

Studies on Fibers Spun from Poly(vinyl alcohol-*b*-acrylonitrile) Emulsions Prepared by Ultrasonic Technique.

I. Characterization of Fiber Structure

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ABSTRACT: The structural characteristics of poly(vinyl alcohol-*b*-acrylonitrile) fibers with different AN contents were studied by comparison with that of PVA and PAN fibers. X-ray diffraction analysis showed that both PVA and PAN blocks in the copolymer fibers formed crystals. Two glass transition temperatures corresponding to PVA and PAN components appeared on the dynamic mechanical spectrum of the copolymer fiber, indicative of their incompatibility in the fiber. SEM intuitively exhibited a longitudinal cracked and grooved surface morphology similar to that of PAN fiber and revealed an internal microdomain separation morphology for the block copolymer fibers. TEM showed a morphological structure intermediate between those of PVA and PAN fibers for the block copolymer fibers. It was also found that the copolymer fiber with the lower AN content has a sheath–core structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 979–988, 2001

INTRODUCTION

Property modification has been a main trend in synthetic fiber science and technology in recent years.¹ Copolymerization plays an important role in fiber modification. We successfully synthesized poly(vinyl alcohol-*b*-acrylonitrile) using an ultrasonic technique, identified its molecular structure,² and studied the spinning performance–composition relationship for aqueous micellar solutions of this type of block copolymers.³ As a part of our continuing work, we report the supermo-

lecular and morphological structure characteristics of the block copolymer fibers, governed by their chemical composition and processing parameters.

EXPERIMENTAL

The synthesis and identification of the block copolymers were reported in ref. 2.

Fiber Preparation

Spinning Emulsions

Initial dilute aqueous emulsions of the block copolymers were heated at 90°C under reduced pressure to remove water until the concentrated emulsions contain about 15% by weight of the block copolymers.

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Table I Characteristics of Fiber Samples

Sample Designation	AN Content (wt %)	Draw Ratio	Heat Treatment	
			Temperature (°C)	Time (min)
B1-4-160	10.80	4	160	5
B1-4-200	10.80	4	200	5
B2-4-160	18.66	4	160	5
B2-4-200	18.66	4	200	5
B3-3-160	26.94	3	160	5
B3-3-200	26.94	3	200	5
B3-4-160	26.94	4	160	5
B3-4-200	26.94	4	200	5
B4-0-160	38.90	Undrawn	160	5
B4-0-200	38.90	Undrawn	200	5
PVA-4-160 ^a		4	160	5
PVA-4-200 ^a		4	200	5
PVA (commercial)				
PVA (commercial)				

^a Prepared from commercial PVA using the same conditions as in the block copolymer fiber preparation.

Block Copolymer Composition

The acrylonitrile content by weight percent of the block copolymers was found according to *N* wt % of the purified block copolymer samples, measured with a Carlo Erba 1106 elemental analyzer.

Spinning

The concentrated spinning emulsions kept at 90°C were filtered, transferred into a cylindrical

vessel at 90°C (by circulation hot water through its jacket), and extruded from the spinneret capillaries, fixed at the bottom of the vessel, by compressed nitrogen gas into the coagulating bath of an aqueous sodium sulfate (Na_2SO_4) solution at 45°C. The coagulating length of the extrudate in the bath is 2 m. The coagulated filaments (as-spun filaments) were wound on a bobbin for subsequent processing and examination.

