

Block Copolymers of *n*-Propyl *p*-Styrene Sulfonate with Isoprene and Styrene: Synthesis, Characterization, and Phase Separation Behavior

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Synopsis

A series of ABA block copolymers based on *n*-propyl *p*-styrene sulfonate (A block) and isoprene or styrene (B block) were synthesized and characterized. The synthesis was based on methods developed previously for the anionic polymerization of *n*-propyl *p*-styrene sulfonate [S. J. Whicher and J. L. Brash, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1995 (1981)], and consisted of forming a polyisopryl dianion by initiation with sodium naphthalene in THF at 0°C. *n*-Propyl *p*-styrene sulfonate was then added and propagated at -94°C. As was the case for *n*-propyl *p*-styrene sulfonate alone, it was found that only limited chain growth of this monomer initiated by living polyisoprene was possible, resulting in maximum A block molecular weights of about 10,000. The phase separation behavior of copolymers having a range of composition, as well as that of a blend of polyisoprene and poly(*n*-propyl *p*-styrene sulfonate) was investigated by examining thin films in the electron microscope. In the copolymers, phase separation was observed with transmission EM when THF was used as the solvent for film casting. Domain morphology was as expected for the various copolymer compositions. When films were cast from chloroform, phase separation was minimal, although it could be improved by annealing. Annealing produced relatively diffuse intermixed domains which occasionally formed unusual triangular patterns. Phase separation of the blend of homopolymers gave domains that were large enough to be mapped with SEM using both secondary electron and EDXA detectors.

INTRODUCTION

Block copolymers of *p*-styrene sulfonic acid and a hydrophobic component have several potential applications such as ion exchange resins^{1,2} and blood compatible materials.³⁻⁵ Block copolymers of an ester of *p*-styrene sulfonic acid would contain polar domains and therefore could also provide interesting materials for blood compatibility studies. The characteristic properties of these materials, and of block copolymers in general, derive from their well-documented phase-separated domain structure.⁶ Segmented polyurethanes, which in some cases also show microphase separation but with poorly defined domain size and shape distributions due to the polydispersity of the "blocks," have been shown to be useful blood contact materials.^{4,7} It is possible that two-phased polymers with more uniform domain size distributions would provide a further improvement over segmented polyurethanes. The present study reports the synthesis and characterization of a series of two-phased polymer materials from ABA block copolymers of *n*-propyl *p*-styrene sulfonate (A block) and isoprene or styrene (B block) by anionic polymerization using sodium naphthalene as initiator. As far as

can be determined, the present paper is the first to report on such block copolymers.

The anionic polymerization of *n*-propyl *p*-styrene sulfonate (npss) and several other esters of *p*-styrene sulfonic acid was previously reported from this laboratory.⁸ The results indicated that only limited MW ($\bar{M}_n = 6000$ –8000) but monodisperse ($\bar{M}_w/\bar{M}_n = 1.06$) polymers could be obtained. The optimum polymerization temperature was -94°C with THF as the solvent. Under these conditions the anions of poly(npss) were stable for up to 400 h but with virtually no further chain growth after 12 h in the presence of excess monomer. It was also found that if the monomer synthesis and purification procedures⁸ were not rigorously followed, polymers with irreproducible molecular weights ranging up to 35,000 and polydispersities between 2 and 3 were usually obtained.

Isoprene was chosen as the B block monomer for most of the present series of block copolymers for the following reasons: (a) phase separation in styrene–isoprene–styrene (SIS) block copolymers is known to occur and has been extensively studied,⁹ and similar behavior would be expected for the corresponding npss copolymers; (b) polyisoprene can be easily stained for contrast in transmission electron microscopy (TEM) studies of the solid polymers using well-documented methods¹⁰; (c) polyisoprene is elastomeric at normal temperatures and therefore would allow the possibility of producing thermoplastic elastomers.

EXPERIMENTAL

Materials

Synthesis and purification of *n*-propyl *p*-styrene sulfonate were carried out according to procedures in the literature^{1,2,11–16} with the important modifications described previously^{8,17} necessitated by the requirement of high purity for anionic polymerization. Sodium naphthalene initiator, THF, and styrene monomer were prepared and purified under high vacuum in previously flamed vessels according to procedures developed by Szwarc,^{9,18} and described in detail elsewhere.¹⁷ Isoprene monomer was distilled from calcium hydride, stirred over three successive sodium mirrors, and stored over calcium hydride. A final distillation was performed just prior to use.

Polymerization

Sodium naphthalene initiates polymerization by electron transfer to the monomer resulting in a radical anion. Dimerization follows before any radical polymerization can occur and propagation of the dianion is bidirectional. This allows for synthesis of ABA block copolymers by just two sequential monomer additions.¹¹ Accordingly, isoprene (or styrene) was added dropwise to a well-stirred solution of initiator, and, when it was fully reacted, the npss was added dropwise to the solution of living polyisoprene (or polystyrene) with continued vigorous stirring. Polymerization of npss was initiated by electron transfer from living polyisoprene (or polystyrene) dianion. Dropwise addition, together with vigorous stirring, promotes uni-

form concentration and temperature, and allows initiation to occur prior to substantial propagation.

The optimum conditions for isoprene polymerization were investigated prior to the synthesis of block copolymers. Initiation was extremely slow at -78 and -94°C , typically taking 5 min for the color change from dark green (initiator) to yellow-orange (isoprene anions). Since slow initiation relative to propagation is known to cause a significant broadening of the molecular weight distribution, polymerizations of the isoprene blocks were carried out at 0°C . The temperature was then decreased to -94°C for polymerization of the *npss* blocks. Figure 1 shows the proton NMR spectrum for polyisoprene synthesized at 0°C . By comparison with spectra in the literature,¹⁹ the individual resonances were assigned as shown and the microstructural composition was estimated as resulting from 40% 1, 4, 50% 1, 2, and 10% 3, 4 additions.

