the low-temperature form to the high-temperature form in *trans*-1,4-polybutadiene domains, which results from microphase separation of the copolymer when cooled from the melt. The second endotherm indicates the melting of the high-temperature crystal form. In the cooling process, the reversible transformations occur, although the corresponding exotherms appear at somewhat lower temperatures.

The X-ray photograph of the drawn sample showed the crystalline fibre pattern, which was quite different from the pattern of a normal, oriented styrene–butadiene random copolymer exhibiting amorphous halos. More than eight diffraction spots, including the innermost equatorial reflection with a spacing of 0.400 nm, were observed and analysed to determine the crystal lattice parameters: $a = 0.885$ nm, $b = 0.908$ nm, $c = 0.479$ nm and

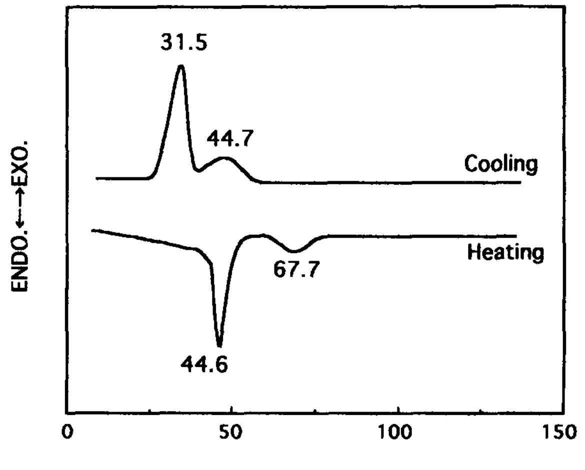

Figure 1 D.s.c. curves of styrene–butadiene block copolymer during the temperature cycle

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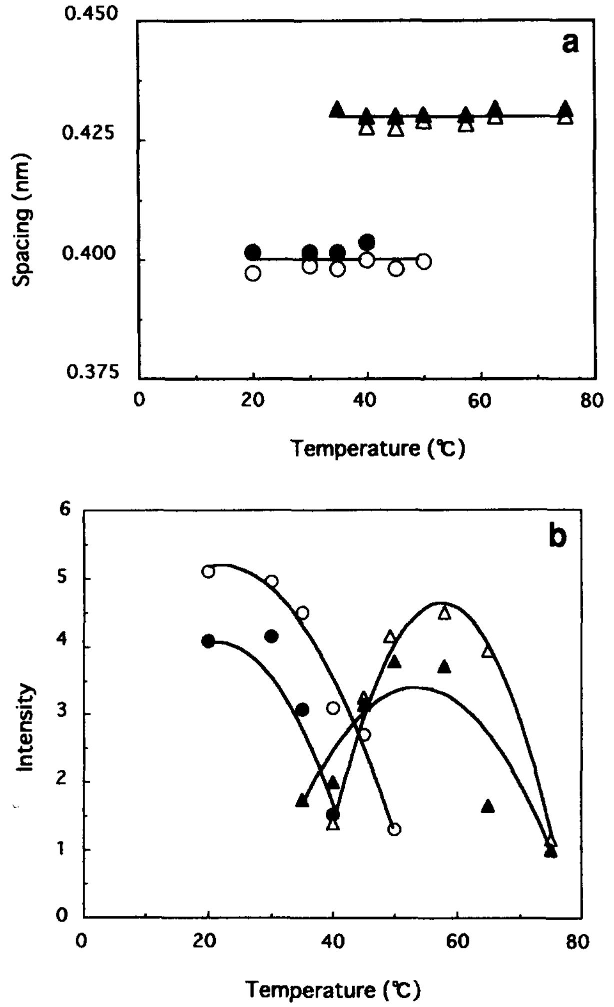

Figure 2 Change of equatorial reflections with temperature: (a) spacing; (b) intensity. ○ and △, Heating process; ● and ▲, cooling process: ○ and ●, low-temperature form; △ and ▲, high-temperature form

$\beta = 113°$. A good agreement was obtained with the parameters for the low-temperature crystal form of *trans*-1,4-polybutadiene proposed by Iwayanagi *et al.*[1]: $a = 0.863$ nm, $b = 0.911$ nm, $c = 0.483$ nm and $\beta = 114°$. It was also confirmed by infra-red analysis that the stereochemical structure of *trans* configuration was preferred in most of the polybutadiene positions of this polymer. Thus, it can be concluded that the X-ray diffraction is caused by the crystals of polybutadiene domains with *trans*-1,4 configuration. The innermost equatorial reflection with a spacing of 0.400 nm is indexed as 200. On heating to temperatures above 40°C, an additional equatorial reflection appears at a spacing of 0.426 nm; this corresponds to the 100 reflection of the high-temperature crystal form proposed by Suehiro and Takayanagi[2]. These innermost equatorial reflections are closely related to the interchain distance.

In order to confirm the crystal transformation, the change of such reflections with temperature was measured, as shown in *Figure 2*. With increasing temperature, the intensity of the 200 reflection of the low-temperature form rapidly decreases to 50°C, while the 100 reflection of the high-temperature form can be observed at almost 40°C; its intensity increases up to 60°C and then decreases to 75°C where the reflection disappears. On the other hand, each spacing of the 200 and 100 reflections remains almost constant during heating. These behaviours coincide well with the thermal behaviour measured by d.s.c. In the heating and cooling cycle, they changed reversibly.

Compared with the homopolymer of *trans*-1,4-polybutadiene, with a crystal transformation temperature of 76°C and melting temperature of 136°C, the copolymer gives much lower transformation and melting temperatures. These facts remind us that depression of the melting point is often observed in polymer blend systems, although the temperature differences are very large in this case. This problem is now being studied from the viewpoint of thermodynamics and morphology.

Conclusions

The crystal structure and crystal transformation of a newly developed styrene–butadiene block copolymer exhibiting shape-memory have been studied. The following conclusions are drawn.

(1) When this copolymer is cooled from the molten state, microphase separation occurs to form an individual domain of polybutadiene and polystyrene, followed by the crystallization of polybutadiene.
(2) The molecules of polybutadiene domains prefer the stereochemical structure of *trans* configuration, i.e. there are mostly *trans*-1,4-polybutadiene molecules.
(3) This copolymer has two crystal modifications: one is stable near room temperature and the other forms above 45°C and melts at about 70°C.
(4) The first-order solid-state transformation between these two forms is reversible in a thermodynamic sense.
(5) This copolymer has much lower transition and melting temperatures than those of the homopolymer of *trans*-1,4-polybutadiene.

References

1 Iwayanagi, S., Sakurai, I., Sakurai, T. and Seto, T. *J. Macromol. Sci.* 1968, **B2**, 163
2 Suehiro, K. and Takayanagi, M. *J. Macromol. Sci.* 1970, **B4**, 39
3 Tatsumi, T., Fukushima, T., Imada, K. and Takayanagi, M. *J. Macromol. Sci.* 1967, **B1**, 459