Block Polymers of Styrene and Acrylonitrile*

ELI PERRY, *Chemstrand Research Center, Inc.,*
Durham, North Carolina

Synopsis

One-to-one block polymers of styrene and acrylonitrile were prepared by a two step process: (*1*) styrene was polymerized in the presence of a dialkylphosphine and (*2*) the polystyrene was used to initiate the polymerization of acrylonitrile. The blocks contained 14–76% acrylonitrile and were 60–100% pure as judged by extraction with toluene at 110°C. Phase and electron microscopy showed that the block polymers consisted of a continuous polystyrene phase when the acrylonitrile content was less than 70% by weight and of a continuous acrylonitrile phase when the acrylonitrile content was above 70% by weight. The polyacrylonitrile dispersed phase was regular and almost spherical. Its measured size equaled the calculated size, assuming that the spheres had a diameter of twice the length of the fully extended polyacrylonitrile chains. Polyblends of homopolymers were similar to the block polymers in structure, except that the dispersed phase was very irregular in size and shape. The physical properties of blocks and polyblends were similar and were inferior to those of polystyrene homopolymers and styrene–acrylonitrile random copolymer except for modulus and for maintenance of modulus over a temperature range. The random copolymer had the highest strength properties, which fact was attributed to the absence of a two phase system and the presence of psuedo-crosslinks. The relatively poor properties of the blocks and polyblends were ascribed to the inability of bulk polyacrylonitrile to absorb energy and to the buildup of stress concentrations at the phase boundaries.
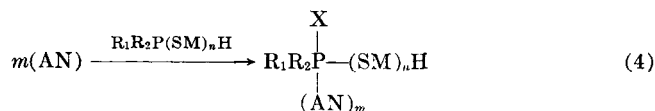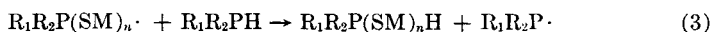
The properties of polymers can be controlled by synthesizing molecules in which the monomer units are arranged in a specific manner. For copolymers, one type of arrangement may involve the number of A and B units which are present in the sequences and, also, the distribution of these sequences. The random placements of A and B follow from the well-known copolymer equation.[1] The nonrandom placements have been the subject of much recent work, most of which is concerned with establishing the existence of block polymers and the differences in solution properties between blocks and mixtures of homopolymers.[2-5] Only scanty information has been published comparing the mechanical properties of blocks with those of polyblends or random copolymers. For alkyd-type blocks, improvements over random polymers in toughness and properties at high temperatures were indicated.[6,7] For blocks of acrylonitrile and methyl methacrylate, a higher glass transition temperature than for the random

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copolymer was reported.[8]   Virtually no information is available concerning the structure of block polymers in the solid state.

This paper discusses a novel method of preparing 1:1 block polymers of styrene (SM) and acrylonitrile (AN), offers some evidence concerning their structure in the solid state, and gives preliminary data comparing the properties of these blocks with those of the homopolymers, polyblends, block polyblends, and random copolymers.

The preparation of the 1:1 blocks depends on two successive reactions: the chain transfer activity of dialkyl phosphines with styrene [eqs. (1)–(3)][9] and the ability of alkyl phosphines to initiate the polymerization of acrylonitrile [eq. (4)]:[10]

$$R \cdot + R_1R_2PH \rightarrow R_nH + R_1R_2P \cdot \tag{1}$$

$$R_1R_2P \cdot + n(SM) \rightarrow R_1R_2P(SM)_n \cdot \tag{2}$$

$$R_1R_2P(SM)_n \cdot + R_1R_2PH \rightarrow R_1R_2P(SM)_nH + R_1R_2P \cdot \tag{3}$$

$$m(AN) \xrightarrow{R_1R_2P(SM)_nH} \begin{array}{c} X \\ | \\ R_1R_2P-(SM)_nH \\ | \\ (AN)_m \end{array} \tag{4}$$

