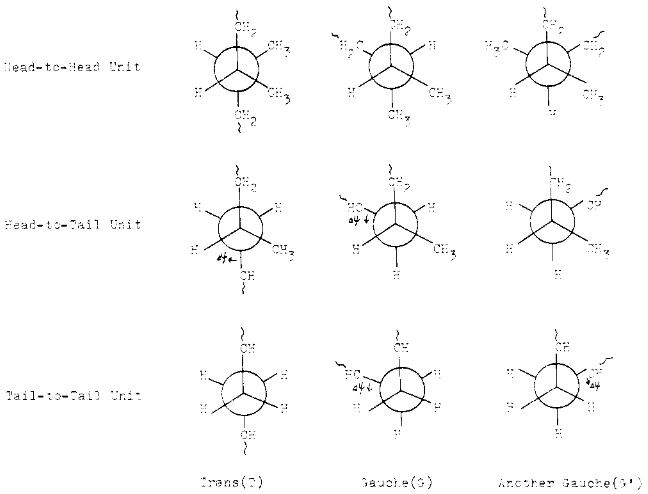

Figure 3. Newman projections of the three-state rotational isomeric states in head-to-head, head-to-tail, and tail-to-tail unit conformations. $\Delta\psi$ represents a distortion of the internal rotational angles from the exact staggering.

mobile (shorter NT_1) than the head-to-tail units. This motional behavior is easily understandable by comparing the conformational environment around the reversal points in the chain with that of head-to-tail unit sequences. According to the three-state rotational isomeric state (RIS) model[13] for polypropylene, each conformational state is assigned to one of the three states, i.e., trans (T), gauche (G), and another gauche (G'), as shown in Figure 3. The repulsive interaction restricting chain rotation occurs in the gauche arrangement between the carbon atom of interest and the carbon atoms separated by three bonds (γ substituents). The number of the carbon atoms participating in the steric repulsion decreases in the order of head-to-head, head-to-tail, and tail-to-tail units, though the repulsive interaction may release by a slight destortion of internal rotational angles ($\Delta\psi \simeq 20°$)[14,15] from the exact staggering as shown in Figure 3. As a result, the motions of CH, CH_2, and CH_3 groups increase in the order of head-to-head, head-to-tail, and tail-to-tail units. Thus, the ^{13}C NMR spin-lattice relaxation data support the previous chemical shift assignment for ^{13}C resonances arising from propylene inversion.

In the sequences containing regular head-to-tail propylene units, the T_1 values of both the methyl and methylene carbons are longer for the isotactic configurational sequences than for the syndiotactic configurational sequences. The dependence of the T_1 values of polypropylene on stereosequence has been pointed out by Randall.[5]

Experimental Section

The polypropylene sample was prepared with a $VOCl_3$-$Al_2Et_3Cl_3$ catalyst system in heptane at -28 °C. It had $\bar{M}_w = 12200$ and $\bar{M}_n = 6100$. It was determined from the ^{13}C NMR spectrum to have a 9.1% content of inverted propylene units.[7] ^{13}C NMR spin-lattice relaxation time measurements were made on a JEOL PS-100 Fourier transform system operating at 25.14 MHz, using a 180°-τ-90° pulse sequence. Eight τ values were used in the measurement, and the integrated intensities of each resonance peak were used in T_1 determinations. The standard errors in T_1 values determined by the method of least squares were less than ±10% for well-resolved ^{13}C resonances, while they were about ±20% for the ^{13}C resonances of $S_{\beta\alpha\alpha\gamma}$ and $P_{\alpha\beta}$ species. The temperature for observation was 123 °C, and the solution was made up in *o*-dichlorobenzene to 100% w/v (1 g of polymer per 1 mL of solvent)[16] without degassing.

