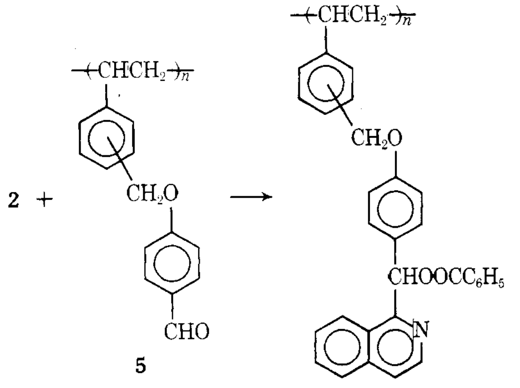
ion, resulting in aromatization.[7] This reaction proceeds with aliphatic aldehydes[7-9] as well as aromatic aldehydes.[7,10,11]

The present report describes the reaction of the anion of the isoquinoline Reissert compound **2** and a polymeric aldehyde as part of our synthetic efforts in this field.

The lack of commercially available polymeric aldehydes necessitates the synthesis of such polymers. For this purpose we utilized the reaction of poly(vinylbenzyl chloride) and phenols which we previously reported.[4] Polymer **1**[4,5] was reacted with *p*-hydroxybenzaldehyde in basic solution; poly[(4′-formylbenzyloxy)styrene] (**5**) resulted in 100% conversion.[4] Its infrared spectrum contains an intense carbonyl band at 1690 cm^{-1}. Its molecular weight distribution (MWD) (2.16) is very similiar to starting polymer **1** (2.11) as determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF). Both GPC and viscometry ($[\eta]$ = 0.21 and 0.20 dl/g for **1** and **5**, respectively, in THF at 25°) indicate the absence of cross-linking and degradation.

The reaction of the Reissert anion **2** and polymeric aldehyde **5** was carried out at 20° under nitrogen in dimethylformamide (DMF).[5] Poly[4-(vinylbenzyloxy)phenyl-1-isoquinolylcarbinyl benzoate] (**6**) was formed in approximately 100% conversion (after purification by several precipitations from THF solution by dropwise addition to hexane and 80% ethanol: *Anal.* Calcd for $C_{32}H_{25}NO_3$: C, 81.51; H, 5.34; N, 2.97. Found: C, 80.85; H, 5.29, N, 2.91) and approximately 100% yield. Its infrared spectrum contains an intense band at 1715 cm^{-1} attributable to the ester carbonyl and shows no evidence of the aldehyde carbonyl band of **5** at 1690 cm^{-1}. The carbonyl band of model monomeric compound **4**, R = C_6H_5,[11] is at 1722 cm^{-1}. The MWD of **6** (2.38 in THF by GPC) is similiar to that of **5**. Thus, GPC as well as viscometry ($[\eta]$ = 0.19 dl/g in THF at 25°) indicate that side reactions leading to cross-linking or degradation are insignificant. Polymer **6** is soluble in THF, benzene, DMF, and chloroform, but insoluble in methanol, ethanol, water, and hexane.



5

6

The ultraviolet (uv) spectrum of polymeric ester **6** in THF contains peaks at 321, 309, and 273 nm. These peaks are characteristic of the 1-benzylisoquinoline moiety;[5,12] thus, their presence in the spectrum of **6** confirms the presence of this moiety.

The excellent conversion obtained in this grafting reaction is noteworthy in comparison to reactions of monomeric aldehydes. Only one reaction of the Reissert anion **2** and an aldehyde, namely benzaldehyde to yield **4**, R = C_6H_5, under these conditions (room temperature, DMF) has been reported and the crude yield was 65%.[13] *p*-Benzyloxybenzaldehyde and **2** lead to a 68% crude yield of the expected ester at −30° in ether–dioxane,[11] while benzaldehyde leads to an 88% yield.[7] In benzene at 80° the latter reaction proceeds in 79% yield.[11] The significance of the high conversion in the present polymeric system is even greater considering the generally sluggish nature of polymers in chemical reactions.[14] While the higher yield in the polymer system may in part be due to ease of isolation, it is believed that the local environment of the reactive center provided by polymer itself enhances the rate of the desired reaction relative to side reactions as previously suggested.[5]