Upon addition of a solution of *npss* in THF to the solution of living polyisoprene, the color changed instantly to red. In cases where less rigorously purified monomer was used, the color of the polymerization mixture changed from red through all or part of the sequence, green to blue to red, as was described for the homopolymerization of *npss*.⁸ The color changes could not be related to any reaction variable and always returned to red before fading during termination. Ethanol was used to kill the living polymers, a process which often took up to 3 h as was the case for the homopolymerizations.^{8,17}

Polymer Characterization

The molecular weights and composition of the polymers were determined by several techniques. In addition the block copolymers and a blend of homopolymers were cast into films and characterized morphologically by electron microscopy.

Following termination the polymers were precipitated in ethanol. They

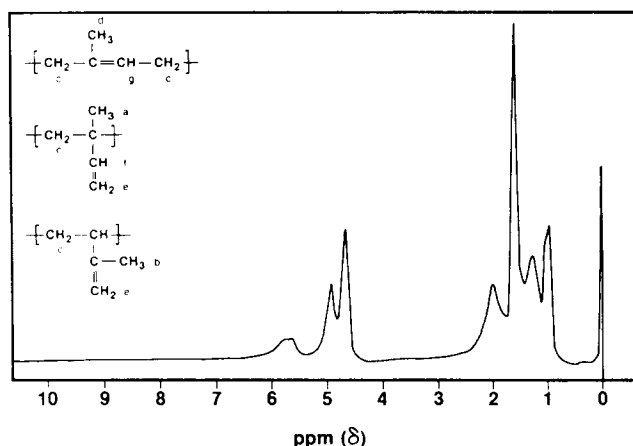


Fig. 1. 90 MHz proton NMR spectrum of polyisoprene (MW = 2×10^5) polymerized anionically using sodium naphthalene in THF. Solvent: chloroform-d. Peak assignments: (a) 0.95; (b) 1.24; (c) 1.57; (d) 1.95; (e) 4.67; (f) 4.92; (g) 5.70.

were then filtered, dried, and extracted with ethanol to remove residual monomer (conversion of npss was incomplete) and weighed.

Molecular weights and compositions (assuming complete conversion of the central blocks) were calculated using either:

$$\bar{M}_n = 2w/I \quad (1)$$

or

$$\bar{M}_n = w/I \quad (2)$$

where w = weight of polymer formed and I = moles of initiator. In the case of ABA triblock copolymers eq. (1) was used for both the total molecular weight and the molecular weight of the B block. For the latter, conversion was assumed to be 100% so w could be taken as the weight of monomer. For the A block molecular weight, eq. (2) was used with w = wt copolymer - wt monomer B. Compositions were calculated from the block molecular weights or estimated independently from proton NMR spectroscopy and elemental analysis. Size exclusion chromatography was used to obtain an independent estimate of the overall styrene equivalent molecular weights, to insure that the copolymers were indeed "single" species as opposed to mixtures of homopolymers and/or diblock copolymers, and to verify complete removal of unreacted monomer. Details of the method of SEC analysis are given elsewhere.^{8,17}

The phase morphology of solution-cast thin films of the ABA block copolymers and a blend of poly(npss) and polyisoprene was examined using various modes of electron microscopy. Samples were prepared for scanning electron microscopy (SEM) from 1 g dL⁻¹ solutions in THF, chloroform, or methyl ethyl ketone cast on glass microscope slides. For transmission electron microscopy, (TEM) thin films were cast from 1.0, 0.5, and 0.2 g dL⁻¹ solutions in THF, chloroform, or DMSO on highly polished KBr disks.²⁰ These films were then scored to fit EM grids, floated off the disks, washed with distilled water, and picked up with grids. In some cases, casting was followed by annealing at 103°C for 12 h *in vacuo* and/or staining by suspending in the vapor of a 1% solution of osmium tetroxide.

RESULTS

The ABA copolymers prepared for this work are listed in Table I. Polymers 1-5 were synthesized in order to establish optimum conditions for polymerization of npss initiated by living polyisoprene. It was found that the upper limit for polyisoprene concentration which allows sufficiently vigorous stirring during npss polymerization at -94°C is approximately 0.1 g dL⁻¹ (experiment 5). Available stirring speeds were too slow in experiments 1-4 with polyisoprene concentrations of 6.24, 2.08, 0.5, and 0.25 g dL⁻¹, respectively.

Despite vigorous stirring in experiment 5, only a very limited molecular weight was achieved for the npss block. This behavior is similar to the

TABLE I
Synthesis of ABA Block Copolymers,^a A = *n*-Propyl *p*-Styrene Sulfonate, B = Isoprene^b

Copolymer	Moles of initiator × 10 ⁴	Monomer B (g)	\bar{M}_n of ^c B block × 10 ⁻³	Monomer A (g)	Reaction time (h)	Reaction temp of A block (°C)	Yield of copolymer (g)	Yield of A block (g)	\bar{M}_n of ^d A block × 10 ⁻³
1 ^e	1.56	15.6	200	4.6	6	0	15.6	—	—
2 ^e	1.56	15.6	200	4.6	4	-78	15.6	—	—
3 ^e	1.56	3.78	48	5	4	-78	3.8	—	—
4 ^e	0.78	1.89	48	5	97	-78	1.9	—	—
5 ^e	0.78	0.78	20	4.6	12	-94	0.95	0.17	2.2
6	3.12	0.78	5	5	12	-94	3.0	2.2	7.1
7	3.12	0.39	2.5	5	12	-94	3.2	2.8	9.0
8	3.12	1.56	10	5	12	-94	4.0	2.4	7.8
9 ^f	1.56	—	—	8	3-4	-78	2.8	—	—
10 ^b	3.12	7.8	50	5	12	-94	10.5	2.7	8.7

^a Polymerizations of B block carried out at 0°C for 2.5 h, solvent = THF, initiator = sodium naphthalene.