where $R \cdot$ is a growing radical, R_1R_2PH is a dialkyl phosphine, R_nH is an inert "waste product," SM is a styrene unit, AN is an acrylonitrile unit, and X is a terminating species.   The desired product from steps (1)–(3) is $R_1R_2P(SM)_nH$, obtained by the chain reactions (2) and (3).   The amount of R_nH can be minimized by choosing conditions which give long kinetic chain lengths.   The concentration of R_1R_2PH must be high enough such that other "waste" products from radical–radical recombination are not large.   On the other hand, if the concentration of R_1R_2PH is too high, the molecular weight of $R_1R_2P(SM)_nH$ will be undesirably low.   Hence, a compromise is necessary and the DP (degree of polymerization) of the styrene was controlled between 300–500 such that more than 95% of all polymer chains contained a P atom in one endgroup.

RESULTS

Preparation and Characterization of the Blocks

The data for reaction steps (1)–(3) are shown in Table I.   The molar ratio of R_2PH to SM was held within narrow limits throughout the reaction by the addition of R_2PH every hour.

The results of initiating AN with the product from steps (1)–(3) are shown in Table II.   The polymerization of AN was not sensitive to the method used to isolate the polystyrene initiator.   The amount of AN in the final product (e.g., the AN sequence length) was controlled by the amount of AN used in the charge.   AN contents ranged from 14 to 76%. Pure AN with no polystyrene (PS) present and AN in the presence of phosphorus-free polystyrene failed to polymerize.

TABLE I
Preparation of Phosphorus-Containing Polystyrene[a]

Run no.	Phosphine	Molar ratio of $R_2PH/SM \times 10^3$	Conversion, %	Degree of polymerization	Method of polymer isolation
P-1	Dibutyl	0.84	19.4	330	Precipitation in MeOH
P-2	Diethyl	1.22	18.3	378	Evaporation
P-3	Diethyl	1.22	19.0	450	Precipitation in MeOH
P-4	Dibutyl	1.06	17.5	285	Precipitation in MeOH

[a] Time 10.0 hr.; temperature 100 ± 0.2°C. for P-1, P-3, and P-4; 99.5 ± 0.2°C. for P-2.

The purity of the block was estimated by extraction with boiling toluene (Table III) and by fractional precipitation. Neither method was completely unambiguous, but the extraction data, which were much more definitive, indicated that the block purity for the polymers ranged between 60 and 100% (see Experimental). Polyblends containing only 1–2% PAN in PS were opaque, while the block sample B-7 with 14% AN was clear and transparent. Also, B-7 was completely soluble in toluene. Other evidence for the presence of blocks came from the appearance of films cast from dimethylformamide (DMF). The purer the block, the more homogeneous the film cast on glass. B-3 and B-7 gave crystal-clear films when observed with the naked eye. B-1, B-2, and B-4 gave films which contained a slight cloud. Polyblends yielded frosty-opaque films. Under the phase microscope, the film from blocks appeared to contain a very fine uniform dispersion while the films from polyblends were discontinuous and were composed of two phases, each containing very large particles. Block

TABLE II
Preparation of Block Polymers[a]

Run no.	Source of PS	Weight of PS, g.	DMF, cc.	AN, cc.	AN in product, %
B-1	P-2	18.5	230	100	64
B-2	P-3	9.6	120	50	76
B-3	P-3	9.6	0	250	68
B-4	P-4	8.9	0	230	54
B-5	P-1	30.0	370	20	21
B-6	P-1	30.0	340	10	22
B-7	P-1	15.0	170	3	14
B-8	b	0.40	0	3	0.1
B-9	—	0	0	10	c

[a] Time 140–160 hr.; temperature 21–23°C. When reaction occurred, the mass turned off-white 1–2 min. after the addition of the AN, a haze formed, and the temperature rose 1–5°C.

[b] Pure P-free polymer, formed by thermal, free radical polymerization at 100°C.

[c] No polymer formation.