Thus, as in the previous example,[5] the reaction of the Reissert anion **2** with a polymeric substrate proceeds in higher yield than with corresponding monomeric substrates. Morever, the virtually complete conversion is unusual for a reaction on a polymer. Although in this case the reaction moiety is at an appreciable distance from the backbone, another sytrene polymer bearing a formyl group on the phenyl ring also reacts to nearly complete conversion. This process, the hydrolysis of polymeric ester **6**, and detailed spectroscopic data will be described in the full paper as we continue to explore these facile chemical modifications of polymers.

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Domain Morphology of Star Block Copolymers of Polystyrene and Polyisoprene

The morphology of linear polystyrene–polydiene block copolymers has received intensive scrutiny over the past several years *via* the application of electron microscopy[1-13] and small-angle X-ray scattering.[14-16] Electron micrographs of these block copolymers show that there is a pronounced tendency for polystyrene (when it is the minority component) to form ordered domains in the polydiene matrix. Small-angle X-ray scattering has also clearly shown the lattice-like arrangement of the polystyrene domains.

The most commonly examined materials have been linear di- and triblock copolymers where the polystyrene content has ranged between 10 and 40 wt %. Contrasting interpretations have been made as to the structure of the phase-

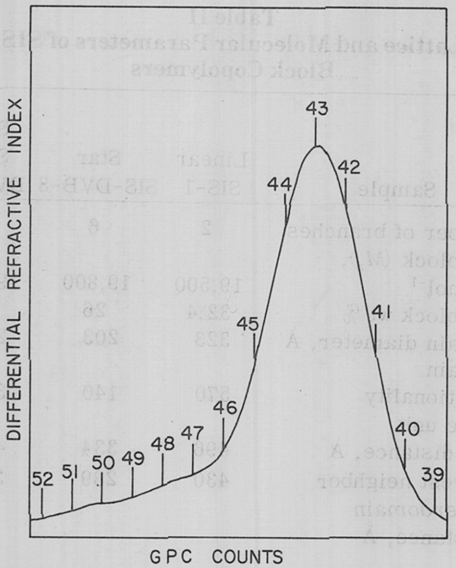


Figure 1. Gel permeation chromatogram of SIS-DVB-4 star block copolymer.

separated polystyrene domains in these block copolymers; *i.e.*, both spherical and cylindrical shaped domains have been reported to exist in these materials. This communication is a preliminary report pertaining to the morphology of "star" block copolymers where the number of arms per star block copolymer ranges from 6 to 9. It will be shown that the morphology of these annealed star block copolymers consists of a body centered cubic arrangement of spherical polystyrene domains.[13]

Experimental Section

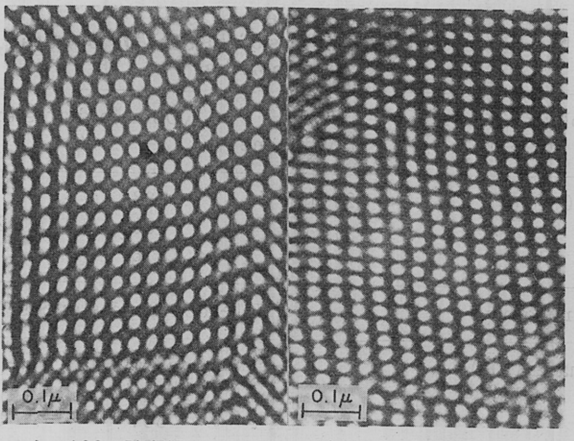
The star block copolymers were synthesized *via* a two-stage sequential anionic polymerization[17] in benzene at 25°. The initiator was sublimed[18] *sec*-butyllithium while the linking agent was *m*-divinylbenzene. The linking reaction was accomplished by the addition of *m*-divinylbenzene to the diblock copolymer solution. This procedure is similar to that used for the preparation of star polystyrene homopolymers.[19–21]