^b In copolymer 10, B = styrene.

^c Estimated by eq. (1), assuming 100% conversion of monomer B.

^d Two blocks of same \bar{M}_n estimated by eq. (2).

^e Reaction media remained red throughout polymerization of A.

^f Isoprene polymerization time = 10 min, temperature = -78°C, very low conversion.

molecular weight limitation observed and studied extensively for the anionic homopolymerization of npss under identical conditions.⁸ Since it was the purpose of this work to investigate the effects of variation in block molecular weight on morphology, it was essential to vary block size. We had observed previously,⁸ for the homopolymerization of npss that when monomer purification was less rigorous, the attainable molecular weight, though still limited, was greater; therefore, subsequent copolymers were synthesized using this type of monomer. In addition, the molecular weight of the polyisoprene was decreased so that copolymers having an appropriate range of compositions could be obtained subject to the constraint that the attainable MW of the npss block is limited. These modifications yielded copolymers with reasonably high npss block molecular weights and an acceptable range of overall compositions. Experiment 10 showed that similar npss block molecular weights could be achieved for a polystyrene central block of MW 50,000 as for polyisoprene central blocks of MW 2500–10,000.

Table II describes the composition of the various polymers obtained by three different methods: gravimetric analysis using the information in Table I, sulfur elemental analysis, and proton NMR spectroscopy. The proton NMR spectra for polymers 8 and 10 are shown in Figures 3 and 4, respectively. Figures 1 and 2 show proton NMR spectra of polyisoprene and poly(npss) for comparison. The broad peaks of these spectra signify that the materials are indeed polymeric. The spectra for the copolymers appear as a combination of the spectra for the two homopolymers. The results of the three methods of analysis are in reasonable agreement with the exception that gravimetric analysis and elemental analysis yield different estimates for the wt % poly(npss) in copolymers 4 and 5. It is to be noted that for copolymers having npss content less than about 10%, neither NMR nor gravimetry was sensitive enough for reliable quantitative analysis.

Table III gives the results of SEC analysis of copolymers 4–10. The chromatograms were analyzed by methods developed by Garcia-Rubio.²¹ All chromatograms were unimodal (e.g., Fig. 5) and the number average mo-

TABLE II
Composition Analyses of ABA Block Copolymers,^a
A = *n*-Propyl *p*-Styrene Sulfonate, B = Isoprene^b

Copolymer ^a	% S by elemental analysis	Wt % A		Mol % A	
		Gravimetric analysis	From sulfur content	From sulfur content	Proton NMR
1	0.32	0	2.3	0.69	—
2	0.51	0	3.4	1.1	—
3	1.06	0	7.5	2.4	~2.5
4	2.01	0	14	4.7	—
5	0.99	18	7.8	2.2	~1.7
6	9.66	74	68	39	34
7	11.71	88	83	59	62
8	8.41	61	59	31	29
9	12.96	—	92	76	77
10	3.50	26	25	13	11

^a See Table I, column 1.

^b In copolymer 10, B = styrene.

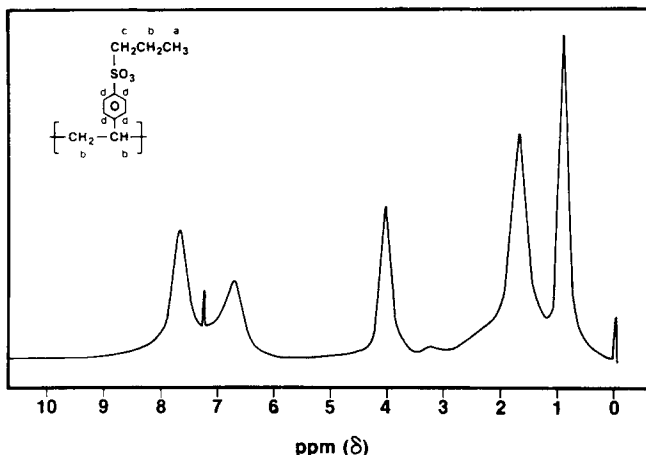


Fig. 2. 90 MHz proton NMR spectrum of poly(*n*-propyl *p*-styrene sulfonate). Solvent: chloroform-*d*. Peak assignments: (a) 0.90; (b) 1.66; (c) 4.18; (d) 7.15.

lecular weights agree in most cases, within experimental error, with results from gravimetric analysis. The discrepancy in the two molecular weights for copolymer 4 leads to different conclusions regarding chain growth of npss from a relatively large isoprene block (MW 48,000). The gravimetric data suggest that the isoprene block is merely "end-capped" while the SEC data suggest moderate chain growth to a block MW of about 6000. It is believed that the gravimetric data are more reliable than the SEC data since the calibration curve for the SEC system was nonlinear in the high MW region.

To determine solid phase morphology the copolymers and a blend of poly(npss) ($\bar{M}_n = 7400$) and polyisoprene ($\bar{M}_n = 200,000$) were cast into films and examined by electron microscopy. The effects of film thickness, casting solvent, and annealing were investigated using both scanning and transmission modes.

The phase morphology resulting from SEM analysis of the homopolymer

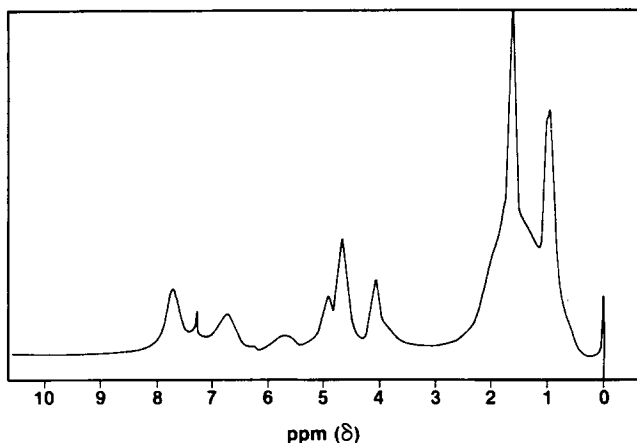


Fig. 3. 90 MHz proton NMR spectrum of block copolymer 8, Table I. Solvent: chloroform-*d*. Peak assignments: see Figures 1 and 2.

