

Morphology and Properties of α -Methylstyrene and Butadiene Diblock Copolymers

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Synopsis

Diblock copolymers of α -methylstyrene and butadiene were synthesized, using *n*-BuLi as initiator, toluene as solvent, and tetrahydrofuran (THF) as accelerator. The addition of a small amount of THF in polymerization solution would greatly increase the 1,2-addition of polybutadiene. However, this effect leveled off gradually as the amount of THF increased. Electron microscopic texture and viscoelasticity of diblock copolymer samples cast from THF, toluene, benzene and CCl₄ were examined. Two peaks were observed in the dynamic mechanical loss ($\tan \delta$) curve at -27 and 145°C , corresponding to segmental motions of polybutadiene and poly- α -methylstyrene, respectively. This showed the microphase separation of the block copolymers. Different electron microscopic textures were observed for same sample cast from different solvents.

INTRODUCTION

The syntheses of block copolymers using the techniques of anionic polymerization, together with the properties of the resulted copolymers, have been studied extensively, especially the block copolymers of poly(styrene-*b*-butadiene) and poly(styrene-*b*-isoprene).¹ However, the block copolymers of α -methylstyrene and butadiene or isoprene have been studied cursorily.² Poly(α -methylstyrene) is well known for its solvent resistance³ and high glass transition temperature ($\sim 170^\circ\text{C}$). The block copolymers from α -methylstyrene and butadiene or isoprene would, therefore, retain some tensile strength at elevated temperature, say up to 100°C , whereas similar copolymers with polystyrene in the end block will lose all their strength.⁴

We have previously investigated the morphology and properties of poly(methylmethacrylate-*b*- α -methylstyrene).^{5,6} In this work, AB diblock copolymers of α -methylstyrene and butadiene are synthesized with *n*-BuLi initiator. The phase separation of these copolymers are examined with electron microscopy and dynamic measurement. The solvent effects on the morphology of the copolymers are also investigated.

EXPERIMENTAL

Materials

α -Methylstyrene was washed successively with 5% NaOH solution and water, predried with MgSO₄, and distilled over CaH₂ under nitrogen. Butadiene was passed through a P₂O₅ column, degassed twice, and stored in a volumetric ampoule before use. Tetrahydrofuran (THF) was distilled twice in the presence of KOH, refluxed three days with KOH and Na chips, mixed with benzophenone,

TABLE I
Characterization of Poly(α -Methylstyrene-*b*-Butadiene)^a

\overline{M}_w	1.53×10^4
\overline{M}_n	1.24×10^4
$\overline{M}_w/\overline{M}_n$	1.23
polystyrene (wt %)	48
polybutadiene (wt %)	52
configurational composition of polybutadiene:	
<i>cis</i> -1,4 (wt %)	27
<i>trans</i> -1,4 (wt %)	17.5
1,2 (wt %)	55.5

^a The mixed solvent used is toluene/THF = 6:1 (v/v); monomer/mixed solvent = 1:3 (v/v).

and then the whole system flushed with nitrogen until the solvent turned to blue-green color and then distilled. Toluene and *n*-heptane were stirred with concentrated sulfuric acid, washed with water, neutralized with 5% NaOH, washed with water again, and then followed the purification procedures for THF. All reagents used were obtained from Wako Chemical Co. (Japan).

Catalyst

n-Butyllithium (*n*-BuLi) was prepared in *n*-heptane according to the procedure of West,⁷ and the concentration was determined by the method of Gilman.⁸

Polymerization Procedures

Polymerization was carried out in a vacuum system ($>10^{-5}$ torr). Toluene, 60 ml, was used as the solvent and *n*-BuLi, 2 ml (9.6×10^{-4} mole, 0.48M in *n*-heptane), as the initiator. In order to increase the yields of poly(α -methylstyrene), THF in amounts of 5–12% by volume on the total amount of monomers, were added as an accelerator.^{9,10} α -Methylstyrene monomer, 15 ml or 0.116 mole, was polymerized first at -30°C for two days. Then butadiene, 10 ml or 0.12 mole, was added and polymerized at 60°C for 4 hr. The presence of an ether