The electron micrographs were obtained on microtomed samples (~400 Å thick) with the aid of the JEOL 120U transmission electron microscope. Microtoming was done, with the aid of a diamond knife, at liquid nitrogen temperature. Following microtoming, the samples were exposed to OsO_4 vapor[22] at room temperature. In all cases, the microtomed samples were obtained from solvent cast films which were annealed for at least 1 week at 95° under vacuum. This was done in order to ensure solvent removal and that the final morphology was as close as possible to the equilibrium state. A 90/10 (v/v) mixture of benzene and *n*-heptane was used to cast the films. Films were cast on cellophane.

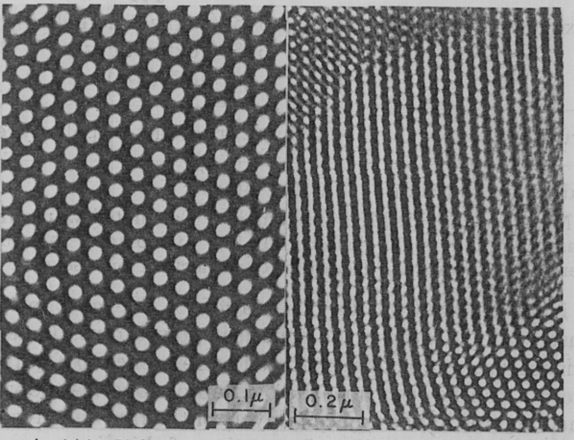
Block copolymer molecular weight characterization was done on Hewlett-Packard 502 and 503 osmometers equipped with S and S-08 membranes. A Waters Ana-Prep instrument was used with a seven Styragel column set with tetrahydrofuran, at 40°, as the carrier solvent. A flow rate of 1 ml min^{-1} was used. At this flow rate the seven-column set had a plate count of 750 plates per foot.

Results and Discussion

This communication concerns itself, in the main, with a presentation of the morphological features of a nine armed star block copolymer, SIS-DVB-4, with a polystyrene content of 27 wt %. Figure 1 is the gel permeation chromatogram of this star block copolymer. It is apparent that this sample does not possess an appreciable amount of low molecular weight material, *i.e.*, unlinked, linear triblock or star copolymer with a limited number of arms, *e.g.*, three or four. However, it must be remembered that gel permeation chromatography will become progressively less sensitive in distinguishing the number of arms in star shaped block copolymers as the degree of branching increases while the arm length, and composition, is kept constant. Hence, the number of arms per star macromolecule must be determined *via* some other technique. As has been shown,[23] number-average molecular weight measurements provide the most reliable method for determining the number of arms in star shaped polymers. Hence, the value of 9 represents the average number of arms in the SIS-DVB-4 block copolymer and was derived from the ratio of the number-average molecular weight of the star copolymer (62.6 × 10^4 g/mol) to that of the unlinked diblock copolymer (7.2 × 10^4 g/mol).



a) 100 PLANE b) 110 PLANE



c) 111 PLANE d) STRIATED STRUCTURE

Figure 2. Electron micrographs of SIS-DVB-4 star block copolymer.

Figure 2 presents representative electron micrographs of the SIS-DVB-4 triblock copolymer. In Figures 2a, 2b, and 2c three separate arrangements of polystyrene domains can be seen, *i.e.*, square (100 plane), rectangular (110 plane), and hexagonal (111 plane). The coexistence of these three polystyrene domain arrangements can be rationalized and explained by reference to the body centered cubic domain arrangement.[13] By the rotation of this lattice around a prescribed crystallographic axis we can go from one morphology to the other. Between these three morphologies are numerous striated transition structures, all of which can superficially be interpreted as being evidence for the presence of cylindrical polystyrene domains.

