New block copolymers: Part VII—Morphology of \((A-B)_{n}\)-type block copolymers

Benimadhab Mahato & Sukumar Maiti*
Polymer Division, Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302
Received 27 November 1990; revised and accepted 8 May 1991

Detailed morphological behaviour of poly(pentamethylene terephthalate)-b-(acrylonitrile-butadiene rubber) copolymer (5GT-b-ATBN) films annealed, benzene etched and iodine stained has been investigated by scanning electron microscopy. The morphology of the copolymer samples depends on the percentage of polyester (hard) segment and on the method of film preparation. Besides hard and soft block phase, a mixed phase has also been detected.

Extensive researches have been carried out to understand the morphology and properties of styrene-butadiene-styrene (SBS) and styrene-isoprene-styrene (SIS) triblock copolymers. These copolymers are totally amorphous and the molecular weights of the blocks are relatively high. It is now widely accepted that many of their usual properties can be attributed to microphase separation of chain segments caused by their thermodynamic incompatibility\(^1\)\(^-\)\(^5\).

In recent years, besides the microphase separation, a particular aspect that has been of interest to polymer chemists is the nature of the domain boundaries. Many of the theories of phase separation in block copolymers are based on the concept of a three-phase system consisting of regions of pure A, pure B and an inter-domain region of mixed A and B\(^6\)\(^-\)\(^9\).

For \((A-B)_{n}\) type block copolymers, domain formation was difficult and in most cases a sponge-like morphology was observed due to the constraints of many valence bonds between the hard and the soft blocks. Phase separation of hard segments of \((A-B)_{n}\) type urethane elastomers into microregions termed domains has been proposed based on the results of electron microscopy\(^1\)\(^1\), X-ray diffraction\(^1\)\(^2\) and viscoelastic property measurements\(^1\)\(^3\).

In this paper we wish to report the study of the surface morphology of 5GT-b-ATBN copolymer samples by scanning electron microscopy (SEM) under various conditions such as, by annealing, etching with benzene and staining with iodine.

**Materials and Methods**

**Preparation of the block copolymers**

Block copolymers having poly(pentamethylene terephthalate) (5GT) as the hard block and amine-terminated butadiene acrylonitrile rubber (Hycar ATBN) as the soft block were synthesized by low temperature polycondensation method\(^1\)\(^4\)\(^,\)\(^5\) by reacting terephthaloyl chloride, pentane-1, 5-diol and ATBN. Variation of copolymer composition was made by procedure as described elsewhere\(^1\)\(^6\).

**Film preparation**

The block copolymers samples were cast from 3\% (w/v) dimethylacetamide solutions, into thin films over glass plates or mercury by evaporating the solvent gradually at room temperature (30°C). The films were completely dried under reduced pressure and annealed up to 75°C. They were treated as follows:

(a) The annealed films were slowly cooled to room temperature and kept in a vacuum dessicator.

(b) The annealed films were etched with benzene by keeping the film in benzene (50 ml) for about 48 hr and benzene was allowed to evaporate slowly at room temperature and finally in vacuo. However, films etched with iodine showed better contrast and resolution than those etched with benzene. Hence iodine etching was also performed.

(c) The annealed films were stained with iodine by keeping the film in iodine solution (50 ml, 1\% solution in ethanol) for 48 hr and then the films were taken out and washed several times with absolute ethyl alcohol and dried in vacuo.

**Morphology study**

The films thus prepared were coated with gold (100 Å) and observed under scanning electron microscopy, ISI-60 model at varying magnifications.

**Results and Discussion**

The copolymer compositions of the block copolymers are presented in Table 1 The general structure of
the block copolymers may be represented as shown in Structure-I.

The characterization, thermal behaviour and chemical properties of these copolymers were reported in a previous communication\textsuperscript{17}.

\begin{equation}
\left\{ \text{Poly(pentamethylene terephthalate)-b-(acrylonitrile butadiene rubber) copolymer (5GT-b-ATBN)} \right\}
\end{equation}
to black continuous region are discerned. Since the copolymer contains 32 wt % of polyester, the white spherical regions are assigned to polyester domains and the grey regions to ATBN (rubber) matrix. Careful examination of Figs 1b, c reveals that polyester domain formation is incomplete. The phase boundary between the two phases is diffuse (Fig. 1c) and there is supposed to be mixing of polyester segments into ATBN segments, since each polyester domain is associated with some rubber matrix (Fig. 1b).

Figure 2 shows that the polyester domains (white regions) are dispersed in the rubber matrix (grey to black regions). The domains are well-defined and interconnected to each other (Figs 2a, b). Figure 2c reveals that the domain formation is complete and there exists a sharp boundary between the matrix and a domain. Figure 2c also shows the presence of some mixed phases (greyish white portion) in the copolymer.

In Fig. 3 discrete small white spherical domains dispersed in grey (black) continuous matrix are obtained. Since the copolymer contains 72% (w/w) polyester, we may assume that the white spherical domains are due to ATBN soft segments and the greyish continuous matrix to polyester segments. The difference between Fig. 3 and Fig. 1 is that the domains are small and have distinct phase boundary in Fig. 3. This may be due to low solubility of dispersed ATBN phase in

![Fig. 3—SEM micrographs of 5GT-72 copolymer films, annealed at 75°C. (a) 200 x and (b) 1600 x](image)

![Fig. 4—SEM micrographs of Kraton D111 Film; 1600 x](image)

![Fig. 5—SEM micrographs of 5GT-32 copolymer films, annealed at 75°C and etched with benzene. (a) 400 x and (b) 3200 x](image)