TABLE III
Extraction With Toluene[a]

Run No.	SM in charge, %	DP of PS	DP of PAN (by calculation)	Total charge g.	Residue		Extract		Minimum purity of block, %[b]
					% of charge	SM, %	% of charge	SM, %	
Blocks									
B-1	36	378	<4050	0.35	73	15	21	100	16
B-2	24	450	<4400	0.36	84	16	9	100	16
B-3	32	450	<2650	0.31	78	24	7	93	27
B-4	46	285	<2000	0.37	72	21	26	100	20
B-5	79	330	<177	0.139	20	16	80	91	10
B-6	78	330	<177	0.195	16	20	84	93	9
B-7[c]	86	330	<114	0.194	<2	—	>98	90	10
B-7[c]	86	330	<114	0.198	<2	—	>96	88	12
Controls (mixtures of homopolymers)									
—	0	—	7	0.102	>99	0	<1	0	<1
—	0	—	71	0.103	>99	0	<1	0	<1
—	50	1400	7	0.37	51	10	40	100	4
—	50	1400	145	0.24	46	7	40	100	1
—	42	3300	460	0.35	55	2	38	100	0.5
[c]	90.6	330	70	0.20	10.5	<8	90.5	100	<0.8
[c]	90.6	330	70	0.20	11.0	<8	89	100	<0.8
—	90.6	330	70	0.20	9.8	<8	90	100	<0.8

[a] For 8 hr. at 110°C.
[b] Calculated as (g. SM in residue + g. AN in extract) × 100/charge weight.
[c] 24 hr. extraction period.

purity below 100% was caused by: (1) the wastage reactions mentioned above and (2) impurities which acted as chain transfer agents in the polymerization of the AN.

Structure in the Solid State

Photographs of representative films made with the phase and electron microscopes are shown in Figures 1–3.   The polyblends (5, 20, 45, and 69% AN) were composed of two phases; the dispersed phase existed in many
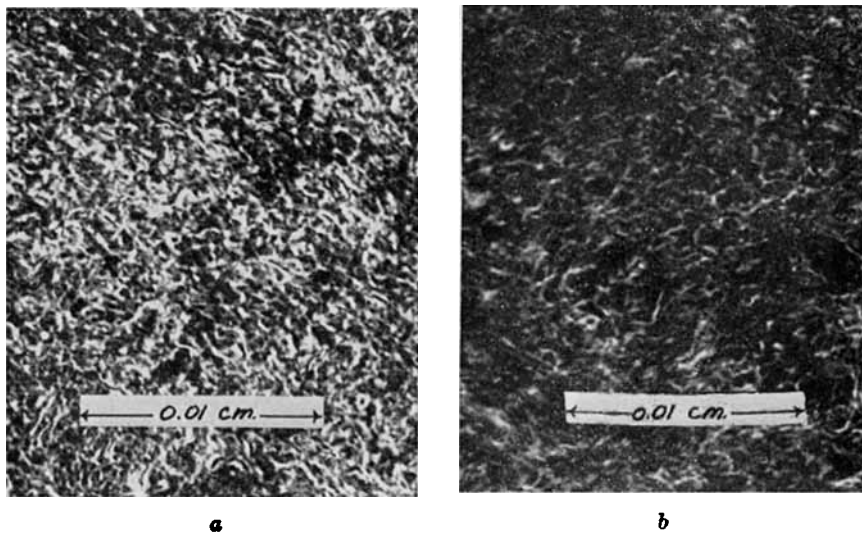

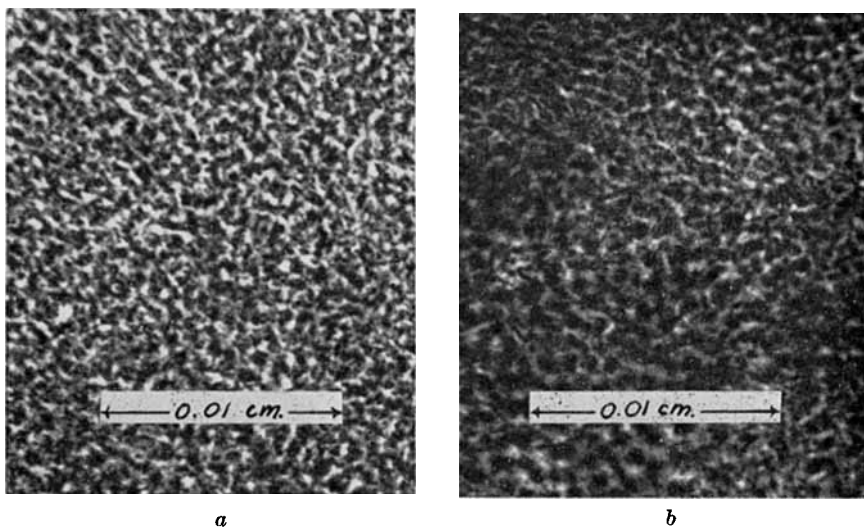Fig. 1. Phase photomicrographs of polyblends: (a) 20% PAN; (b) 79% PAN.