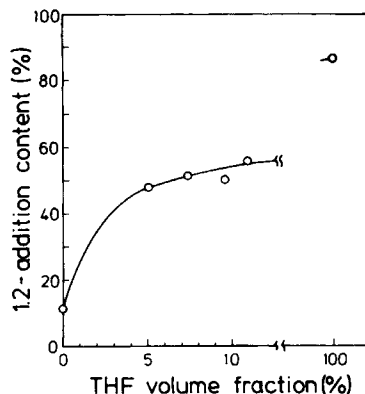


Fig. 1. 1,2-Addition content of PB block segment of MS-B diblock copolymer vs. THF volume fraction.

not only increased the polymerization rate of α -methylstyrene but also the rate of cross-addition of butadiene to poly(α -methylstyrene).¹¹

Identification of Block Copolymer

The characteristic color of living poly(α -methylstyrene) anion is dark red, and that of living polybutadiene anion is yellow. Therefore, the sequence of polymerization can be observed by the color change of the system. The microstructure of polybutadiene segment in the blocks was examined by IR (Perkin-Elmer, 567) and NMR (Jeol, JNM-C-60 HL) spectroscopy, and the molecular weight distribution and average molecular weight of these samples were analyzed by gel permeation chromatography (GPC) (Waters Associates, ALC/GPC, 502/401). In each case, a single narrow peak was observed. This substantiated the formation of block copolymers.

Dynamic Viscoelasticity

Dynamic viscoelasticity was measured at a frequency of 110 Hz with a direct-reading dynamic viscoelastomer (Toyo Baldwin, Rheovibron DDV-II-C) over the temperature range of -80 to 170°C . The specimen was cast from solution on a mercury surface and dried first at room temperature and then under vacuum. The specimens obtained from solution in THF, toluene, benzene, and CCl_4 were symbolized as *F*, *T*, *B*, and *C*, respectively. However, samples cast from CCl_4 solutions were too brittle to be measured. Dimensions for the specimen were about $(0.4\text{--}0.8) \times 5 \times 20$ mm.

Electron Microscopy

Block copolymers were dissolved in THF, toluene, benzene, or CCl_4 , and diluted to a concentration of 0.1%. Films were cast on a distilled water surface and were stained with a 2% OsO_4 solution for 1 hr. The thickness of the film obtained was about 700 Å. The transmission electron microscopy (TEM) employed was Hitachi HU12A. The magnification was 50,000 \times .

RESULTS AND DISCUSSION

The characterization of typical poly(α -methylstyrene-*b*-butadiene) synthesized in our laboratory is shown in Table I.

The effect of THF on 1,2-addition content of polybutadiene is shown in Figure 1. The 1,2-addition content of polybutadiene synthesized in the absence of THF was as low as 11.6%. Block copolymers of α -methylstyrene and butadiene prepared in the presence of THF contained an increasing amount of 1,2-addition of butadiene units. The effect of THF on the mode of butadiene polymerization became less pronounced as the amount of THF was increased. In a THF solvent, the content of 1,2-addition of butadiene could reach as high as 87%.¹² Wise reported that the addition of a small amount of diethyl ether did not alter the microstructure of the polybutadiene to any great extent.¹¹ In our work, THF had a great influence on the mode of butadiene polymerization.

The storage modulus E' and loss tangent $\tan \delta$ were plotted as a function of