### Table 1—Copolymer composition and thermal characteristics of the block copolymers

<table>
<thead>
<tr>
<th>Block copolymer code</th>
<th>Hard block</th>
<th>Soft block</th>
<th>T_g, °C</th>
<th>T_m, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5GT-32</td>
<td>32</td>
<td>—</td>
<td>-58.0</td>
<td>not detectable</td>
</tr>
<tr>
<td>5GT-54</td>
<td>54</td>
<td>—</td>
<td>-56.5</td>
<td>40</td>
</tr>
<tr>
<td>5GT-72</td>
<td>72</td>
<td>—</td>
<td>-54.1</td>
<td>44</td>
</tr>
<tr>
<td>5GT</td>
<td>100</td>
<td>—</td>
<td>—</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
</tr>
</tbody>
</table>

747
Fig. 6—SEM micrographs of 5GT-54 copolymer films, annealed at 75°C and etched with benzene. (a) 200 × and (b) 3200 ×

continuous polyester matrix, but in the case of Fig. 1, the solubility of polyester in ATBN matrix is higher. Its morphology is comparable to the morphology of Kraton D1111 where the less soluble polystyrene domains are dispersed in polyisoprene matrix (Fig. 4).

Morphological behaviour of annealed and benzene etched films
Figures 5-7 show the scanning electron micrographs of annealed and benzene etched films of 5GT-32, 5GT-54 and 5GT-72 respectively. A very striking morphology is seen in these specimens. Since benzene dissolves ATBN very well, continuous ATBN phase and the 5GT as the dispersed phase are expected to be seen.

In 5GT-32 (Fig. 5a) white polyester domains dispersed in the grey to black ATBN continuous matrix are observed. By carefully observing the micrograph (Fig. 5a), some white polyester portions which do not form any domain are identified. Probably these are the ATBN solubilized polyester portions. The domains have got a distinct phase boundary (Fig. 5b) compared to that seen in Fig. 1.

In 5GT-54, the morphology of benzene-etched film (Fig. 6) is almost similar to that of annealed specimen (Fig. 2). But in this case the polyester domains are less defined (Fig. 6a), and the phase boundary (Fig. 6b) is prominent together with some phase mixing (see Figs 6a, b).

An interesting morphology is observed in 5GT-72 copolymer sample (Fig. 7). Large polyester domains are connected with crystalline polyester (Fig. 7b) which are dispersed in a continuous ATBN matrix. Besides that a crack is observed in each polyester domain. This type of morphology has not been reported in any other block copolymer.

Morphological behaviour of annealed and iodine stained films
Figures 8-10 show the scanning electron micrographs of annealed and iodine stained films of 5GT-32, 5GT-54 and 5GT-72 respectively. In Fig. 8 (for 5GT-32), white lamellar sponge-like domains dispersed in grey to black continuous regions are observed. Since iodine selectively reacts with polybutadiene-olefinic bonds, the grey to black regions are assigned to amorphous ATBN portion and white regions to crystalline polyester domains. Figure 8 also indicates that the phase separation between the domain and the continuous matrix is not complete and gives a diffuse phase boundary (Fig. 8c).
Figure 8—SEM micrographs of 5GT-32 copolymer films, annealed at 75°C and stained with iodine. (a) 50 x, (b) 200 x and (c) 1600 x.

Figure 9—SEM micrographs of 5GT-54 copolymer films, annealed at 75°C and stained with iodine. (a) 200 x, (b) 400 x and (c) 3200 x.

Figure 9 is similar to Fig. 2 (morphology of annealed films) and Fig. 6 (morphology of benzene-etched films). But in this case the polyester domains are more well-defined compared to those of the others.

An interesting morphology is observed in 5GT-72 copolymer sample (Fig. 10) wherein black ATBN domains encircled with white portion are dispersed in greyish continuous polyester matrix. It may be assumed that the white portion is the interfacial boundary of the two phases which may be regarded as a third phase. In all 5GT-b-ATBN copolymer samples a third phase (interfacial boundary or mixed phase) is present but in this case it is more prominent probably because of high percentage of polyester content in the copolymer and large amount of amorphous polyester (5GT) is solubilized in the soft ATBN segment. This may also be explained by the increase of interfacial mixing. Several evidences are available for the occurrence of this third phase and of the hard phase toward low temperatures, or that of the mixed phase. Annighofer and Gronski showed the presence of a three-phase system in styrene-isoprene copolymer by electron microscopy.

Recently, Koberstein and Russell found a microphase mixing transition of polyether based polyurethane block copolymers. These authors also concluded that the transition was evidenced by a dramatic

749
in the diffuse microphase boundary thickness.

In conclusion, we may say that the morphology of 5GT-b-ATBN copolymer samples depends on the weight percentage of polyester segments and on the conditions of film preparation. Although, the morphology of 5GT-54 copolymer sample is almost the same in all the films (independent of film preparation) its morphology is prominent in iodine-stained films. Perhaps oxidative role of iodine contributes to its better performance as an etchant and staining material to polymer films. Benzene does not enjoy such property. This is true in other copolymer samples, viz. 5GT-32 and 5GT-72 also. Besides the two phases, viz. polyester and ATBN, the presence of a mixed phase is detected in all the copolymer samples. But it is prominent in 5GT-72 sample where the polyester percentage is high. These results are in agreement with the results obtained by thermal analysis.17.

Acknowledgement
The authors wish to thank the B.F. Goodrich Company, USA for a gift of Hycar ATBN, the Department of Science & Technology and the CSIR, New Delhi for partial financial support.

References

Fig. 10—SEM micrographs of 5GT-72 copolymer films, annealed at 75°C and stained with iodine. (a) 200 x, (b) 400 x and (c) 6400 x