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(13) P. J. Flory, "Statistical Mechanisms of Chain Molecules", Interscience, New York, 1969. Recently, a five-state RIS model for polypropylene conformation has been proposed by Suter and Flory,[14] who took into account not only the minima in the conformational energy map but also the character of the energy surface in the vicinity of the minima. However, the simple three-state RIS scheme seems to be sufficient for the qualitative explanation of the ^{13}C T_1 data of polypropylene.
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Communications to the Editor

Synthesis and Morphological Behavior of a New ABC Three-Block Polymer

A carefully prepared specimen of a well-designed block copolymer such as an SBS thermoplastic elastomer is known to exhibit a regular periodic microphase structure which depends primarily on the volume fraction of the constituent blocks[1] and also, to some extent, on the conditions of preparation. Recently, studies on several ABC three-block polymers have been reported.[2-5] However, their morphologies are still not clearly understood, partly because of the complexities of their domain structure and partly because of the difficulty in staining these specimen to distinguish three phases. For instance, in the case of a polystyrene (PS)-polyisoprene (PI)-poly(2-vinylpyridine)

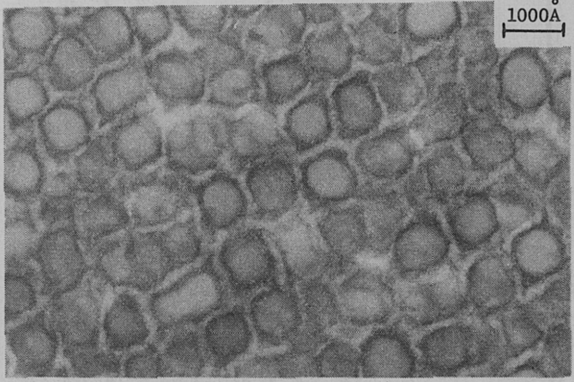
Table I
Characteristics of Polymer Samples

	block mol wt, $10^{-3}M_n$		
code	PS	PB	P4VP
SBP-1	20.2	22.0	32.3
SBP-2	23.3	45.2	22.3
SBP-3	13.0	76.7	22.8

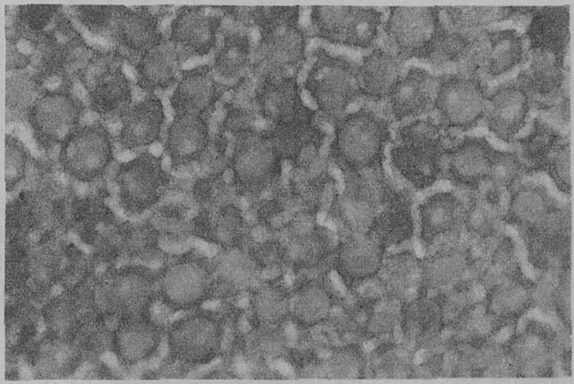
0024-9297/80/2213-0455$01.00/0

(P2VP) three-block polymer reported by Price et al.,[2] PI domains were stained with OsO_4 while P2VP domains were stained with $AgNO_3$. Therefore a comparison of the two photographs and some speculation is required to deduce the morphology. We have also synthesized a new ABC three-block polymer which is composed of PS, polybutadiene (PB), and poly(4-vinylpyridine) (P4VP) and have found that the domain morphology can be fairly easily distinguished by staining only with OsO_4. We report the results herein.

