Morphological Characteristics of SEBS Thermoplastic Elastomer Gels

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Received May 20, 1996

Modification of the morphology and properties of a microphase-ordered block copolymer can be readily achieved through intramicrodomain incorporation of either a parent[1−4] or block-selective[4−8] homopolymer. Previous efforts have conclusively demonstrated that the equilibrium morphology of such copolymer/homopolymer blends is strongly dependent on several factors, including the bulk composition of the blend, the mass of the homopolymer (M_h) relative to that of the host block (M_b), and the chemical selectivity of the homopolymer. Results from both experimental[9,10] and theoretical[11,12] studies reveal that reduction in molecular weight of the homopolymer lessens the repulsion between homopolymer and the insoluble (nonhost) block. Consequently, the spatial distribution of homopolymer within its resident microdomain becomes increasingly more uniform and less localized. If $M_h \ll M_b$, the additive can be envisioned as a preferential solvent that swells the compatible block of the copolymer while inducing self-assembly of the insoluble block.

While early studies of ordered block copolymers addressed the impact of solvent preference on copolymer morphology *upon* solution casting, recent studies by Reynaers and co-workers[13−15] have focused on an interesting variation of this theme, namely, thermoplastic elastomer gels. These gels are composed of a triblock copolymer with glassy end blocks and a rubbery midblock in the presence of a midblock-selective, nonvolatile oil of relatively low molar mass. Small-angle X-ray and neutron scattering (SAXS and SANS, respectively) have been utilized thus far to examine the morphological characteristics of such gels, and, as illustrated in Figure 1, suggest that these gels are stabilized by a three-dimensional network of end block micelles that serve as physical cross-links. In this work, we employ transmission electron microscopy (TEM) to investigate and compare the morphologies of several of these gels produced by both solution casting and mechanical mixing.

Two poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (SEBS) triblock copolymers, with compositions ranging from 31 (Kraton G1654) to 33 (Kraton G1651) wt % S, were obtained from the Shell Development Co. Their molecular weights were 150 000 and 240 000, respectively, and their polydispersities were less than 1.04.[16] The viscosity of the saturated aliphatic white oil used as an extender in this study (Hydrobrite 380 PO, from Witco Corp.) was 75 cSt at 40 °C (its molecular weight is about 468, according to ASTM D2502). Gels containing oil weight fractions (ω_{oil}) of ≥ 0.70 were prepared via two routes. In the first, predetermined masses of the copolymer and oil were added to cyclohexane to yield a 5% (w/v) solution. Once these solutions were cast into Petri dishes, they were quickly dried (for 3 days) at ambient temperature. In the second sample preparation route, the copolymer and oil were mechanically mixed under vacuum for 1 h in a Ross LDM 1-qt. double planetary mixer maintained at 180 °C. Resultant gels were sectioned at −100 °C in a Reichert-Jung Ultracut-S microtome and stained with the vapor of 2% RuO_4(aq) for 5 min. Electron micrographs were recorded on a Zeiss EM902 electron spectroscopic microscope, operated at 80 kV and ΔE between 50 and 100 eV.

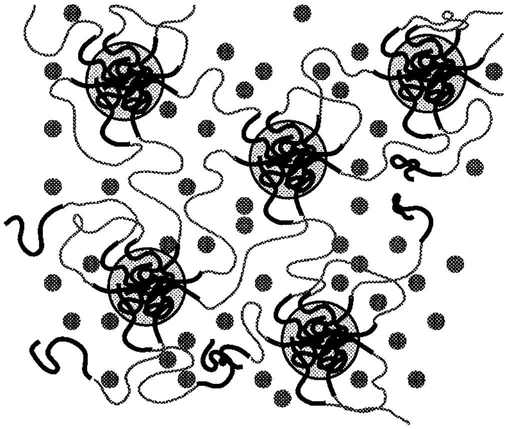

Figure 1. Illustration of a dispersed micellar morphology in a SEBS gel, as inferred from SAXS and SANS measurements.[13,14] The glassy S micelles stabilize the gel by serving as physical cross-links for the EB matrix containing solubilized oil.