Fig. 2. Phase photomicrographs of block polymers: (a) 14% PAN; (b) 68% PAN.
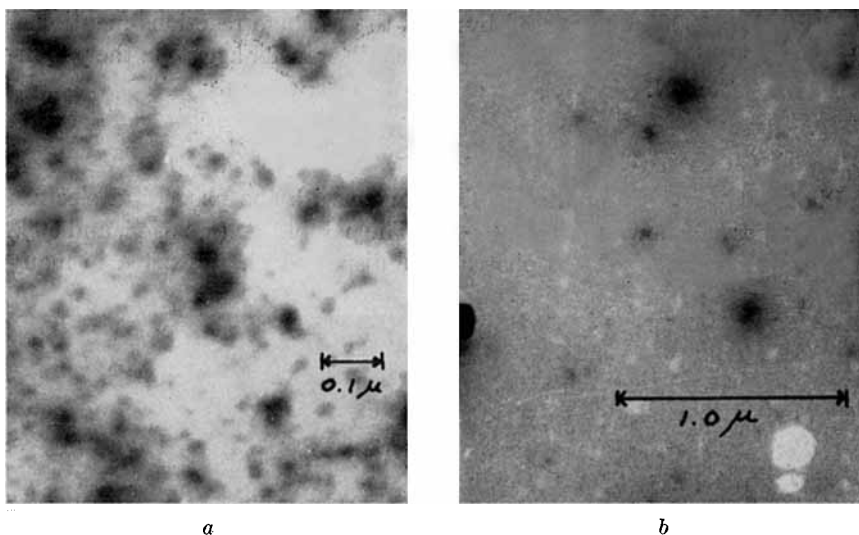
a   b

Fig. 3. Electron photomicrographs of block polymers: (a) 14% PAN, film cast from toluene; (b) 21% PAN, film cast from toluene.

irregular shapes so that it was difficult to speak of an average particle size. The PS was the continuous phase except for the 69% PAN polyblend, in which the PAN was partially continuous. The dispersed phase in the blocks was much more uniform and spherical. In the block containing 76% PAN, the PAN became the continuous phase while the PS was the continuous phase in all of the other samples. The block containing 14% PAN was completely soluble in toluene; the block containing 21% PAN was mostly insoluble in toluene, so that the electron photomicrograph made of the solution-cast film showed a much lower PAN content than did the electron photomicrograph of the 14% PAN sample (Fig. 3). The random copolymer containing 27% AN showed no dispersed phase in an electron microscope which was capable of a resolution below 20 A. A calculation indicated that this copolymer had over 95% of the AN in sequences of 1 or

TABLE IV
Particle Size of the Dispersed Polyacrylonitrile Phase in Block Polymers

AN content, wt.-%	Calculated average particle size, A.[a]	Measured particle size, A.[b]
14	<560	100–500, mostly 200–300
21	<890	110–500 (of the toluene-soluble fraction only)
68	<13,200	11,000–22,000

[a] See text for method of calculation.
[b] From photomicrographs.

