Polymer Bulletin 12, 71-77 (1984)

**Polymer Bulletin**

# Synthesis and Characterization of α-Methylstyrene-Butadiene-α-Methylstyrene Linear Block Copolymers

**Alberto Gandini, Giovanni Perego, Arnaldo Roggero, Roberto Vitali and Alessandro Zazzetta**

ASSORENI, Polymer Research Laboratories, 20097 San Donato Milanese, Italy

## SUMMARY

α-methylstyrene-butadiene-α-methylstyrene linear block copolymers with a 'pure' block structure were prepared by sec-butyllithium and coupling agent in a four-step process. Their morphology is built up of microdomains of poly-α-methylstyrene, including the unbonded segments, dispersed in a polybutadiene matrix. Cylindrical domains arranged in a hexagonal lattice or irregularly shaped domains in a disordered phase are observed, depending on the molecular weight of the poly-α-methylstyrene segment.

## INTRODUCTION

The presence of rigid glassy microdomains dispersed in a rubbery matrix confers to the ABA block copolymers high tensile properties; however, the tensile strength is markedly depressed at temperatures approaching the Tg of the hard A component. Hence, it is of great interest to obtain A blocks of high temperature capability. In this connection α-methylstyrene (MS) constitutes certainly a suitable monomer, since the polymer is known to have a Tg > 170°C (1,2). The preparation of MS and isoprene based ABA block copolymers is reported in literature (3,4); moreover, α-methylstyrene-butadiene-α-methylstyrene (MSBMS) 'tapered' block copolymers were synthesized (5).

We have carried out the synthesis of MSBMS block copolymers by using monofunctional catalysts in the absence of polar activators in order to achieve "pure" triblocks and minimize the vinyl content in the polydiene block.

It is the aim of this paper to report in detail the results concerning the synthesis, and the characterization of these materials. A qualitative description of the morphology is also reported.

## EXPERIMENTAL

Monomers, catalyst, solvent and coupling agent were used according to the procedure described in (6). Polymerization was carried out under a dry argon atmosphere in a pyrex reactor equipped with stainless steel head, stirrer, thermocouple, manometer and inlets for argon and reactants. A typical run was performed according to the following procedure. 50 g of MS were polymerized by sec-butyllithium ($10^{-3}$M) at room temperature for 1 h. Subsequently, butadiene (2 g) was added and the reaction was allowed to proceed for 15 mins. After dilution with 400 ml of cyclohexane, further addition of butadiene (35 g) lead to complete the synthesis of the diblock. Finally, the coupling reaction was accomplished at 95°C for 15 mins., using diphenyldichlorosilane ($0.5 \times 10^{-3}$M) and a little amount of tetrahydrofuran. Polymer was stabilized with a phenolic antioxidant, coagulated in methanol and dried under vacuum.

Molecular weights of ABA triblock, AB diblock and A homopolymer present in MSBMS, were determined using a Waters HP GPC equipped with $\mu$-Styragel columns. The instrument was calibrated with poly-MS and polybutadiene standards. The peaks in the chromatogram were integrated in order to obtain the weight fraction of ABA, AB and A species. The overall content of MS and the diene microstructure were determined by a Bruker CXP 300 NMR spectrometer at 300 MHz from $CCl_4$ solution.

Morphology of MSBMS was investigated on samples obtained by compression molding at 210°C. SAXS patterns were recorded by a Kratky camera; the scattering data were corrected for slit smearing using an infinite slit correction. Additional SAXS experiments were performed on samples showing preferred orientation by using a kiessig camera. Transmission electron microscopy (TEM) observations were performed on microtomed thin sections, stained with a 1% $OsO_4$ solution for 2 h.