Figure 2 shows a pair of transmission electron micrographs obtained from two Kraton G1654 gels in which $\omega_{oil} = 0.70$. Dark characteristics in these and subsequent images correspond to S-rich microdomains, which are preferentially stained with electron-dense RuO_4. The gel featured in Figure 2a is produced by the solution casting route described above, whereas the one displayed in Figure 2b illustrates the effect of mechanical mixing. Both gels exhibit comparable morphologies consisting of a combination of randomly oriented cylindrical and spherical microdomains measuring between 20 and 26 nm in diameter. It is of interest to note that the gel produced via mechanical mixing also possesses some locally ordered regions in which spherical S micelles are arranged on a body-centered cubic (bcc) lattice.

While no scattering data are yet available for the $\omega_{oil} = 0.70$ gels described in Figure 2, the morphological characteristics of gels with $0.82 \leq \omega_{oil} \leq 0.94$ can be quantitatively compared with the SAXS and SANS data of Mischenko *et al.*[13,14] Provided in Figure 3 is a pair of micrographs obtained from two Kraton G1654 gels with $\omega_{oil} = 0.90$. In both cases, the morphology clearly consists of spherical S micelles measuring about 15−22 nm across (as discerned from the NIH Image analysis software package), uniformly dispersed in an EB/oil matrix. Since these morphologies do not exhibit long-range order, a micellar periodicity cannot be accurately estimated from electron micrographs such as those displayed in Figure 3. The network of micelles clearly evident in Figure 3a,b is responsible for rigidifying and stabilizing these thermoplastic elastomer gels principally through *inter*microdomain midblock bridging.[17,18] While the micrographs in Figures 2 and 3 suggest that the gross morphological characteristics of thermoplastic elastomer gels are moderately dependent on the sample preparation routes employed in this work, slight varia-

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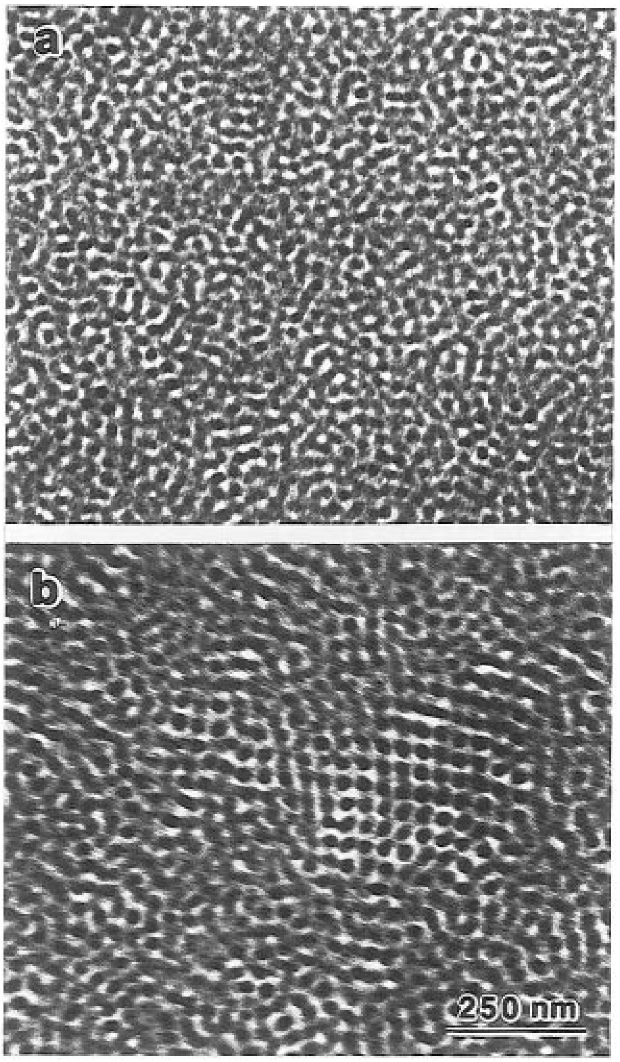