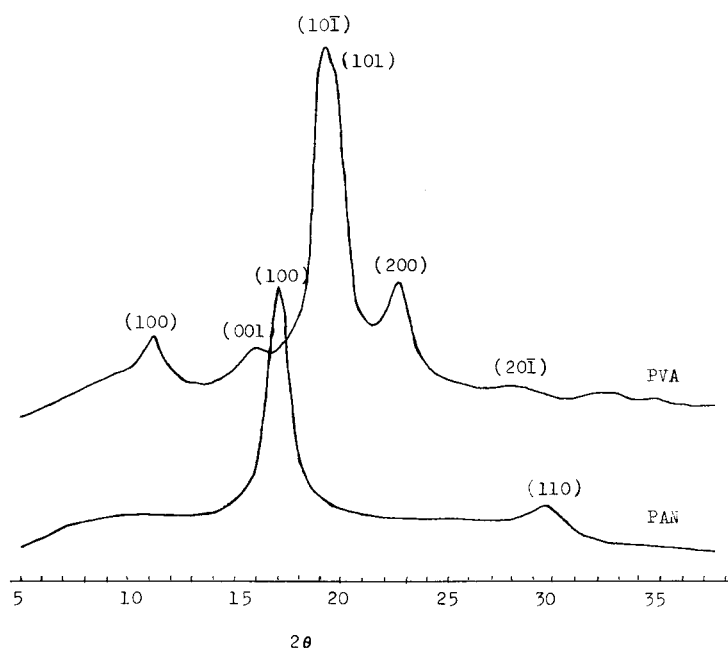


Figure 1 WAXD patterns of PVA and PAN fibers (commercial).

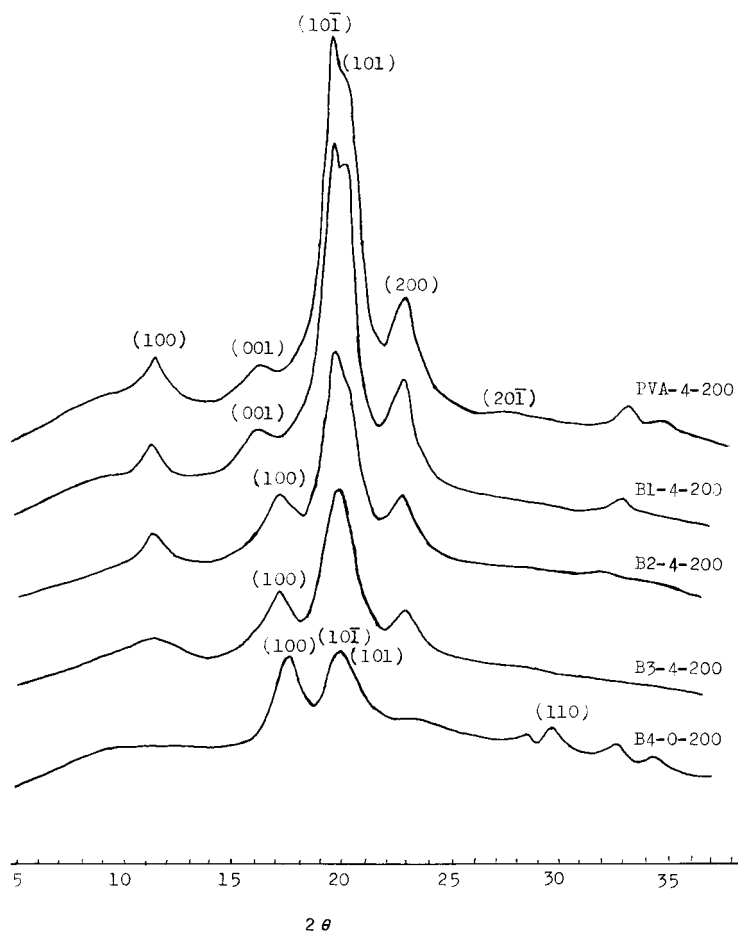
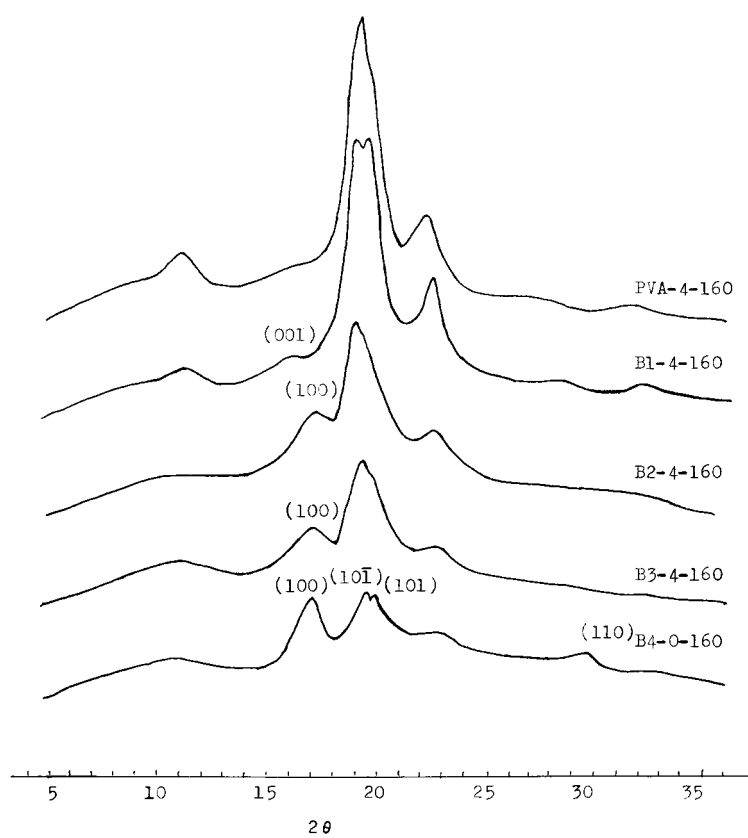