TABLE V
Physical Data

Identification	Composition, % AN[a]	Tensile strength, psi	Elongation at break, %	Tensile modulus × 10⁻⁶ psi	Izod impact, ft.-lb./in.	Glass transition temp. T_g, °C.	Dynamic modulus, psi	
							× 10⁻⁴ at T_g − 10°C.	× 10⁻² at T_g + 10°C.
Polyblend with DP (PS) 1400, DP (PAN) 460	5	5400	3.85	1.74	0.22	120	1.3	1.2
"	20	3960	2.27	1.99	0.21	120	1.5	1.3
"	45	3080	1.84	2.16	—	106	4.5	60.0
"	69	2100	1.56	1.77	—	—	—	—
Block B-7	14	—	—	—	—	105	14.5[b]	1.4[b]
Block polyblend of B-1 and Lustrex 2020	5	4520	2.5	1.96	—	106	7.0	10.0
Block polyblend of B-2 and Lustrex 2020	20	3470	1.9	2.13	—	119	2.3	1.4
Random copolymer Lustran A	27	8960	6.93	1.66	0.48	112	7.0	2.5
Lustrex 2020, DP (PS) 1300	0	5620	3.85	1.84	0.25	99	—	—

[a] Polyblends, block polyblends, and blocks containing more than 15% AN yielded opaque moldings. Polystyrene, random copolymer, and blocks containing less than 15% AN yielded clear, transparent moldings.
[b] Via vibrating reed. All other values via torsion pendulum.

2 monomer units.   Particle size measurements were made of the dispersed phase of the blocks (Table IV).

The true particle size of the 14 and 21% AN blocks was beyond the resolution of the light microscope.   Therefore, only the particle size of the soluble fraction of the 21% block could be measured.

Polymer Properties

Some properties of SM–AN blocks, polyblends, homopolymers, and random copolymers are shown in Table V.   When compared to PS, block polyblends and polyblends of homopolymers had a higher modulus which was, also, less sensitive to temperature change as long as two separate phases were present.   PS was superior to block polyblends and polyblends of homopolymers in tensile strength, elongation, toughness, and flow.   The difference between the properties of polyblends of homopolymers and block polyblends was not great.   The polyblend of homopolymers had a slightly greater tensile strength, elongation, and toughness; the block polyblend had a slightly higher modulus which was less affected by temperature change.   Random copolymers had the greatest tensile strength, elongation, and toughness.   They were inferior to blocks and polyblends in modulus and in maintaining the modulus over a temperature range.   No data are shown for pure PAN, since it could not be molded without decomposition. Likewise, blocks containing more than 50% AN were too brittle to handle and test.

DISCUSSION

The nature and behavior of blocks, polyblends, and random copolymers of SM and AN could be rationalized in terms of the following proposal concerning their structures in the solid state.   The blocks in all cases were 1:1 attachments of PS and PAN.   PS and PAN were incompatible such that mixtures as blocks or polyblends formed separate phases.   PAN had the larger cohesive energy density, δ, and tended to form the dispersed phase ($\delta_{PS} = 8.56$ and $\delta_{PAN} = 15.4$).[11]   The degree of dispersion of PAN in the blend was a function of the dispersion technique and the mobility of the chains.   For block polymer, the agglomerate size was limited to about twice the length of the PAN chain.   Growth to larger spheres would have
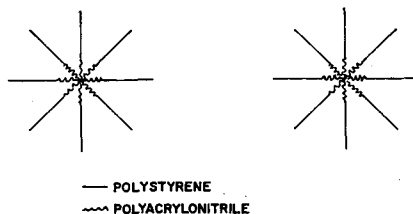

— POLYSTYRENE
〜〜 POLYACRYLONITRILE

Fig. 4. Schematic representation of the structure of the block polymers in the solid state: PAN fully extended; PS randomly coiled.

required that the PS be pulled into the PAN phase (see Fig. 4). Measurements with the phase and electron microscopes confirmed that polyblends had PAN agglomerates of irregular shape and varying particle size (10,000–64,000 A.). For the blocks, the calculated size was in the same range as the observed size when the diameter of the dispersed phase was estimated assuming that this diameter was twice the length of the fully extended PAN chains (with each monomer unit contributing 2.5 A. to the overall length of the chain). The agglomerate size increased with the molecular weight of the PAN, as expected. A critical size was reached when the spheres became large enough to touch, corresponding to 74% by volume (the closest packing of spheres) or 76% by weight PAN. (The density of PS was taken to be 1.05[12] and that of PAN to be 1.18[13]). Above this critical volume, the dispersed phase changed to PS (as observed in the microscope), and the properties resembled those of PAN. For example, fine powders of block polymer which contained less than 70% PAN stuck to a heated bar at temperatures between 130°C. (for pure PS) and 250°C. (for 68% PAN). Above 70% PAN, the block was infusible on the bar even at higher temperatures. The critical PAN content for blends was found to be about the same as for blocks, as expected, because the closest packing volume is not sensitive to particle size. Below this critical volume, blocks and polyblends differed in structure only because the size and shape of the PAN agglomerates in blends could not be controlled readily while the size and shape of the PAN agglomerates in blocks were controlled automatically. For blocks, below a certain molecular weight of the PAN the PAN spheres became so small as to scatter very little light[14] and the block polymer was completely transparent to the eye and under the light microscope (cf. B-7 of calculated PAN particle size <560 A.).

