The Effect of Coagulant on the Structure and Properties of Poly(*p*-Phenylene Benzobisthiazole) Fibers [PBZT]

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Synopsis

Fibers spun from anisotropic solutions of a lyotropic rigid-rod polymer, poly(para-phenylene benzobisthiazole) [PBZT], were coagulated into homogeneous nonsolvents including a solution of 18% iodine/82% ethanol, ethanol, and water. The effect of these coagulants on the structure and mechanical properties of the PBZT fibers was studied. Structural and mechanical studies were performed on as-spun fibers. Wide-angle X-ray diffraction techniques have shown that fibers coagulated in the presence of iodine anions had *d*-spacings that were unique, as well as *d*-spacings that were characteristic of PBZT or iodine anions. Tensile and shear properties were highest in a fiber having a spin/draw ratio of 3 which contained 19.5% iodine species by weight. For these fibers, an average tensile strength of 2.2 GPa and a torsional modulus of 1.14 GPa was recorded. For fibers having this spin/draw ratio, and undergoing no post-processing heat treatment or tension drying, these values are much higher than would be expected.

INTRODUCTION

Recently, a number of investigators have been interested in the molecular and macroscopic changes that occur when certain polymers, such as nylon 6[1,2] are exposed to iodine in solution or in the vapor phase. When a nylon 6 film having the α crystal structure is exposed to aqueous iodine/potassium iodide solution, its interchain hydrogen bonding is destroyed and a nylon 6–iodide complex is formed. This new material can be easily drawn in order to increase the tensile modulus; when the iodide anions are removed, the crystal structure transforms to the γ form.[3]

The complexes formed by interactions between iodine and certain small molecules were studied as early as the 1940s. By the late 1960s, Mulliken and others had shown that iodine and its compounds often form an association with nitrogen-containing molecules that can be stronger than van der Waals forces.[4] Examples of such systems are iodine in solution with pyridine, triethylamine, or benzene/benzamide.[5]

This work shows that iodine can form a complex with a lyotropic polymer, poly(*p*-phenylene benzobisthiazole) [PBZT]. PBZT, a rigid-rod polymer developed by the Air Force Ordered Polymers Program, is generally spun into high-modulus/high-strength fibers and films via a dry-jet wet spinning process. The phase transition from ordered nematic solution to solid is caused by coagulation into a nonsolvent, typically water. In our work, processing conditions

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were utilized to introduce iodine into the fiber structure by replacing the conventional water bath with an iodine/ethanol solution. Wide-angle X-ray scattering (WAXS) shows that such fibers exhibit some new d-spacings; also, the thermal and mechanical properties of these fibers have changed.

EXPERIMENTAL

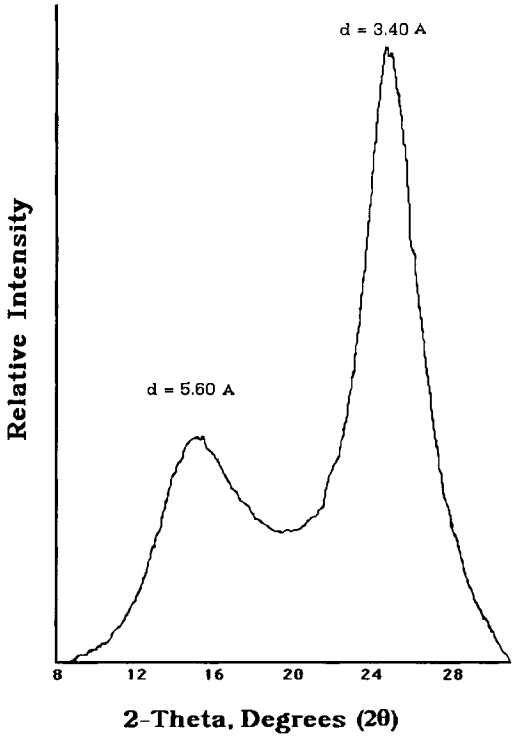
PBZT [Stanford Research Institute, IV = 25, M_w = 36,000, 15.5% solids in poly-phosphoric acid (PPA)] was heated to 80°C and spun into fibers via a dry-jet wet spinning process, with an air gap of approximately 8 in. The coagulants used were distilled water, 95% ethanol, and an 18% iodine/ethanol solution (w/w). Fibers were allowed to soak in fresh aliquots of coagulant overnight to leach out any remaining acid. All fibers were allowed to air dry while on the take-up wheel; those coagulated in iodine/ethanol were first rinsed with ethanol to remove surface iodine.

Previous studies by Cohen,[6] DeTeresa,[7] and Rakas[8] had shown that conventionally spun PBZT fiber that is kept wet after coagulation (and thus retains a more expanded, swollen structure) is readily impregnated by a variety of materials via a solution exchange method. This technique was employed in order to determine differences, if any, between fibers coagulated in an iodine/ethanol solution and those produced by the impregnation technique. PBZT fibers were spun from the same solution, coagulated in a water bath, and washed to remove excess acid. Then the water in the fiber was slowly replaced with ethanol, until the fiber's environment consisted of 100% ethanol. At this point, enough iodine was added to the ethanol to make a 20% solution (w/w). The fiber remained in this environment for one week; it was then removed, quickly rinsed in ethanol to remove surface iodine, and allowed to air dry.