Figure 2 WAXD patterns of PVA and poly(vinyl alcohol-*b*-acrylonitrile) fibers.

Table II Half-Peak Breadth of Diffraction Peaks and Spacing, d , of Diffraction Planes of Fibers

Fiber Samples	Half-Peak Breadth ($^{\circ}$)		Spacing d (\AA)	
	PVA (101)	PAN (100)	PVA (101)	PAN (100)
PVA (commercial)	1.8		4.491	
PAN (commercial)		1.5		5.174
PVA-4-160	1.8		4.489	
B1-4-160	1.8		4.459	
B2-4-160	2.2	2.3	4.503	5.191
B3-4-160	2.3	2.2	4.471	5.121
B4-4-160	2.5	2.1	4.500	5.189
PVA-4-200	1.7		4.476	
B1-4-200	1.7		4.509	
B2-4-200	1.8	2.2	4.476	5.176
B3-4-200	1.9	2.0	4.491	5.180
B4-4-200	2.2	1.9	4.594	5.245

Drawing

Drawing of the as-spun filaments was performed in an aqueous saturated sodium sulfate solution at 80°C for the desired draw ratio.

Heat-Treatment

The drawn filaments were dried and heat-treated at different temperatures for 5 min.

Acetalization

The heat-treated fibers were acetalized with a formaldehyde solution under conditions as employed in commercial PVA fiber production.

Structure Characterization

X-Ray Diffraction Measurement

A fiber sample was cut into powder. Its wide-angle X-ray diffraction (WAXD) spectrum was recorded with a Rigaku D/mas-III A Model X-ray diffraction instrument at 35 kV, 20 mA, X-rays were monochromatized with a nickel filter to obtain $\text{CuK}\alpha$ radiation.

The size of the crystallites of PVA and PAN components in the copolymer fibers was measured by the breadths of the half-peak height of the superimposed diffraction peaks from reflecting planes (101) and (101), positioned at $2\theta = 19.7^{\circ}$ for PVA crystals,⁴ and of the main diffraction peak from reflecting plane (100), positioned at $2\theta = 17.07^{\circ}$ for PAN crystals, respectively, from their diffraction patterns.

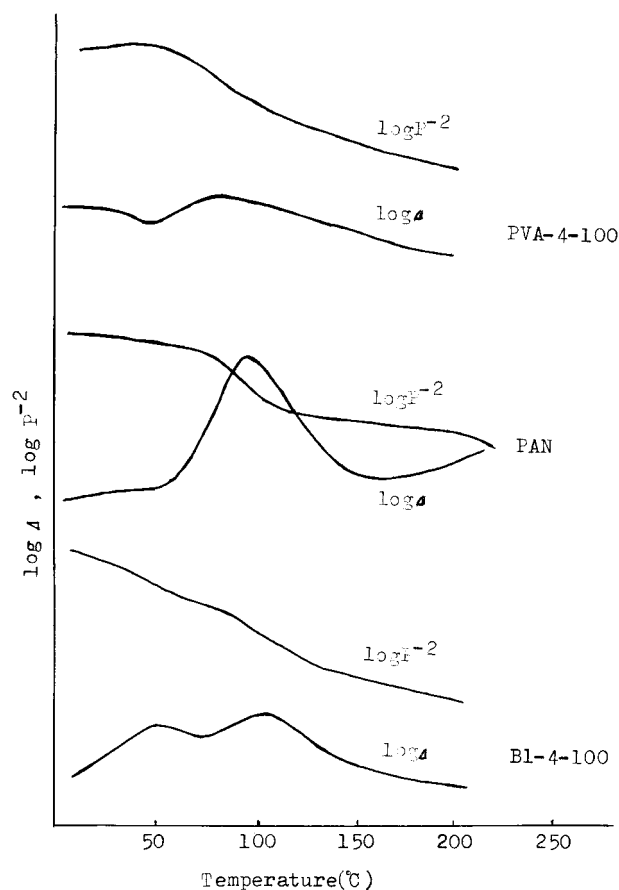
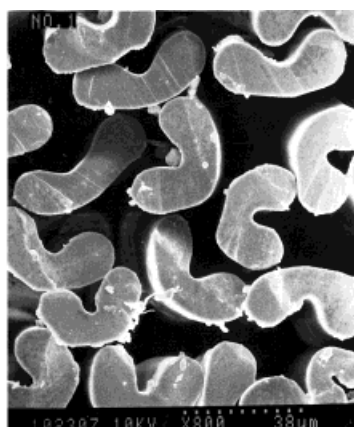
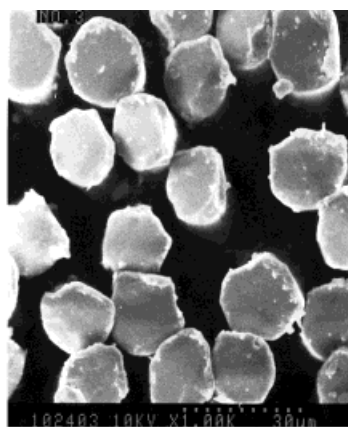