## RESULTS AND DISCUSSION

The synthesis of MSBMS was performed by a four-step process. In the first step, the A block was obtained by a bulk polymerization at room temperature, using sec-butyllithium without polar activators. In spite of the low ceiling temperature of MS (ca. 60°C for neat monomer), molecular weights adequate to serve as end blocks in ABA copolymers were obtained. Polymerization temperature, which is known to affect the stability of the living ends (7-9), was carefully controlled so that a narrow molecular weight distribution was achieved. In the second step, a very fast crossover reaction from the MS carbanion to butadiene took place when a small amount of butadiene was added. The capping reaction prevented depolymerization of poly-MS in the subsequent step. After dilution with cyclohexane, the polymerization of butadiene was carried out to give the AB diblock (step 3). Though some unreacted MS was present in the reaction medium, little, if any, MS was incorporated in the polybutadiene block, due to the absence of polar activators. This was proved by separate tests in which butadiene was polymerized as in step 3 in the presence of MS. Finally, the coupling reaction by diphenyldichlorosilane was easily carried out (step 4).

A list of the synthesized MSBMS copolymers is reported in Table 1 together with the corresponding molecular parameters. They generally contained varying amounts of uncoupled AB diblock and unbonded poly-MS (A') (see Figure 1). The weight fraction of A' ($X_{A'}$) ranged from 0.05 to 0.16; the weight fraction of A bonded in both ABA and AB ($X_A$) ranged from 0.13

Table 1
Characterization of MSBMS triblock copolymers.

| Sample | $X_A$ a) | $X_{A'}$ b) | $X_{AB}$ c) | $X_{ABA}$ d) | $\bar{M}n$ e) x $10^{-3}$ | $M_w/M_n$ | $M_A$ f) x $10^{-3}$ |
|---|---|---|---|---|---|---|---|
| MSBMS- 1 | 0.234 | 0.070 | 0.250 | 0.680 | 55.6 | 1.20 | 7.00 |
| MSBMS- 2 | 0.203 | 0.072 | 0.018 | 0.910 | 66.3 | 1.20 | 7.25 |
| MSBMS- 3 | 0.286 | 0.084 | 0.165 | 0.751 | 50.0 | 1.25 | 7.80 |
| MSBMS- 4 | 0.240 | 0.070 | 0.170 | 0.760 | 63.1 | 1.22 | 8.15 |
| MSBMS- 5 | 0.235 | 0.095 | 0.180 | 0.725 | 67.6 | 1.15 | 8.78 |
| MSBMS- 6 | 0.130 | 0.050 | 0.290 | 0.660 | 130.0 | 1.15 | 8.87 |
| MSBMS- 7 | 0.190 | 0.090 | 0.180 | 0.730 | 84.3 | 1.25 | 8.80 |
| MSBMS- 8 | 0.200 | 0.090 | 0.160 | 0.750 | 94.1 | 1.20 | 10.34 |
| MSBMS- 9 | 0.250 | 0.160 | 0.230 | 0.610 | 72.5 | 1.18 | 10.80 |
| MSBMS-10 | 0.202 | 0.123 | 0.017 | 0.860 | 100.4 | 1.25 | 11.56 |
| MSBMS-11 | 0.220 | 0.120 | 0.320 | 0.560 | 103.5 | 1.15 | 12.95 |

a) Weight fraction of A segments in AB and ABA.
b) Weight fraction of A homopolymer.
c) Weight fraction of AB.
d) Weight fraction of ABA.
e) Number average molecular weight of ABA.
f) Number average molecular weight of A segment in AB and ABA.

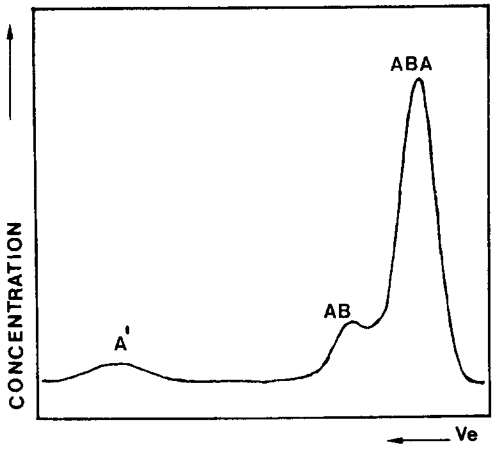

Fig.1. Gel permeation chromatogram of a typical MSBMS.

to 0.29. Molecular weight distribution of ABA triblocks was very narrow, Mw/Mn ranging from 1.15 to 1.25. The number-average molecular weight of A, $M_A$, was in the range 7-13 x $10^3$. As expected, for each sample, the molecular weight of A' was found to be very close to the corresponding value of A. The polybutadiene microstructure was found to contain ca. 88% 1,4 units.