Figure 2. Electron micrographs of two SEBS gels in which $\bar{M}_n$ = 150 000 and ω_{oil} = 0.70. The gel in (a) was cast from cyclohexane solution, whereas the one in (b) was mechanically mixed at 100 °C.

tion in processing can have a pronounced effect on the mechanical properties of such gels.

An electron micrograph of a Kraton 1651 gel with ω_{oil} = 0.90 produced via mechanical mixing is displayed in Figure 4. As in Figure 3, this micrograph reveals that this gel, composed of a higher molecular weight copolymer than the one used in the gels shown in Figures 2 and 3, is likewise stabilized by dispersed S micelles measuring about 15−20 nm in diameter. Complementary small-angle scattering measurements[14] of mechanically mixed Kraton G1651 gels possessing comparable ω_{oil} (=0.88 and 0.94) yield a micellar periodicity between 63.5 and 81.3, nm, respectively. By assuming a dispersed spherical micelle morphology in their SANS model calculations, Mischenko *et al.*[14] report that the mean diameter of the S micelles in this gel lies between 19.4 and 22.4 nm, in excellent agreement with the results presented here. An intriguing feature of the micrographs in Figures 3b and 4 is that some of the EB/oil appears to be imbibed within the S-rich micelles. An enlargement illustrating this morphological peculiarity, which is not believed to be a defocus artifact (as verified by through-focus series, energy-filtering, and objective lens astigmatism variation), is provided in Figure 5. This feature has not been reported for block copolymer micelles in copolymer/homopolymer blends and may

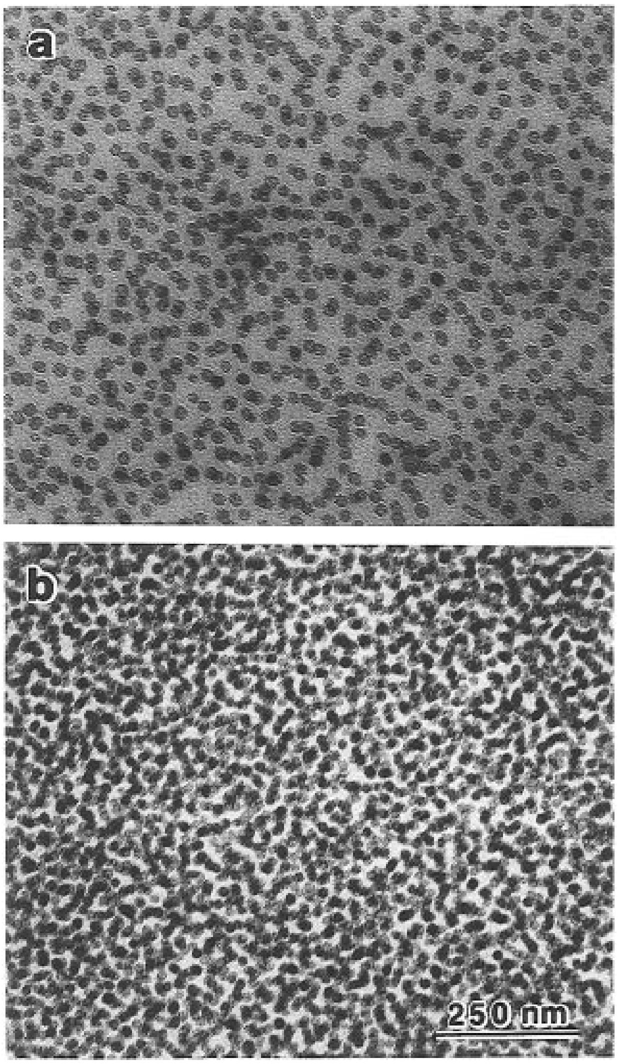

Figure 3. Electron micrographs of two SEBS gels in which $\bar{M}_n$ = 150 000 and ω_{oil} = 0.90. The gel in (a) was cast from cyclohexane solution, whereas the one in (b) was mechanically mixed at 100 °C. Spherical S micelles (stained with RuO_4) are clearly evident in each.