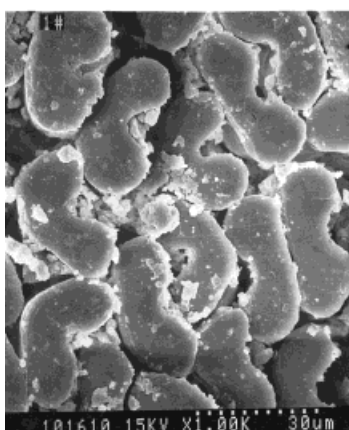
Figure 3 Transitions obtained from dynamic mechanical spectra of PVA, PAN, and poly(vinyl alcohol-*b*-acrylonitrile) (10.80% AN content) fibers (dried at 100°C). Δ is the logarithmic decrement (natural logarithm of the ratio between two successive displacements); P^{-2} is the relative stiffness of the material tested.



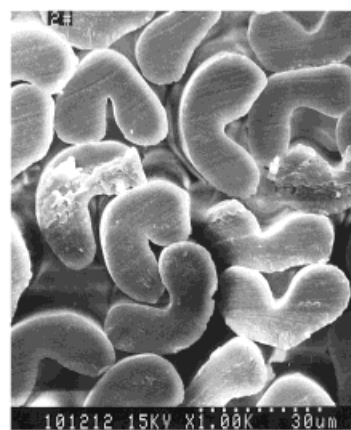
(a)



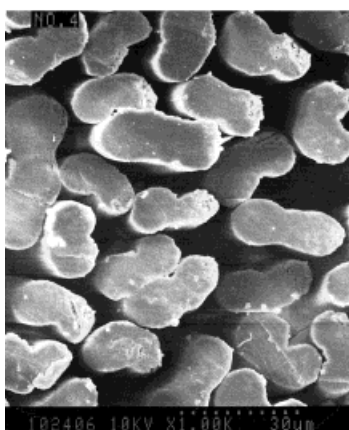
(b)



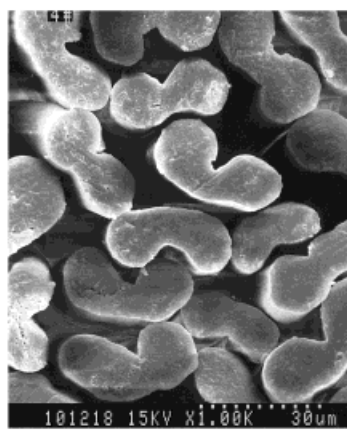
(c)



(d)



(e)



(f)

Figure 4 Scanning electron micrographs of cross-sectional shapes for fibers: (a) PVA-4-200; (b) PAN; (c) B1-4-160; (d) B1-4-200; (e) B3-4-160; (f) B3-4-200.