Two phases were present for both blocks and polyblends. For the polyblends, there was little adhesion between the PAN and PS phases. For both types of material, the PAN acted as an inert filter of high modulus to yield a high modulus product.[15–17] The strength properties varied in the same manner for both materials, with stress concentration centers developing at the interfaces between the phases. The slight difference in properties between the blocks and the polyblends may have been due to differences in the particle shape and size of the dispersed phase.[18] The inability of the PAN phase to contribute to the strength and toughness properties is suggested by analogy to blends of rubber and polystyrene in which imcompatible mixtures with little adhesion between the phases are, nevertheless, much tougher than pure polystyrene. Apparently, adhesion between the phases becomes a governing factor only in those cases in which the dispersed phase is able to absorb substantial amounts of energy. The random copolymer differed from the polyblend and the 1:1 blocks in that, for each polymer molecule, many AN sequences were tied to many SM sequences through chemical bonds in a homogeneous system. Problems of stress concentration and adhesion did not arise. The short AN sequences acted as pseudo-crosslinks to improve strength properties. Above the glass

transition temperature, the "crosslinks" broke, and the strength properties deteriorated rapidly; the material flowed readily. Since a second phase was not present, the modulus at room temperature was comparable to that of PS. Thus, the optical and mechanical properties of the blocks and polyblends were consistent with the proposed picture of the physical arrangement of the materials in the solid state.

The results with the electron microscope suggested that it may be a valuable tool not only for studying the nature of the solid state of polymers but also for studying the solubility characteristics of polymers. For example, from Figure 3 it could be deduced that a 1:1 block of PS of DP 330 with PAN is soluble in toluene at 25°C. only when the PAN has a DP of less than 160. It might be informative, also, to study random copolymers of higher AN content to determine at which AN content a second phase appears in the solid state.

EXPERIMENTAL

Purification of Raw Materials

The all-glass apparatus was flamed three times successively under dry argon, and the reagents were handled and stored under argon. Polymer grade SM (Monsanto Chemical Company, >99.7%) was dried with four portions of $CaSO_4$ and the center cut from a fractionation was collected. Polymer-grade AN (Monsanto Chemical Company) was dried with three portions of CaH_2, and the center cut from a fractionation was collected. AR-grade DMF was dried with five portions of P_2O_5, and the center cut from a fractionation was collected. The dialkyl phosphines were prepared according to proven procedures.[19] Argon (>99.996%, dew point $< -78°F.$) was dried to less than 1 ppm water by passage over molecular sieves.

Pure PS of 1400 DP was obtained by reprecipitating Lustrex 2020 (Monsanto Chemical Company) three times into MeOH from toluene and drying at 50°C. and 0.1 mm. Hg.

Preparation of Polymers

The all-glass apparatus was flamed three times under argon, and the reactions were conducted under argon. Phosphorus-containing polystyrene was prepared by charging a stirred three-necked flask with the calculated amounts of SM and phosphine and heating the flask at the reaction temperature for 10 hr. Phosphine was added hourly to maintain a constant (+10%, −0%) molar ratio of phosphine to SM. All additions were made via pipets which had been baked at 140°C. and cooled under argon. The polymer was isolated either by evaporation of unreacted material under vacuum at 25°C. or by precipitation in excess MeOH, and was dried to constant weight at 0.10 mm. Hg and 40°C.