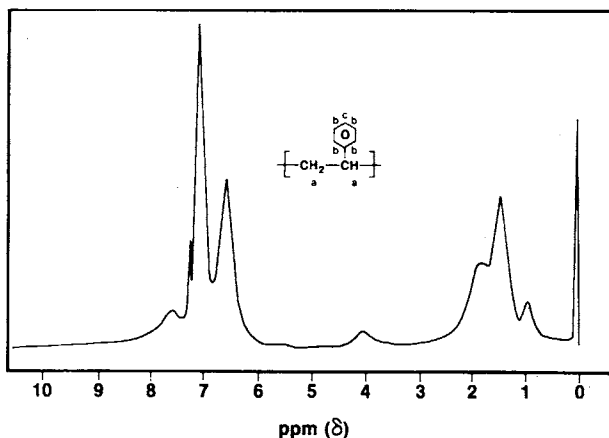


Fig. 4. 90 MHz proton NMR spectrum of block copolymer 10, Table I. Solvent: chloroform-d. Peak assignments: see Figure 2 for assignments relating to npss block; (a) 1.50; (b) 6.58; (c) 7.09.

blend is shown in Figure 6. When cast from THF, phase separation is such that sufficient contrast exists for mapping both by secondary electron analysis and by EDXA for sulfur as shown in Figures 6(a) and 6(b). Both methods show that the dispersed phase consists of circular islands with a size distribution varying over an order of magnitude. EDXA identifies the dispersed phase as the poly(npss). This analysis provides an estimate of the resolution limit for EDXA based on sulfur in this system. Domains with diameters of 4–5 μm are the smallest that can be resolved by sulfur-based EDXA; smaller domains could be observed using secondary electrons. Contrast in films cast from THF was not improved by annealing. When the same blend was cast from chloroform, no phase separation could be detected by SEM. Upon annealing, however, some sulfur clustering was identified by EDXA at very slow scanning rates as shown in Figure 6(c).

As would be expected from the resolution limit shown for domains in the blend, EDXA could not be used to map phase morphology for the copolymers whether or not the films were annealed. Therefore, TEM was used to char-

TABLE III
Size Exclusion Chromatography of ABA Block Copolymers,^a
A = *n*-Propyl *p*-Styrene Sulfonate, B = Isoprene^b

Copolymer ^a	\bar{M}_n^c	\bar{M}_p^d	Polydispersity ^e
4	48,700	60,000	1.24
5	24,400	25,000	1.50
6	19,200	15,000	2.13
7	20,500	15,000	1.68
8	25,600	20,000	3.18
9	35,900	25,000	2.65
10 ^b	67,300	70,000	1.10

^a See Table I, column 1.

^b In copolymer 10, B = styrene.

^c Estimated by gravimetry.

^d \bar{M}_p = styrene equivalent peak MW obtained by SEC.

^e Estimated from styrene equivalent \bar{M}_n and \bar{M}_w obtained by SEC.

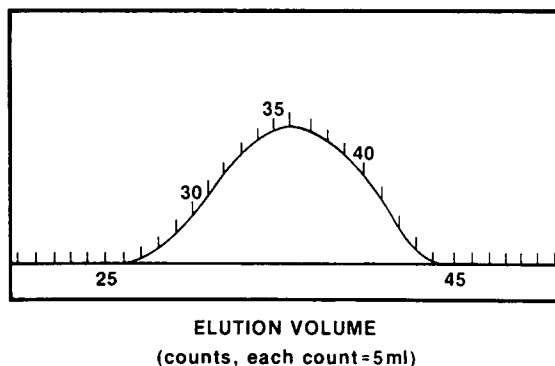


Fig. 5. Representative size exclusion chromatogram for ABA block copolymer. Solvent: THF/dioxane, 80/20 (v/v). Packing: CPG glass, pore sizes, 75, 170, 240, and 500 Å; 4 columns, each 4 ft × 0.25 in.

acterize the copolymers. Films cast from 1 g dL⁻¹ THF solutions and stained with OsO₄ had sufficient contrast for mapping using TEM as shown in Figures 7(a), 8(a), 9(a), and 10. Annealing did not appear to improve phase separation. In contrast, films cast from chloroform (or DMSO in the case of copolymer 8) showed little or no phase separation in TEM unless they were annealed (Figs. 7, 8, and 9). Even after annealing, phase separation was not as distinct as for films cast from THF, and it was accompanied by