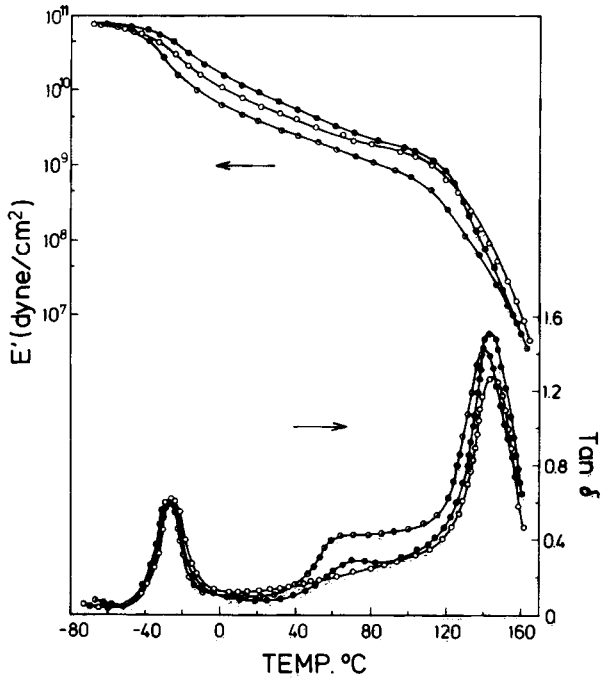


Fig. 2. Dynamic mechanical properties of MS-B diblock copolymer cast from different solvents: (●) benzene, (◐) toluene, and (○) THF.

temperature in Figure 2. Two peaks were observed at -27 and 145°C , which can be attributed to the onset of segmental motion of polybutadiene and poly- α -methylstyrene, respectively. This could be accounted for in terms of a two-phase structure originating from microphase separation of the block segments. There appeared a third peak (around 70°C) in samples cast from toluene or benzene (Fig. 2). This probably indicated the presence of a new phase that had

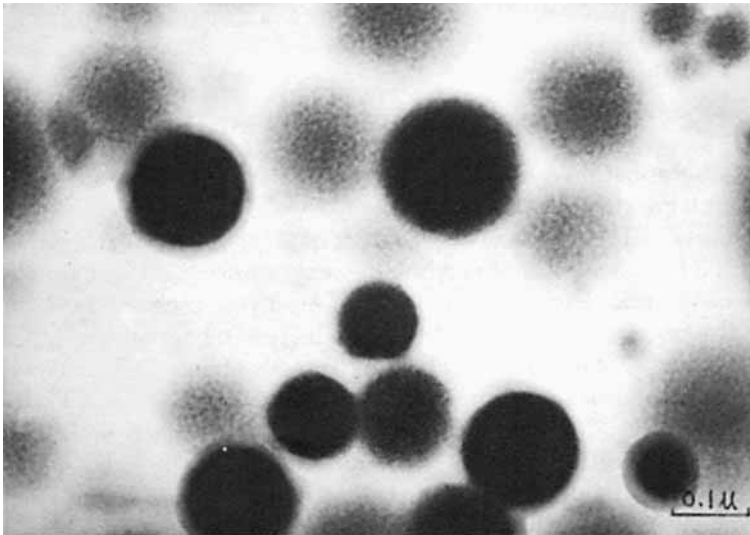


Fig. 3. Electron micrograph of MS-B block copolymer cast from THF solution.

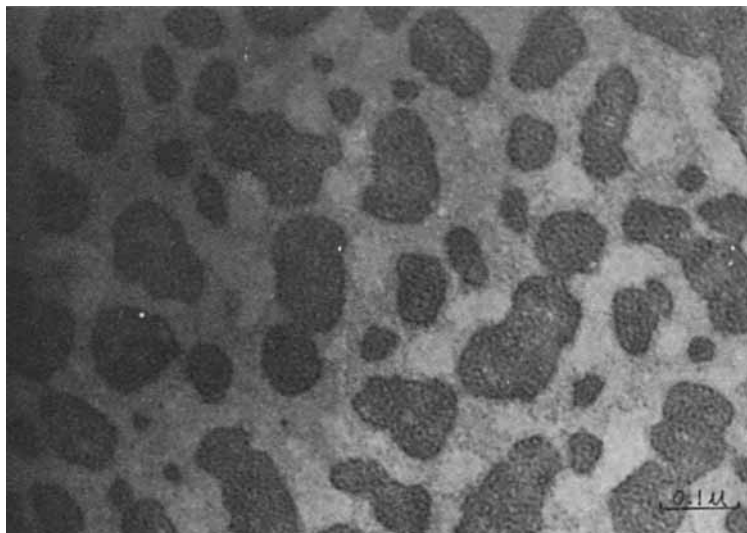


Fig. 4. Electron micrograph of MS-B block copolymer cast from toluene solution.

a chain mobility different from those in the homopolymer domains. This phase may be an intimate mixing of polybutadiene and poly- α -methylstyrene caused by incomplete phase separation.