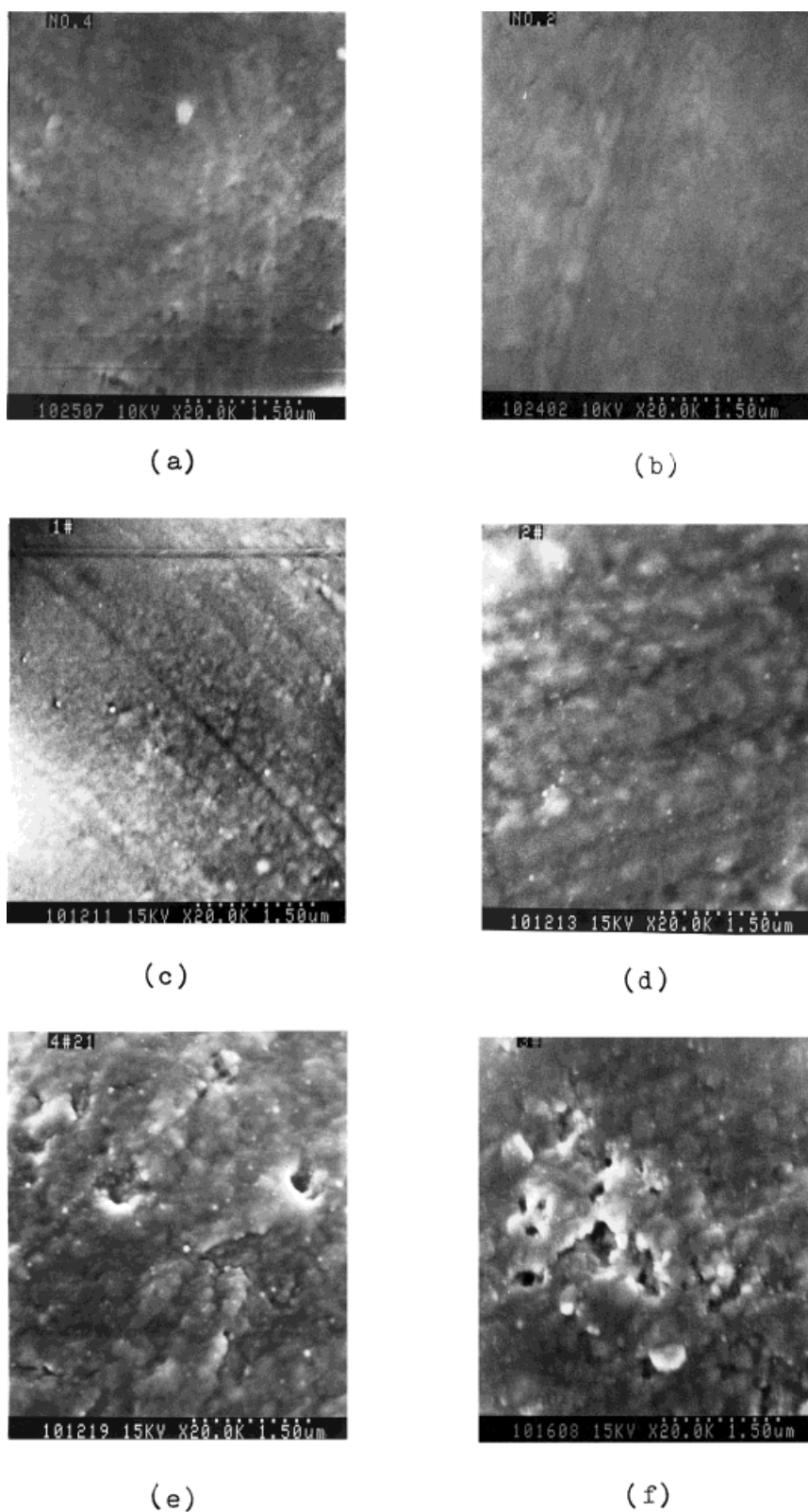
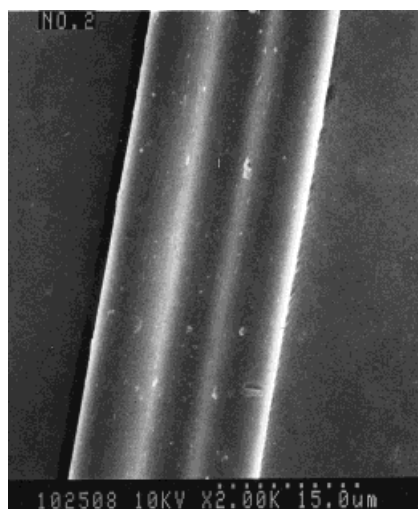
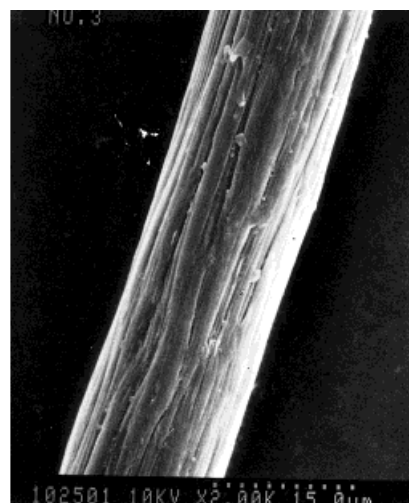