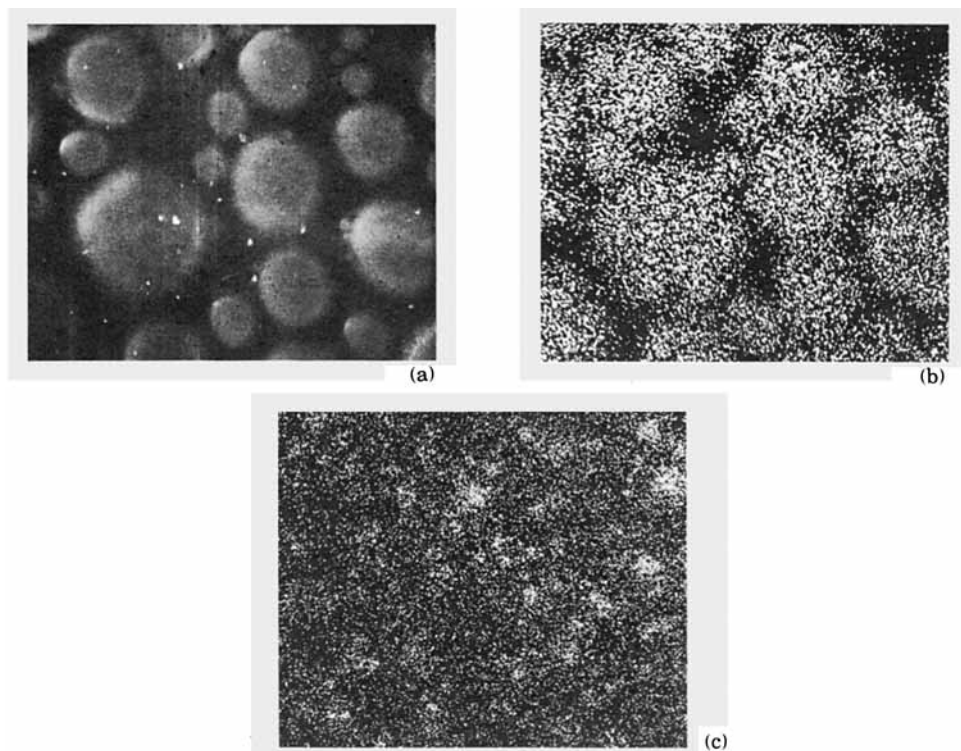


Fig. 6. SEM of a blend of poly(*n*-propyl *p*-styrene sulfonate) and polyisoprene (magnification, 4000): (a) secondary electron image when cast from THF; (b) matching sulfur X-ray image; (c) X-ray image when cast from chloroform and annealed.

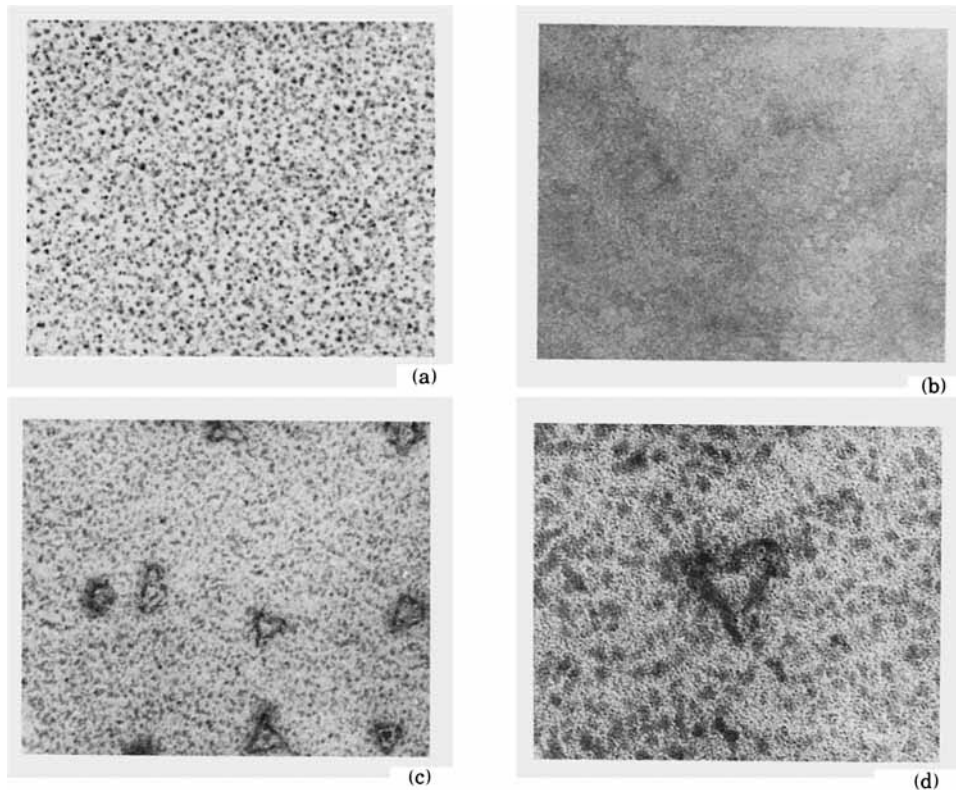


Fig. 7. TEM of block copolymer 6, Table I (magnification, 7×10^4): (a) cast from THF; (b) cast from chloroform; (c) cast from chloroform and annealed; (d) high magnification (2.5×10^5) view of (c).

some clustering of the dispersed polyisoprene domains in copolymers 6 and 7. Micrographs such as those in Figures 6–10 were used to calculate domain sizes and area fractions of the two phases. This information is provided in Table IV. Since the domain morphologies of copolymers 1–5, all containing less than 15% npss, were essentially indistinguishable, only one of them (copolymer 4) is described in Table IV.

For copolymer 10 where the central block is polystyrene, no phase contrast was expected because unsaturation is needed for OsO_4 staining. Therefore, phase domain morphology could not be observed.