The transmission electron micrographs of the block copolymers are shown in Figures 3–6. The dark regions are the stained polybutadiene (PB) blocks and the light regions are the poly- α -methylstyrene (PMS) blocks. The domains of polybutadiene cast from THF solution are spherical and dispersed (Fig. 3). This suggests that THF is a better solvent for PMS than PB, and there is a clear phase separation between these two polymer blocks. The phase separation in a film cast from toluene solution (Fig. 4) is not so clear as in the film cast from THF. The PB domains which are dispersed irregularly in PMS phase appear to contain

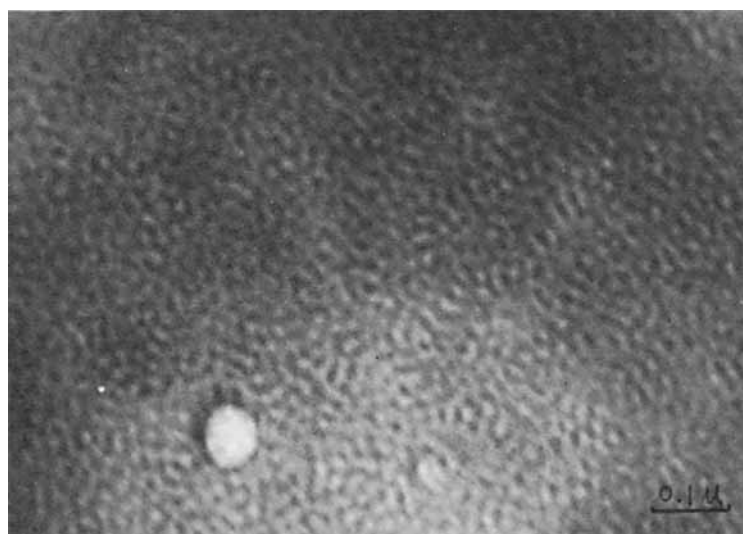


Fig. 5. Electron micrograph of MS-B block copolymer cast from benzene solution.



Fig. 6. Electron micrograph of MS-B block copolymer cast from CCl_4 solution.

small PMS domains. Toluene seems to be a better solvent for PMS than PB. However, the difference in solubility of these two polymer blocks in toluene is not so contrasty as in THF. The size and shape of the domains of each block in films cast from benzene are almost the same (Fig. 5), indicating a still closer solubility of each polymer block in benzene. Figure 6 shows a film cast from CCl_4 . The film is almost homogeneous, which suggests that CCl_4 may dissolve both polymers.