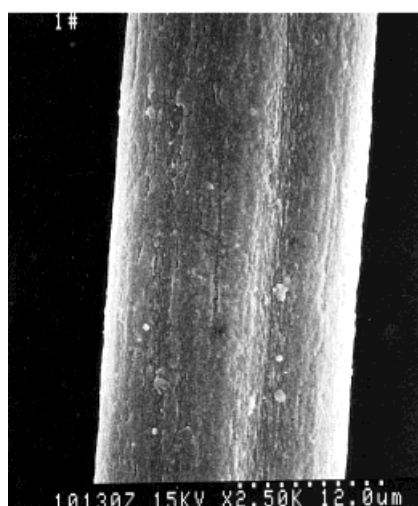
Figure 5 Scanning electron micrographs of enlarged cross sections for fibers (magnification: $\times 20,000$): (a) PVA-4-200; (b) PAN; (c) B1-4-160; (d) B1-4-200; (e) B3-3-160; (f) B3-5-200.



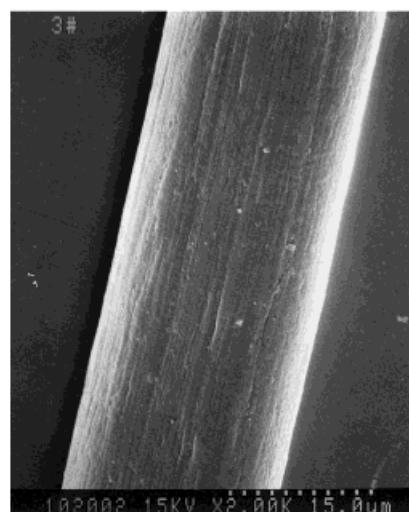
(a)



(b)



(c)



(d)

Figure 6 Scanning electron micrographs of surface morphology for the same fibers as in Figure 5: (a) PVA-4-200; (b) PAN; (c) B1-4-160; (d) B1-4-200.

Dynamic Mechanical Analysis

The dynamic mechanical spectrum of the fibers were recorded with a Model NB-1 torsional braid analyzer.

Scanning Electron Microscopy

A X-650 scanning electron microscope (SEM) was employed to examine the longitudinal surface and the cross-section morphologies of the block copolymer fibers after they were silver-plated.

Transmission Electron Microscopy

The internal texture of the block copolymer fibers was observed with a JEOL JEM-100CX transmission electron microscope (TEM) through their microtomed longitudinal and transverse sections.

RESULTS AND DISCUSSION

Experimentally, it was demonstrated that aqueous concentrated emulsions of poly(vinyl alcohol-*b*-acry-