The presence of cylindrical domains in solvent cast films of linear as well as tri- and tetraarmed star block copolymers of 20–30 wt % polystyrene has been suggested by some[8,10–12] whereas others[2,3,5,6,13–16] have presented evidence that spheres are the dominant shape for these polystyrene domains. In our opinion, the belief that cylindrical domains exist in these block copolymers, for the case of well annealed solvent cast films, is in error and is apparent-

Table I
Morphological Parameters of the SIS-DVB-4 Star Block Copolymer

Diblock mol wt, g/mol	Wt % polystyrene	Domain diameter, Å	
72.0×10^3	27(nmr)[a]	283	
		280	280
		278	
Morphology		Interdomain distances,[24] Å	
Square (100)		310	
		328	
		307	323
		333	
		341	
Hexagonal (111)		376[b] (nearest neighbor)	375[c]
		646[b] (next nearest neighbor)	648[c]
Structure	Volume fractions of polystyrene		
Body centered cubic	0.245 (nmr)[a]		0.24[d]

[a] Measured *via* 300 MHz instrument. [b] Calculated values from measured interdomain distances in the 100 plane. [c] Measured interdomain distances. [d] Determined *via* electron microscopy.

ly, in part, based on the observation of the morphologies caused by the overlap of spherical polystyrene domains. This feature can be demonstrated by reference to Figure 2d where it can be seen how the overlap of spherical polystyrene domains in two adjacent layers of the film can give rise to the striated structures. Inspection of this figure reveals the presence of the individual polystyrene spheres in this "overlap" arrangement. Thus, it is clear that striated structures can result from various three-dimensional distributions of spherical polystyrene domains located on different crystallographic planes.

This latter view of the domain arrangement would be impossible if cylinders were the dominant morphology. The same can be said for the fact that the square and rectangular domain arrangements coexist with the hexagonal array, *i.e., their presence precludes the existence of polystyrene* cylinders. Hence, we can only conclude that the predominating polystyrene domain structure for this star block copolymer is that of spheres and that these spheres exist in a body centered cubic arrangement.

This conclusion is fortified by the results presented in Table I where the lattice and molecular parameters of the SIS-DVB-4 block copolymer are presented.

Particularly gratifying is the good agreement between the observed and calculated interdomain distances for the hexagonal array of domains. It should also be noted that the body centered cubic model yields good agreement between the measured and calculated values of the volume fractions of polystyrene. Similar results have also been obtained for linear and hexaarmed SIS block copolymers.[25] Parenthetically it can be noted that if cylinders are taken as the domain configuration for SIS-DVB-4 the calculated (from the 111 plane) volume fraction of polystyrene is 0.51.

The validity of the body centered cubic arrangement gains support from an analysis of a structural model built according to this latice arrangement of polystyrene domains. Inspection of this model (ref 13) reveals that the body centered array accounts for the observed morphology of the star SIS-DVB-4 block copolymer. This lattice arrangement of spherical polystyrene domains has also been found to apply to both linear and hexaarmed SIS block copolymers.[25] A summary of these findings is given in Table II. These results are based on over 250 electron micrographs taken of these block copolymers and are the result of measurements involving only those domains that were perfectly circular. A complete presentation of the details pertaining to the morphology of these star block copolymers and aspects of their synthesis and stress-strain behavior will be presented at a later time.

Table II
Lattice and Molecular Parameters of SIS Block Copolymers

Sample	Linear SIS-1	Star SIS-DVB-8	Star SIS-DVB-4
Number of branches	2	6	9
End block $\langle M_n \rangle$, g mol^{-1}	19,500	19,800	19,500
End block wt %	32.4	26	27
Domain diameter, Å	323	203	280
Domain Functionality	570	140	368
Cubic unit Cell distance, Å	496	334	457
Nearest neighbor Interdomain distance, Å	430	289	396

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