DISCUSSION

One intended application for the polymers synthesized in the present work was to investigate the effect of sulfonate ester groups (and then following hydrolysis, sulfonate ions) on blood compatibility. More precisely, it was desired to know how distribution of these groups in domains according to different patterns, as opposed to a random nondomainal distribution, would affect blood platelet reactivity. The effect of such variables as the identity of the discontinuous phase, domain size distribution, domain shape, and overall composition are of interest. The series of copolymers and the homopolymer blend described here provided a sufficient basis for these biological investigations, and the results have been published elsewhere.²²

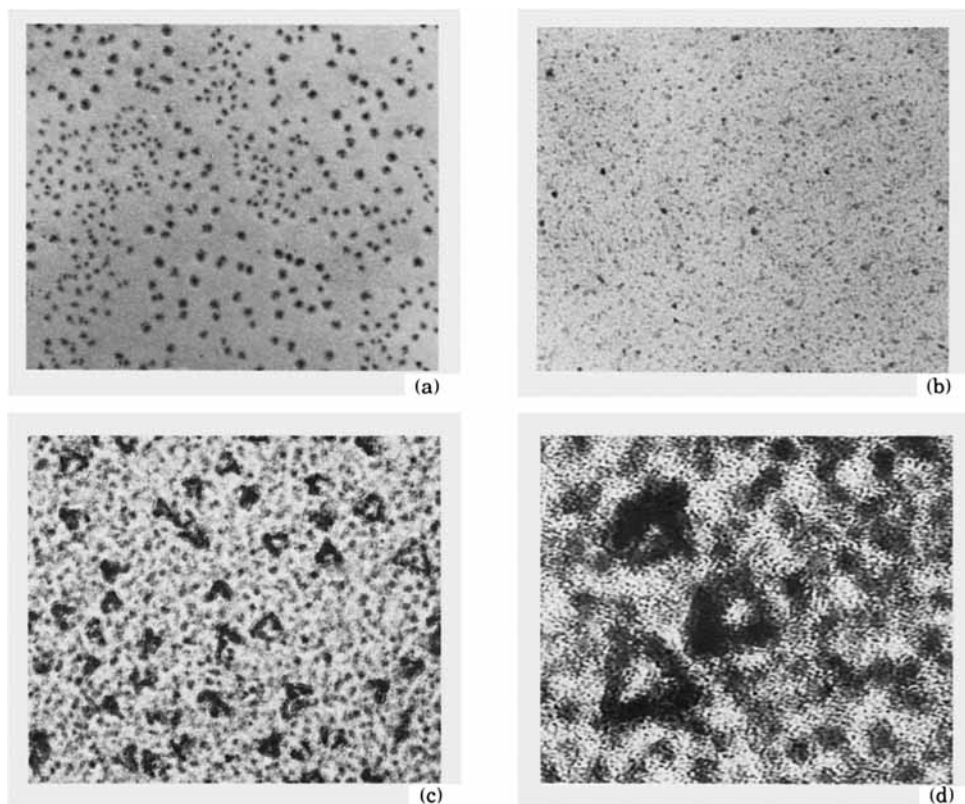


Fig. 8. TEM of block copolymer 7, Table I (magnification, 7×10^4): (a) cast from THF; (b) cast from chloroform; (c) cast from chloroform and annealed; (d) high magnification (2.5×10^5) view of (c).

Of more direct relevance for the present discussion are (a) the polymerization of npss initiated by living polyisoprene compared to that initiated directly by sodium naphthalene as reported previously,⁸ and (b) the variation of domain morphology of the block copolymers with composition.

The polymerization behavior of npss initiated by living polyisopryl dianion is very similar to that for sodium naphthalene initiation. As was the case for the latter, it was found that only limited molecular weight of poly(npss) could be achieved. For both initiators the molecular weight of poly(npss) appears to be limited to about 10,000. It seemed possible that the achievable chain length might be related to the total chain length of the polymerizing species. If estimates of total copolymer chain length in terms of the number of chain carbon atoms are made using the gravimetrically derived molecular weights in Table III (these are believed to be the more reliable of the two molecular weight estimates given), the values range from about 2100 (copolymer 4) to 270 (copolymer 7). In the case of copolymer 4 with a polyisoprene block of MW 48,000, only a very few npss monomers were added, i.e., the polyisopryl dianion was merely "end-capped." Evidently, the total chain length in this case was already great enough that no real growth would occur when npss was added. The remaining isoprene copolymers, 5-9, have npss chain lengths of about 20, 60, 80, 70, and 145, respectively, and central block chain lengths of about 890,

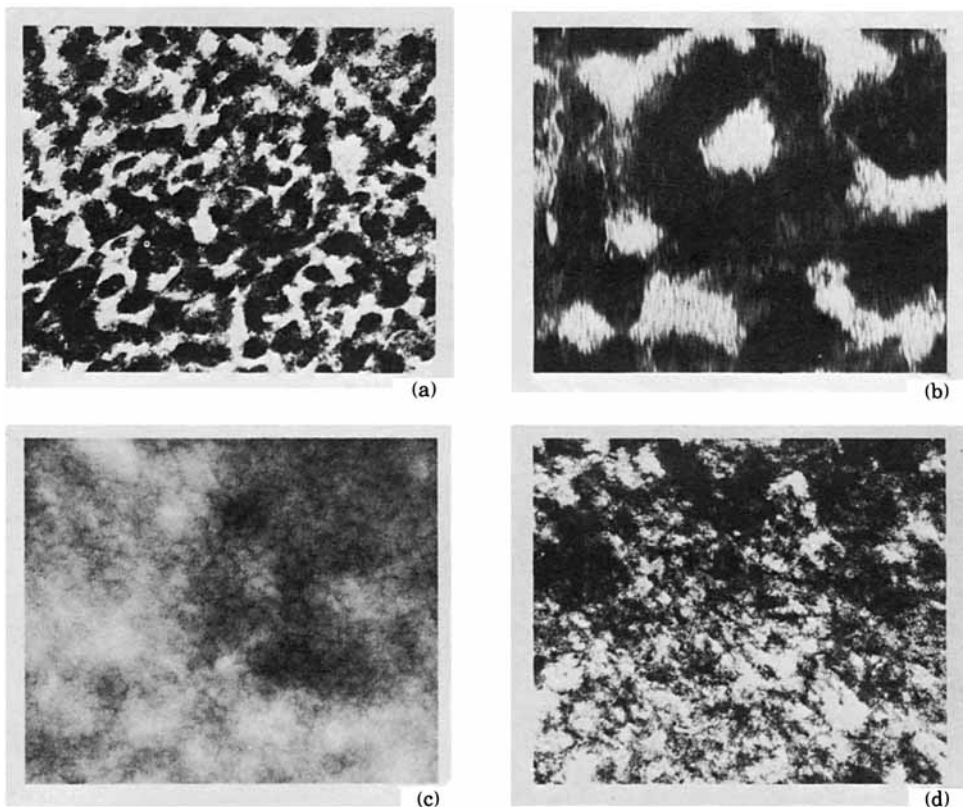


Fig. 9. TEM of block copolymer 8, Table I (magnification, 7.7×10^4): (a) cast from THF; (b) high magnification (2.5×10^5) view of (a); (c) cast from DMSO; (d) cast from DMSO and annealed.