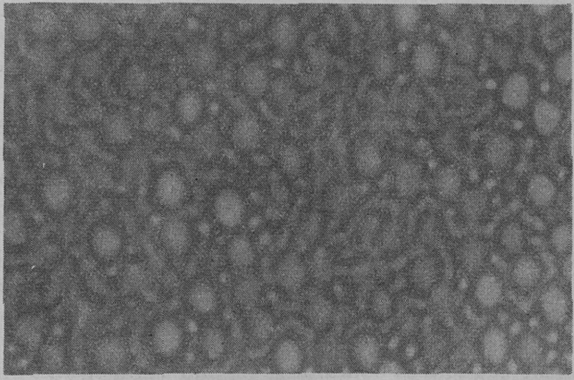
A few samples of PS–PB–P4VP three-block polymer (SBP) were synthesized by a living anionic polymerization method. The reaction was a three-stage sequential addition of styrene, butadiene, and 4-vinylpyridine (4VP) in benzene with *sec*-butyllithium as the primary initiator for styrene. Aliquots were taken at the end of the first and second stages to recover PS and SB diblock precursors, respectively. Butyllithium-initiated polymerization of 4VP in hydrocarbon media including benzene is heterogeneous with respect to the insolubility of the homopolymer in the solvent.[6] However, in our synthesis at the final addition of 4VP, the colorless transparent solution, which contained butadienyl anions, rapidly changed to a brick-red colored solution of 4-vinylpyridinyl anions. No precipitates were observed. This shows that the propagation of 4VP blocks proceeded in a homogeneous fashion. Hence, we expected stoichiometrically predicted molecular weights and fairly narrow molecular weight distributions for the final products. Among more than 30 single solvents examined, we found that only chloroform, *n*-butyraldehyde, and pyridine are solvents for the SBP three-block polymers. Molecular weights were determined by gel permeation chromatographic analysis of PS and SB precursors, combined with composition analysis by UV absorption and elemental analysis.[7] Luxton et al.[8] reported that the block copolymerization of 4VP to PS–polybutadienyllithium in benzene has revealed, via gel permeation chromatography (GPC) with tetrahydrofuran (THF) carrier, that some chain linking occurs to yield star-branched material. However, we failed to make a similar observation. Our SBP samples did not dissolve but gave opalescent solutions in THF, which then could not be used as the GPC solvent. Also in GPC runs with $CHCl_3$ as the carrier solvent, we observed that extensive adsorption of the polymer by the Styragel columns takes place and the elution of the polymer is severely retarded. Therefore, for the characterization we carried out the sedimentation velocity and osmotic pressure measurements in $CHCl_3$. The former revealed that the molecular weight distributions are fairly narrow and neither unreacted PS and SB precursors nor rapidly moving high molecular weight components exist in the SBP's.[7] The latter gave number average molecular weights which agreed with the stoichiometric values, as anticipated. Table I lists the characteristics of the SBP samples. The amount of star-branched components, if any, is too small to be detected by the present methods of characterization. This might be due to the fact that we carried out the polymerization at about 10 °C, which is lower than the range reported by Luxton et al.



(a) SBP-1/$CHCl_3$



(b) SBP-2/$CHCl_3$

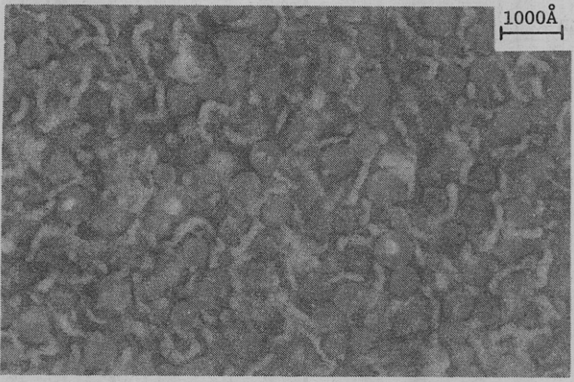


(c) SBP-3/$CHCl_3$

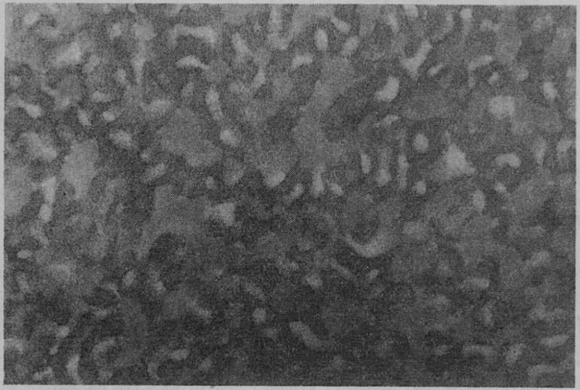
Figure 1.

We have examined the morphology of the SBP's cast from $CHCl_3$ and other solvents. Figure 1 shows electron micrographs of the SBP's, all cast from $CHCl_3$. In SBP-1/$CHCl_3$ we observe black, grey circular, and light continuous regions. Since OsO_4 selectively reacts with PB-olefinic bonds and less strongly with nitrogen atoms of pyridine rings, we assigned the black regions to PB domains, the grey regions to P4VP domains, and the light regions to PS domains. Since two ultrathin sections, which are cut perpendicular to each other as well as to the film surface, give essentially identical micrographs, we conclude that in SBP-1/$CHCl_3$ a large P4VP globe is held in a thick-walled PS cube and PB fills the gap. This is an unprecedented original structure we have never seen in any other ABC three-block polymers and AB diblock copolymers. Incidentally, the calculated volume ratio of the components of the "ball-in-a-box" or "cell" structure is comparable with ABC composition in the polymer.