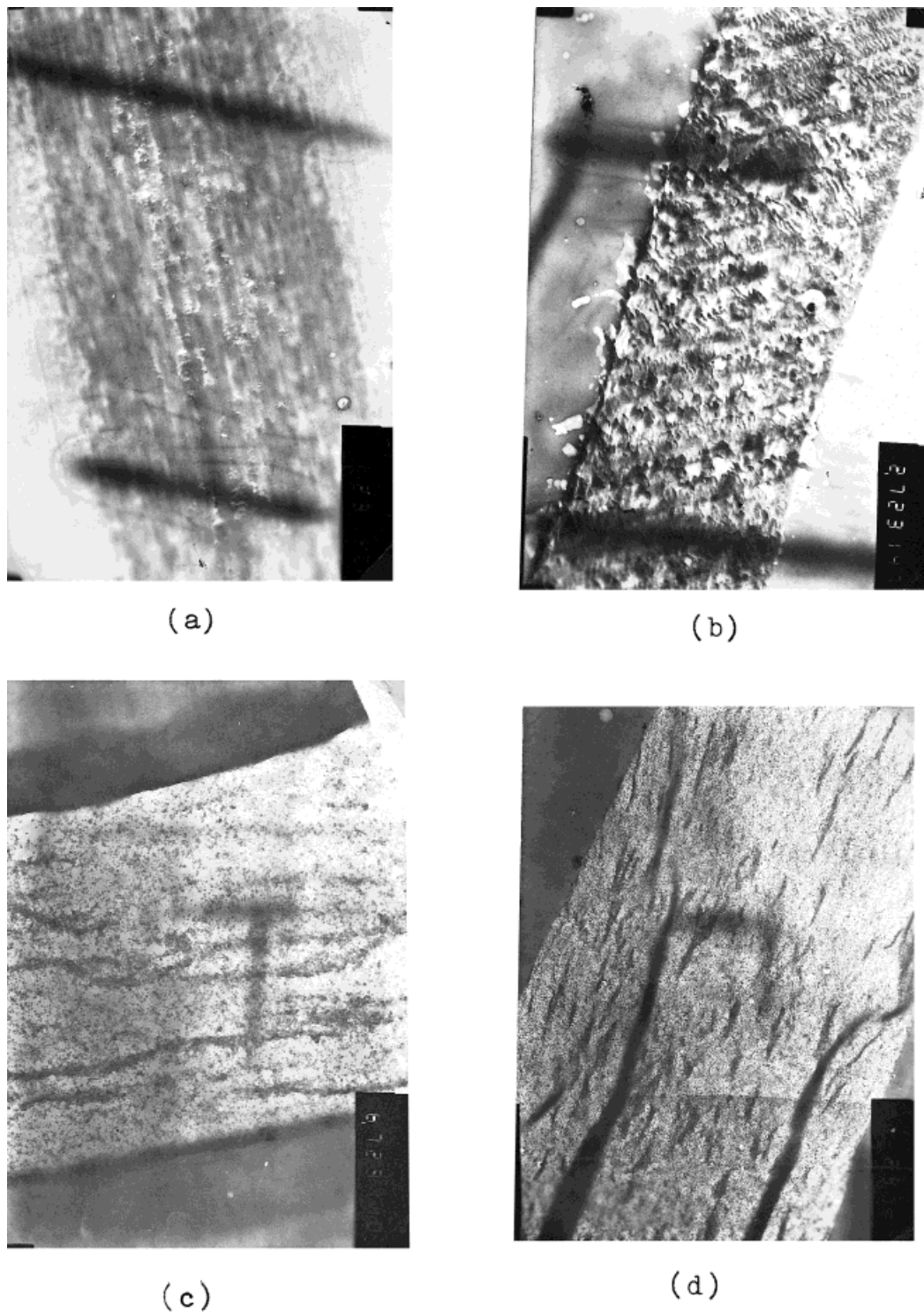


Figure 7 Transmission electron micrographs of longitudinal sections of fibers: (a) PVA-4-200; (b) PAN; (c) B2-4-160; (d) B3-5-200.

lonitrile), the AN content of which was lower than 30 wt %, could be smoothly spun into continuous filaments with good drawability.³ Table I shows the chemical composition, draw ratio, and heat-treat-

ment conditions of the block copolymer fibers studied in this work. The as-spun sample B4 was brittle and thus has no drawability because of its high AN content up to 38.90 wt %.