Block polymers were made by charging a stirred three-necked flask with phosphorus-containing polystyrene and further drying the polymer at

50 °C. and <0.005 mm. Hg for 60–72 hr.   The reactor was brought to atmospheric pressure with argon, and solvent and AN were added.   The reaction was terminated after a predetermined time by pouring the mixture into excess MeOH.   Drying was accomplished at 50 °C. and <0.2 mm. Hg.

PS of degree of polymerization 3300 was prepared by thermal polymerization at 100 °C. and purified as described for Lustrex 2020.

PAN was prepared according to literature techniques.[20]   The random copolymer was Lustran A (Monsanto Chemical Company) which contained 27% AN.

Preparation of Polyblends

Polyblends of block polymer with PS were made directly on the mill rolls. Polyblends of PAN and PS homopolymers could not be formed on the mill rolls due to compatibility problems.   They were prepared by dissolving the homopolymers in DMF and precipitating the solution rapidly in MeOH.

Measurement of AN Content

The AN content of blends and blocks was determined either by elemental analysis for N or by infrared spectroscopy by using the ratios of the absorption of the 695 and 2245 cm.$^{-1}$ bands.   For the infrared method, special care was required because the PAN and PS polymers were incompatible. Best results were obtained by dissolving the sample in DMF, mixing the solution with powdered KBr, drying in a vacuum oven, and pressing the disk.   A calibration curve based on synthetic mixtures was required.

Degree of Polymerization

The DP was obtained viscometrically for pure PS[21] and for pure PAN.[22] The DP of the PAN in the block was calculated from its AN content.

Estimation of Block Purity

The best estimate of purity came from data on toluene extraction in a Soxhlet at 110 °C.   The values in Table III of 16–27% for minimum purity of the blocks containing 24–46% SM had to be multiplied by a factor of 3–4, since the minimum figure did not allow for the content of AN, which was the major constituent.   Hence, the assumed block purity of >60% for these polymers was conservative.   For blocks containing 78–86% SM, the situation was reversed.   SM was the major constituent, while the minimum block purity was based only on the AN content.   The facts that (1) the moldings for blocks with 14% AN were transparent while a polyblend of 1–2% PAN with PS was opaque and (2) there was no residue for this 14% block after extraction with toluene, even though pure PAN of DP as low as 7 was insoluble in toluene, both indicate that this block purity was close to 100%.

Qualitative indication of the presence of blocks was obtained by fractional precipitation (with a 50–50 by weight mixture of DMF and toluene

as a solvent with MeOH as the precipitant) and by casting of films from DMF on glass slides. The procedure and solvent–precipitant system used for fractional precipitation[23] may not have been optimum for the present monomers, which fact may have been responsible for the relative insensitivity of the method. When casting films, solutions in DMF of less than 3% concentration were used to avoid two-phase systems. The films were air-dried at 40–50 °C. until they were not tacky and further dried at 50 °C. and 0.02 mm. of Hg for 24 hr.

Microscopy

Phase Microscopy. Samples were prepared by pressing polymer powder for 2 min. at 180°C. and then cooling rapidly. The films were immersed in Dow 712 silicone oil and pictures were taken with a Reichert microscope (anoptral phase illumination).

Electron Microscopy. Polymer B-7 and the soluble fraction of B-5 were dissolved in toluene and cast on glass slides. Lustran A films were cast from a cyclohexanone solution. Pictures were taken with a Philips EM-200 electron microscope with a maximum resolution of 8 A.

Physical Data

Polymer was densified on a 6 in. mill roll at 185–195 °C. A homogeneous sheet was formed in 1–1.5 min. and milling was continued thereafter for 5 min. Sample slabs were prepared by flash molding in a "picture frame" mold. Polymer was preheated at 180°C. for 5 min. at contact pressure, 2000 psi was applied for 1 min., and the press was cooled to 70°C. within 6–8 min. The specimens were $3^3/_4 \times {}^3/_8 \times 0.030$ i n. for mechanical tests and $4 \times {}^3/_8 \times 0.045$ in. for torsion pendulum tests. Izod specimens were $2^1/_2 \times {}^1/_2 \times 0.130$ in.