The stress-strain curve of a typical MSBMS is shown in Figure 2. The tensile strength and the elongation behaviour of our materials are higher than those reported for the same triblocks (5). This reflects the 'pure' block structure of the former copolymers with respect to the 'tapered' block structure of the latters.

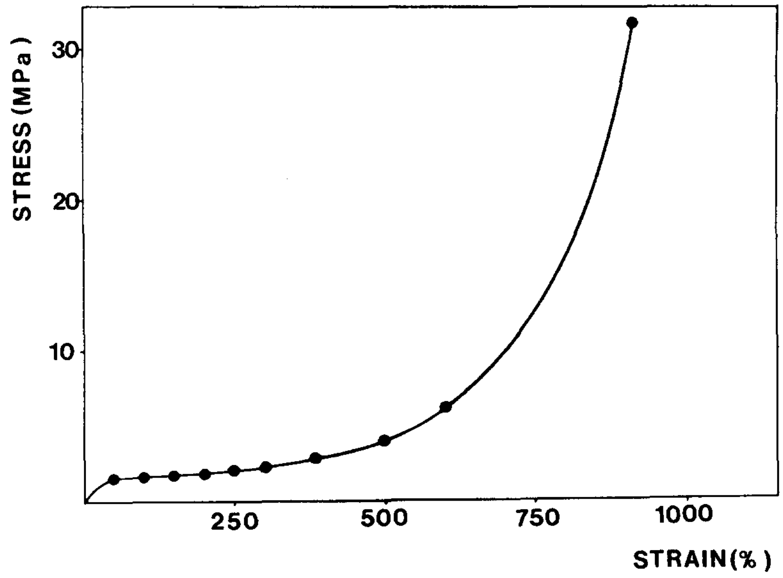

Fig.2. Stress-strain properties of MSBMS-5

Preliminary investigation of dynamic-mechanical properties of MSBMS shows that the substitution of MS for styrene (S) gives rise to an increased length of the rubbery plateau (about 45°C) in terms of storage modulus-temperature relationship. Similar results were obtained for MSBMS tetrachain block copolymers (10). However, it must be stressed that the improvement in terms of rubbery plateau is lower than that expected on the basis of the difference between the Tg of MS and that of S (about 80°C). Further investigations are in progress in order to explain this feature.

TEM micrographs of compression molded MSBMS show microdomains of poly-MS dispersed in a polybutadiene matrix. No macroscopic segregation of the homopolymer fraction in separate domains is evident. In the samples with $M_A$ greater than 8 x $10^3$, the microdomains, cylindrical in shape, are