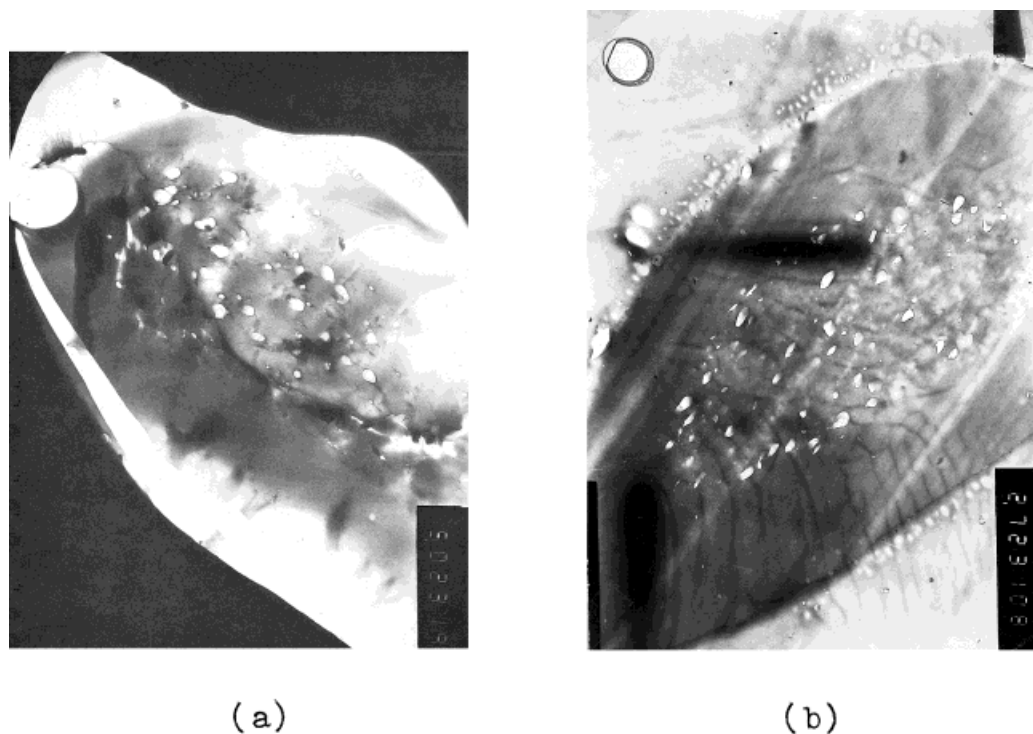


Figure 8 Transmission electron micrographs for cross sections of fibers: (a) PVA-4-200; (b) B1-4-160.

Characterization of Crystallinity

X-ray diffraction patterns of the heat-treated PVA and PAN fibers exhibit sharp diffraction peaks, as shown by Figure 1. The PVA molecular chain assumes a planar “zigzag” conformation and forms a monoclinic crystalline structure;⁵ PAN possesses a three-dimensional helix conformation and constructs a hexagonal paracrystal.⁶ Thus, they are not expected to form a cocrystal or a mixed crystal. In fact, as shown by Figure 2, the two components of the block copolymer fibers crystallize entirely independently. Because of the very small amount and high dispersion of PAN blocks in samples B1-4-160 and B1-4-200, no crystalline diffraction peak appears on the diffraction patterns of them, although the latter was heat-treated at high temperatures. With increasing AN content in the fiber, the crystallization of PAN blocks was progressively displayed by their diffraction patterns. Figure 2 and Table II show that with an increasing heat-treatment temperature the crystal size estimated with the half-peak breadth increases, but with increasing AN content, it decreases indicating somewhat mutual bothering of the two components with their crystallization. Table II also shows that the spacings of lattice in the block copolymer fibers are basi-

cally unchanged with their composition and processing conditions, showing the respective crystallization of the PVA and PAN components.

Dynamic Mechanical Analysis

Figure 3 shows two glass transition temperatures, T_{g1} and T_{g2} , on the dynamic mechanical spectrum of the block copolymer fiber sample B1-4-160, corresponding to PVA blocks and PAN blocks in the copolymer. This phenomenon demonstrates the presence of microphase separation in amorphous regions of the copolymers, caused by the incompatibility between the two kinds of blocks.

Morphological Structure

Scanning Electron Microscopy

Figure 4 indicates that with increasing heat-treatment temperature the cross-section shape of the block copolymer fiber becomes more bent and that with an increasing AN content in block copolymer fiber the bending degree of its cross section decreases. It could be expected that with further increase of the AN content the block copolymer fiber will have a certain circular section similar to that of the PAN fiber [Fig. 4(b)].

Figure 5 presents enlarged scanning electron micrographs for the cross sections of the fibers. Obviously, the microdomain separation intensified with increase of the AN content and heat-treatment temperature, leading to the formation of voids.

Figure 6 shows that the surface morphology of the block copolymer fiber is intermediate between that of the PVA fiber and that of the PAN fiber. A number of longitudinal cracks or grooves on the copolymer fiber surface can be clearly seen.

Transmission Electron Microscopy

Figure 7 shows that the internal longitudinal morphology of the block copolymer fibers are endowed with that of the PVA fiber and that of the PAN fiber. Figure 8 displays that the block copolymer fiber possesses a skin-core structure similar to that of the PVA fiber.

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