Tensile strength was measured according to ASTM D-882. Because of slippage in the grips, the results were relative and not absolute. The data shown were the average from three samples.

Izod impact strength was determined according to ASTM D-256 with 0.010 in. notch radius.

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Résumé

Des polymères en bloc 1:1 de styrène et d'acrylonitrile ont été préparés par un processus en deux étapes: (*1*) le styrène est polymérisé en présence d'une dialkylphosphine et (*2*) le polystyrène est employé pour initier la polymérisation de l'acrylonitrile. Les polymères en bloc contenaient 14–76% d'acrylonitrile et étaient purs à raison de 60 à 100% comme on a pu en juger par extraction avec le toluène à 110°C. La microscopie de phase et la miscroscopie électronique montrent que les polymères en bloc consistent en une phase continue de polystyrène quand le contenu en acrylonitrile est inférieur à 70% en poids, et d'une phase continue en acrylonitrile quand le contenu en acrylonitrile était supérieur à 70% en poids. Le polyacrylonitrile dispersé dans la phase était de forme régulière et presque sphérique. Son volume mesuré égale son volume calculé, en supposant que les sphères avaient un diamètre de deux fois la longueur des chaînes de polyacrylonitrile étirées à l'extrème. Des mélanges d'homopolymères ont des structures semblables à celles des polymères en bloc sauf que la phase dispersée était très irrégulière en volume et en forme. Les propriétés physiques des polymères en bloc et des mélanges sont semblables et inférieures à celles des homopolymères et du copolymère styrène-acrylonitrile statistique sauf en ce qui concerne le module et pour le maintien de la valeur du module pour une série de températures. Le copolymère statistique avait des propriétés de résistance plus fortes; on a attribué ce fait à l'absence d'un système à deux phases et à la présence de pseudo-pontage. Les faibles propriétés des polymères en bloc et des mélanges sont attribuées à l'incapacité des blocs dep olyacrylonitrile d'absorber l'énergie et à la formation d'importantes concentrations aux zônes de séparation de phases.

Zusammenfassung

Eins-zu-eins-Blockpolymere aus Styrol und Acrylnitril wurden durch einen zweistufigen Prozess hergestellt: (*1*) Styrol wurde in Gegenwart eines Dialkylphosphins polymerisiert und das Polystyrol wurde (*2*) zum Start der Acrylnitrilpolymerisation verwendet. Die Blocks enthielten 14–76% Acrylnitril und waren nach der Extraktion mit Toluol bei 110°C zu urteilen, 60–100% rein. Phasenkontrast und Elektronenmikroskopie zeigten, dass die Block-polymeren bei einem Acrylnitrilgehalt geringer als 70

Gewichtsprozent aus einer kontinuierlichen Polystyrol- und bei einem Acrylnitrilgehalt über 70% aus einer kontinuierlichen Acrylnitrilphase bestehen. Die dipserse Polyacrylnitrilphase war regulär und fast sphärisch. Ihre gemessene Grösse entspricht der berechneten unter der Annahme, dass die Kugeln einen Durchmesser entsprechend der doppelten Länge der völlig ausgestreckten Polyacrylnitrilketten haben. Polymergemische aus Homopolymeren waren in der Struktur den Blockpolymeren ähnlich, nur war die disperse Phase von sehr unregelmässiger Grösse und Gestalt. Die physikalischen Eigenschaften der Blocks und der Polymermischungen waren ähnlich und schlechter als die der Polystyrolhomopolymeren und statistischer Kopolymerer von Styrol–Acrylnitril bis auf den Modul und die Stabilität des Moduls über einen Temperaturbereich. Das statistische Kopolymere hatte die besten Festigkeitseigenschaften, was dem Fehlen eines Zweiphasensystems und der Anwesenheit von Pseudovernetzung zugeschrieben wird. Die relativ schlechten Eigenschaften der Blocks und Polymermischungen wurden der Umfähigkeit von Bulk-Polyacrylnitril zur Energieabsorption und zum Aufbau von Spannungskonzentration an den Phasengrenzen zugeschrieben.