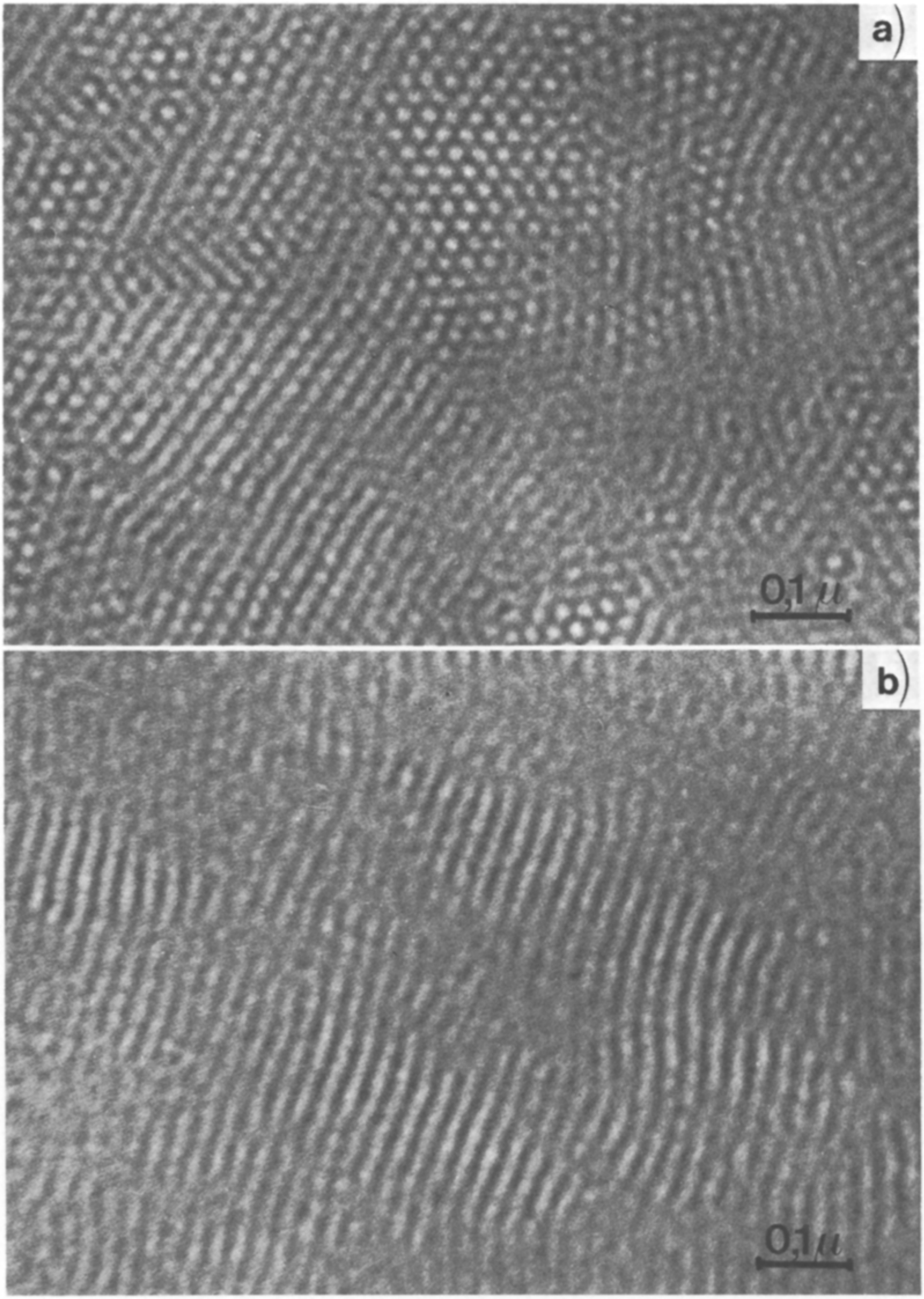

Fig.3. Transmission electron micrographs of MSBMS-5: view of the structure along the direction parallel (a) and perpendicular (b) to the axis of the cylinders.

arranged in the typical two-dimensional hexagonal lattice, as indicated by SAXS diffraction lines with reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$ (corresponding to the 100, 110, 200, 210 Bragg reflections respectively). The broadening of the Bragg reflections in the SAXS patterns varies among these samples, suggesting different extent of structural order. Because some of these samples display a considerable preferred orientation, TEM micrographs of appropriately microtomed sections allow to visualize the hexagonal structure along the directions parallel (Figure 3a) and perpendicular to the axis of the cylinders (Figure 3b) respectively.

Copolymers with $M_A$ lower than $8 \times 10^3$ display an essentially disordered phase. The structure is built up of irregularly shaped microdomains of poly-MS with spatial arrangement characterized by short-range order (Figure 4). This feature is confirmed by the fact that one discrete peak only is detectable in the corresponding SAXS patterns. A similar behaviour has been observed in styrene-isoprene diblock and triblock copolymers. In these materials, a transition from an ordered lamellar phase to a disordered phase occurs when lowering the molecular weight of the hard segment below $9 \times 10^3$ (11).