225, 110, 440, and 135. It could be argued that there is a tendency for chain length of the npss block to decrease with increasing chain length of the central block. However, the npss chain lengths of copolymers 6, 7, and 8 are very similar (60, 80, and 70, respectively), while the central blocks vary considerably (225, 110, and 440, respectively). Thus, it is probably best to

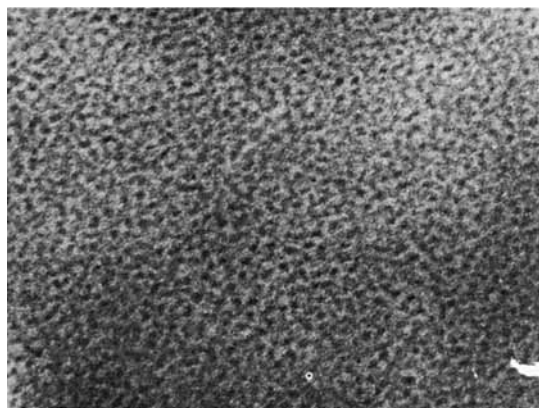


Fig. 10. TEM of block copolymer 9, Table I (magnification, 7.7×10^4), cast from THF.

TABLE IV
Surface Characteristics of Two-Phase Polymer Systems Incorporating Poly(*n*-Propyl *p*-Styrene Sulfonate) (A)

Surface	Polymer ^a	Figure	Continuous phase	Casting solvent	Annealing	$\bar{M}_n \times 10^{-3}$ B block ^b	$\bar{M}_n \times 10^{-3}$ A block ^c	Weight ^d fraction A	Area ^e fraction A	Average domain diameter discontinuous phase (nm)
1	4	—	Polyisoprene	THF	Yes	48	3.5 ^f	0.14	—	—
2	6	7(a)	Poly(npss)	THF	Yes	5	7.1	0.68	0.66	9-12
3	6	7(b)	—	Chloroform	No	—	—	—	No phase separation	—
4	6	7(c),(d)	Poly(npss)	Chloroform	Yes	—	—	—	0.61	30
5	7	8(a)	Poly(npss)	THF	Yes	2.5	9.0	0.83	0.77	9-26
6	7	8(b)	Poly(npss)	Chloroform	No	—	—	—	—	10-20
7	7	8(c),(d)	Poly(npss)	Chloroform	Yes	—	—	—	0.71	30
8	8	9(a),(b)	—	THF	Yes	10	7.8	0.59	0.57	No disc. phase
9	8	9(c),(d)	—	DMSO	Yes	—	—	—	—	—
10	9	10	Poly(npss)	THF	Yes	3.1 ^f	16.4 ^f	0.92	0.73	27
11	10	—	Polystyrene	THF	Yes	50	8.7	0.25	—	—
12	Blend	6(a),(b)	Polyisoprene	THF	Yes	200	7.4	0.50	0.50	500-8000

^a See Table I, column 1.

^b See Table I, column 4.

^c See Table I, column 10.

^d See Table II, column 4.

^e From Figures 6-10.

^f From elemental analysis data.

conclude that no strong correlation exists between ultimate MW of the npss block and that of the central isoprene block.

It was also conceivable that propagation could be different in the sodium naphthalene and polyisopryl anion systems due to the fact that in the sodium naphthalene case one has bidirectional growth starting from a small dianion, whereas, in the block copolymer case, one has effectively unidirectional growth from each end of a relatively large dianion. Again this difference does not seem to affect the reaction, and it appears that limited chain growth is an intrinsic characteristic of this anionic system. As was discussed for the sodium naphthalene initiator,⁸ one can only speculate as to the explanation of such behavior. Among the possibilities is that the propagation becomes diffusion-controlled; this seems unlikely in view of the low overall concentration of solids in THF (less than 5%) and, consequently, the low viscosity of the reaction mixture. It seems more likely, as we speculated for the anionic homopolymerization of npss,⁸ that stable complexes between the anionic chain end and pendant sulfonate ester groups on the polymer are formed rendering the anions "dormant."

Turning to consideration of phase separation and morphology it can be seen (Table IV) that poly(npss) is the discontinuous phase in the blend of homopolymers and in copolymers 4 and 10, while polyisoprene is the discontinuous phase in copolymers 6, 7, and 9. For copolymers 4 and 10, having poly(npss) as the discontinuous phase, the details of domain morphology could not be observed using electron microscopy. The domain dimensions are too small in copolymer 4 and the polystyrene phase of copolymer 10 could not be observed; however, poly(npss) is assumed to be the discontinuous phase since it is the minority component. The morphology of the domains of the discontinuous phase in the bulk is generally spherical at concentrations below 20–25% and cylindrical between 20% and 40%. Both domain types can manifest themselves at surfaces and in thin films as circles, although cylindrical domains can also appear as lamellae. It therefore seems reasonable to assume that the sulfonate domains are circular in copolymers 4 and 10 in which they are present at 14% and 25%, respectively.