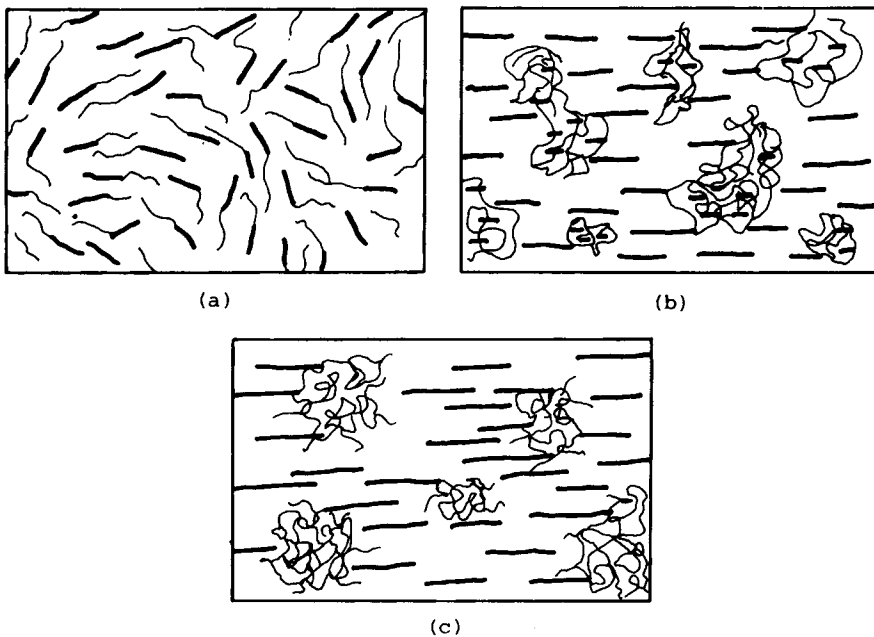


Fig. 7. Possible scheme of spatial arrangement of PMS and PB block segments. (a) Benzene CCl_4 cast film; (b) toluene cast film; and (c) THF, MEK cast film. (—) PMS block segment; (---) PB block segment.

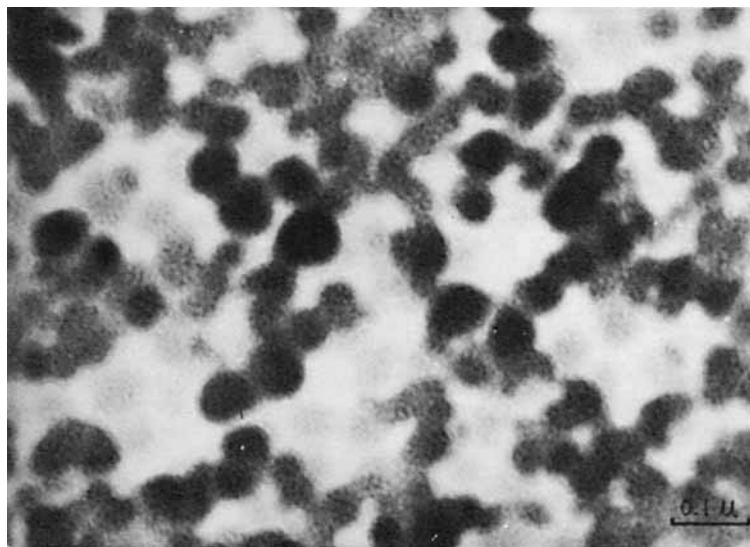


Fig. 8. Electron micrograph of MS-B block copolymer cast from MEK solution.

Films cast from CCl_4 solution were very brittle. The measurement of dynamic viscoelastic properties became difficult with such specimen. The rubbery domains became so small that they could not bear the tensile or impact stress.¹³

The extendability of individual block in a specific solvent is different. In a relatively good solvated state, the chains are extended. In a relatively bad solvated state, the chains would be coiled. A possible scheme of spatial arrangement of block copolymer can be depicted as in Figure 7.

The solubility parameters of PB, PMS, CCl_4 , benzene, toluene, and THF are 8.1, 8.9, 8.6, 9.2, 9.0, and 9.1, respectively. A qualitative description of solubility behavior of block copolymers from solubility parameters becomes difficult, to say nothing of quantitative descriptions. For example, the transmission electron micrograph of poly(α -methylstyrene-*b*-butadiene) cast from methyl ethyl ketone (MEK) (Fig. 8) showed less contrast in phase separation than that cast from THF, even though MEK has a higher solubility parameter (9.3). The solvent effect on morphology can only be explained as that different solvent will show different interaction with each block. Films cast from different solvent will therefore show different morphological behavior.¹⁴ The two-phase structure of block copolymers in the solid state obtained from solvent casting is influenced by the configurations of the polymer chains in solution, even in relatively dilute solution.¹⁵ The molecular conformation depends on the nature of interactions between solvent and polymer molecules. The difference of these interactions between blocks will affect its morphological behavior. Other factors such as the evaporation rate of solvent and the supporting material for casting will also change the morphology, especially when mixed solvents are used.¹

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