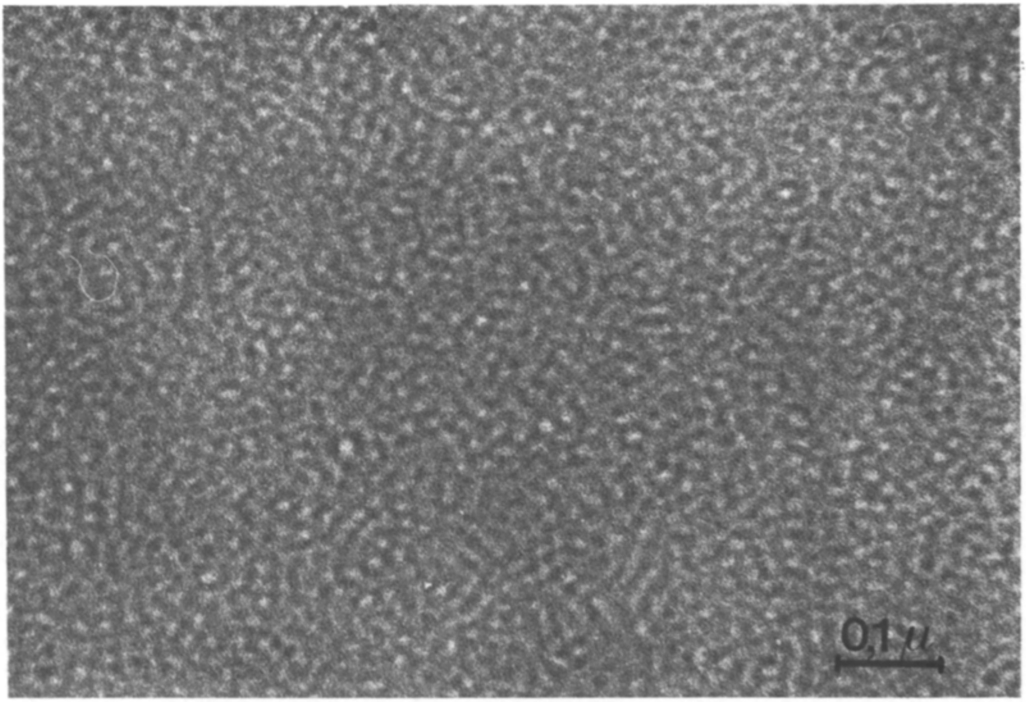

Fig.4. Transmission electron micrograph of MSBMS-1

For the samples displaying cylindrical morphology, the average value of the domain radius, R, was derived, starting from the dimensions of the hexagonal lattice obtained by SAXS measurements. The trend of R as a function of $M_A$ clearly indicates that the domains are formed by both A and

A' segments, in agreement with the results of TEM analysis. This feature will be reported in detail in a subsequent paper.

## REFERENCES

1. J.M.G. Cowie and P.M. Toporowski, Eur. Polym. J. 4, 621 (1968).
2. S.L. Malhotra, Ly Minh and L.P. Blanchard, J. Macromol. Sci. Chem. A12(1), 167 (1978).
3. L.J. Fetters and M. Morton, Macromolecules 2, 453 (1969).
4. G. Karoly, A.C.S. Polym. Prepr. 10(2), 837 (1969).
5. R.E. Cunningham, J. Appl. Polym. Sci. 22, 2907 (1978).
6. H.L. Hsieh, Rubber Chem. Tech. 49, 1305 (1976).
7. D.P. Wyman and I.H. Song, Makromol. Chem. 115, 64 (1968).
8. I. Mita and H. Okuyama, J. Polym. Sci. 9, 3437 (1971).
9. D. Ades, M. Fontanille and J. Leonard, Can. J. Chem. 60, 564 (1982).
10. F. Mistrali and L. Gargani, Kautschuk und Gummi, submitted for publication.
11. G. Hadziioannou and A. Skoulios, Macromolecules 15, 258 (1982).

*Accepted May 14, 1984*