In copolymers 6, 7, and 9, polyisoprene is the discontinuous phase. In these copolymers polyisoprene is the minor component and the poly(npss) weight fractions are 0.68, 0.83, and 0.92, respectively. For all three of these polymers the domains of the discontinuous phase are roughly circular (Figs. 7, 8, and 10) as would be expected on the basis of composition.

In copolymer 8 there is no discontinuous phase. The concentration of poly(npss) in this copolymer is 60%, near the expected upper limit for the existence of lamellar domains in the bulk.⁶ The phase structure in the thin films prepared for electron microscopy is an interlacing swirling pattern as shown in Figure 9.

Finally the domain structure of the blend of homopolymers (Fig. 6) with 50% of each component indicates poly(npss) is the discontinuous phase. The domains are spherical and have a rather broad distribution of diameters. Such distributions have been noted previously for blends of polar and non-polar polymers.²³ The domains of the blend were mapped using both secondary electron and EDXA modes. Contrast in the secondary electron map

is probably due to thickness variations, and the thicker sulfonate domains thus appear lighter. The reverse was observed for a blend of polystyrene and polyethylene oxide where the thicker phase was the nonpolar polystyrene.²³ Thickness differences between domains were also observed in copolymers of polystyrene and polyethylene oxide.²³ Such thickness variations between domains were not observed in the copolymers in the present study, presumably either because they do not exist, are too small for detection, or are masked by staining effects.

The effect of solvent was investigated for copolymers 6, 7, and 8, which were each cast from two solvents. THF, a good solvent for both components, resulted in a degree of phase separation which was not measurably improved by annealing as shown in Figures 7–10. Similar behavior was also seen for the homopolymer blend, as shown in Figure 6. When chloroform (or DMSO for copolymer 8 which would not dissolve in chloroform) was used as the casting solvent, no phase separation occurred which could be resolved by TEM (Figs. 7 and 9) except in the case of copolymer 7 where there were some rather indistinct polyisoprene domains [Fig. 8(b)]. That phase separation occurred for copolymer 7 but not for copolymer 6 when cast from chloroform may be related to the fact that the polydispersity of copolymer 7 is considerably smaller (see Table III).

When a film of copolymer 8 cast from DMSO was annealed at 130°C for 12 h under vacuum only a slight rearrangement of the two components occurred, resulting in a structure with poorly defined domains as shown in Figure 9(d). On the other hand, when films of copolymers 6 and 7 cast from chloroform were annealed, rearrangement into well-defined domains resulted. For copolymer 6, Figure 7(c) shows that polyisoprene domains have formed where none existed prior to annealing. For copolymer 7, Figures 8(b) and 8(c) show that the domains which are poorly defined prior to annealing have rearranged into a structure similar to that in Figure 7(c). The domains formed by annealing of chloroform-cast films [Figures 7(c) and 8(c)] are less distinct than those in films cast from THF [Figures 7(a) and 8(a)] and are somewhat intermixed, as is typical for block copolymers cast from a solvent which is a poor solvent for one of the components.²⁴ Occasionally the domains are clustered together in triangular aggregates; these are unusual structures whose origins are not understood. They may represent a tendency toward more complete phase separation under annealing conditions, although no increase in the number or size of these aggregates was observed on increasing the annealing time. Domain clustering has been observed in other systems when the casting solvent is a good solvent for one of the blocks and a poor solvent for the other,²⁴ as was the case for chloroform in the present system.

Various types of data from Figures 7–10 are compiled in Table IV. The different surfaces are categorized with respect to casting solvent, annealing, composition, and copolymer MW. In columns 9 and 10 the weight fraction of poly(npss) in the copolymers is compared to its area fraction in the thin films. For surfaces 2, 5, and 8, cast from THF, a very close agreement exists between these two parameters, although the area fraction is always slightly smaller probably due to some intermixing with the isoprene phase. These data demonstrate very good phase separation with THF as solvent. There

was also good phase separation and minimal intermixing of phases for the homopolymer blend, surface 12, for which the area fraction equals the weight fraction. For surfaces 4 and 7 cast from chloroform, the area fraction of poly(npss) is considerably lower than the weight fraction. This shows that while annealing enhances phase separation, complete separation is not possible by annealing alone. Intermixing of the domains is also indicated by their rather diffuse appearance in the electron micrographs [Figs. 7(c), 7(d), 8(c), and 8(d)].

The domains in copolymer 9 cast from THF (Fig. 10) are also diffuse, probably due to its relatively broad molecular weight distribution as indicated by the polydispersity (Table III). The polyisoprene block is small for this copolymer because both initiation and propagation were very slow, and polymerization of the npss block was started before complete conversion of the isoprene block. As a result the area fraction for poly(npss) in this surface is considerably smaller than its weight fraction.

The data in column 11 of Table IV describe the domain dimensions as measured from the corresponding figures. These data lead to two main conclusions. First, the domains in films cast from THF are more compact than in those cast from chloroform. Second, the domains of the blend are 2 orders of magnitude larger than those of the copolymers where the MW of the poly(npss) is of the same order of magnitude. This demonstrates the restrictions on phase separation imposed by covalent bonding between the blocks. While restricting domain size, this bonding appears also to make the domains more uniform, as can be seen by comparing Figure 6(a) with Figures 7(a) and 8(a).

CONCLUSIONS

It has been shown that ABA block copolymers of *n*-propyl *p*-styrene sulfonate (A block) and isoprene or styrene (B block) can be formed by addition of *n*-propyl *p*-styrene sulfonate to living polyisoprene or polystyrene. The MW of the *n*-propyl *p*-styrene sulfonate block could not be extended beyond about 10,000 because of a fundamental limitation on anionic chain growth of this monomer. Various block copolymers showed phase separation behavior analogous to that of the styrene isoprene system.

The authors acknowledge the financial support of this research by the Natural Sciences and Engineering Research Council of Canada.

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Received May 10, 1984

Accepted October 2, 1984