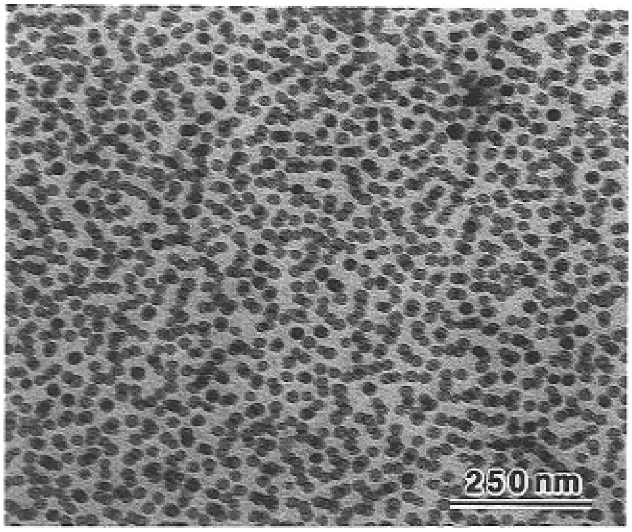

Figure 4. Electron micrograph of a SEBS gel in which $\bar{M}_n$ = 240 000 and ω_{oil} = 0.90. As in Figure 3, this gel consists of dispersed S micelles. This gel was mechanically mixed at 100 °C.

reflect, in addition to the possibility of kinetic entrapment during gel preparation, greater compatibility

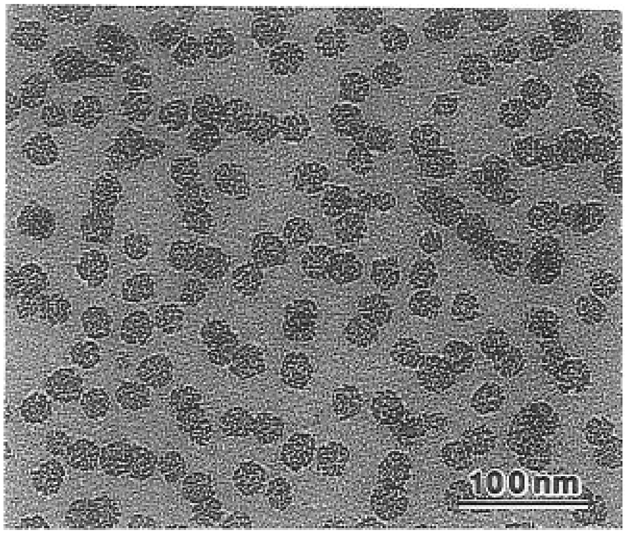

Figure 5. Enlargement of Figure 3b demonstrating that some of the S-rich micelles contain unstained EB/oil.

between S and the oil utilized here, in contrast to S and, for example, a homopolydiene.

In this communication, we have demonstrated that the morphological features of oil-rich thermoplastic elastomer gels can be discerned directly with TEM. The gels examined here consist of SEBS triblock copolymers and at least 70 wt % of a midblock-selective oil. They are stabilized at these relatively high oil concentrations by dispersed S micelles, a fraction of which are physically cross-linked via midblock bridging.[17,18] Microstructural dimensions estimated from the TEM micrographs presented in this work are found to be in favorable quantitative agreement with previously reported SAXS and SANS measurements.[13,14]

Acknowledgment. This work was supported by the Raychem Corp. and the Shell Development Co. and, in part, by the National Science Foundation (CMS 941-2361).

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MA9607271