In electron micrographs of SBP-2 and SBP-3/$CHCl_3$, we no longer observe the "ball-in-a-box" structure. In the former, globular P4VP domains and a semicontinuous PS phase are dispersed in a PB matrix. In the latter, globular P4VP and worm-like PS domains are dispersed in a PB continuous phase. Mechanical properties of these samples were found to be consistent with these microphase structures.[7] Figure 2a shows a micrograph of SBP-1 cast from a benzene/methanol (9:1) mixture. The previous regular cell structure is lost, but some similarities still exist.



(a) SBP-1/[benzene/methanol(9:1)]



(b) SBP-2/pyridine

Figure 2.

It should be noted that in the above results the morphologies do not comply with a rule given by Molau,[1] namely, that P4VP always forms large globular domains rather than cylindrical or lamellar domains in spite of the P4VP content being varied from 0.10–0.24. In contrast to this, Nagasawa reported that the morphology of an ABC three-block polymer of PS–(poly[(4-vinylbenzyl)dimethylamine])–PI exhibits a combination of Molau's morphologies.[5] We suspect that strong inter- and intrablock coherence of P4VP blocks predominates over other interactions[9,10] and that the P4VP domains tend to keep the interfacial area as small as possible.

To prevent the coagulation of the P4VP phase into globules, we also cast SBP-2 from pyridine, which is a good solvent for P4VP. Figure 2b shows its morphology, in which P4VP formed neither globular domains nor a clear continuous phase but curious amoeba-like domains. This result suggests a possibility of controlling the morphology of SBP's, to some extent, by choosing suitable casting conditions.

Note Added in Proof. Recently we were able to obtain a new morphology, a "three-lager lamellar" structure, in which the three phases alternate as . . .SBP·PBS·SBP. . . in the SBP-1 cast from *n*-butyraldehyde/$CHCl_3$ (9:1 v/v) mixture. The details will be reported soon.

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Formation of Soluble Polyethylene by Hydrogenation of Alkali-Metal-Doped Polyacetylene

The semiconducting organic polymer polyacetylene $[(CH)_x]$ or polyvinylene $[-(CH{=}CH)_x-]$ has recently been the subject of much experimental[1-12] and theoretical[13-20] study because of observations that its conductivity can be changed many orders of magnitude by doping it with various acceptors and donors.

Infrared,[21] Raman,[22] and absorption[22] spectral data are consistent with a linear conjugation of cis and/or trans C=C double bonds. The insolubility and infusibility of this conjugated polymer, however, make it difficult to obtain various information on molecular weight, its distribution, cross-linking, branching, etc. More detailed structural information is necessary for understanding chemical as well as physical properties of the as-prepared polyacetylene.

In this short communication, we present preliminary results on the formation of soluble polyethylene by hydrogenation of alkali-metal-doped polyacetylene.

Recently we have found that the alkali-metal-doped polyacetylene catalyzes the H_2–D_2 exchange reaction under very mild conditions and that hydrogen in the doped polyacetylene is also able to exchange with H_2 in the gas phase at higher temperature (>160 °C).[23] During the course of the hydrogen exchange study, we have observed that the doped film becomes partly transparent after several hours when the reaction is carried out at 200 °C and 85 Torr of H_2, suggesting that there is a possibility of hydrogenation of the conjugated double bonds in the doped polyacetylene.

The sodium doped films were prepared by treating the *trans*-polyacetylene films[24] (0.05–0.1-mm thickness) with a solution of sodium naphthalide in THF (~0.5 M) for about 1 h. The doped films were washed repeatedly with THF by trap-to-trap distillation from the sodium naphthalide solution until the washed solution became colorless. After being dried under vacuum, the films were allowed to react with hydrogen (550 Torr) at 200 °C for 7 h. Silvery films of the sodium-doped polyacetylene turned to transparent pale brown material, which became opaque to some extent on cooling to room temperature. The hydrogenated product was treated with methanol vapor and then immersed into a methanol–water mixture to dissolve the doped sodium in the films. Since hydrogen evolution was observed by this treatment, it was suggested that sodium in the hydrogenated film was present in the form of either the metal or sodium hydride. The entire operation was carried out under vacuum or inert gas.