A Statton camera and a Siemens D-500 X-ray diffractometer, both utilizing Cu Kα radiation, were used in WAXS studies. Fibers were wrapped in bundles around cardboard mounts; when using the diffractometer, a lead shield was placed over the cardboard to prevent extraneous scattering. Equatorial scans were taken on the diffractometer using line focus collimation, with incident beam slits of 0.3° (2θ) with a final slit of 0.15° (2θ). In Statton studies, unless stated otherwise, sample-to-film distances are identical for the set of coagulated fibers and for the set of impregnated fibers.

Fiber tensile properties were measured on 30-mm gage length samples in an Instron Universal Tester equipped with a 2-kg load cell. Tensile moduli are corrected for machine compliance. Torsional moduli were measured on 20-mm gage length samples using a torsion pendulum device that has been described elsewhere.[9] Fiber diameters greater than 70 μm were measured by using a Vickers optical microscope with a calibrated eyepiece; smaller fibers were measured by a diffraction method that used a laser.[10] Fiber densities were obtained by measuring exactly 1 m of fiber, then weighing it on a Mettler balance that was accurate to 10^{-6} g. The sample was weighed three times and an average was taken. An average of 100 diameters was used in calculating the density. Unless stated otherwise, all mechanical and physical data was obtained from as-spun fibers.

Heat treatment of selected fibers was done in a tube furnace. Keeping in mind that iodine sublimes at room temperature and that PBZT is stable under



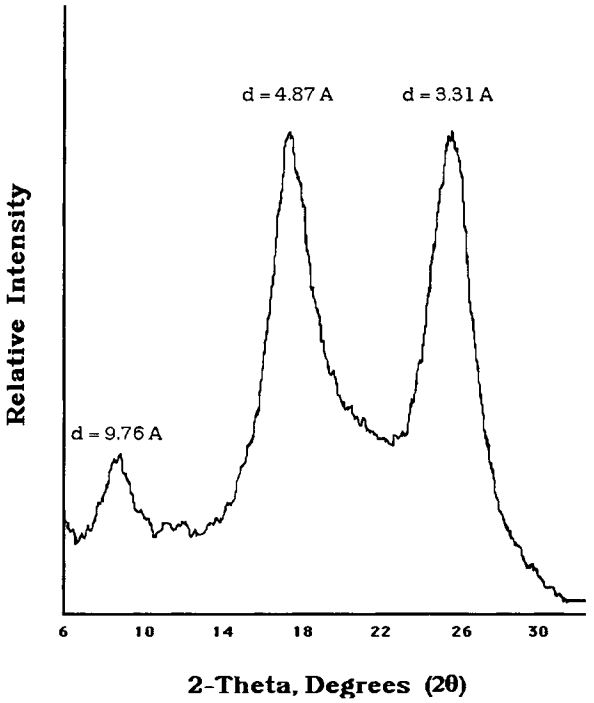


Fig. 1(A). Wide-angle X-ray diffractometer equatorial scan of PBZT coagulated in water, spin/draw = 9.7 [PH9].

Fig. 1(B). Wide-angle X-ray diffractometer equatorial scan of PBZT coagulated in iodine/ethanol solution, spin/draw = 9.7 [PI9].

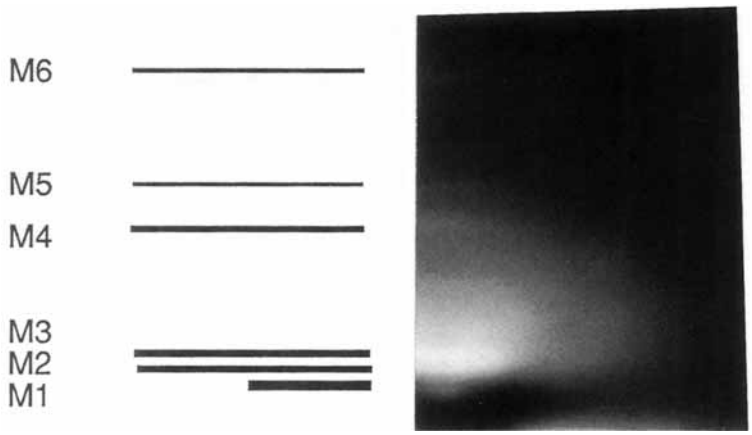


Fig. 2. WAXS print of PBZT coagulated in iodine/ethanol, spin/draw = 9.7 [PI9]. Meridional reflections are emphasized.

nitrogen up to 600°C, fibers were quickly heated to 395°C under nitrogen, held at this temperature for 5 min, then slowly allowed to cool to room temperature. Before and after heat treatment 100 diameters were measured along the fiber length, as well as the weight.

Dr. Chih Chang performed resonance Raman spectroscopy on all fibers coagulated in iodine/ethanol.

RESULTS AND DISCUSSION

Figure 1 shows wide-angle X-ray equatorial scans of PBZT fibers with a spin/draw ratio of 9.7 coagulated in water or in the iodine/ethanol solution

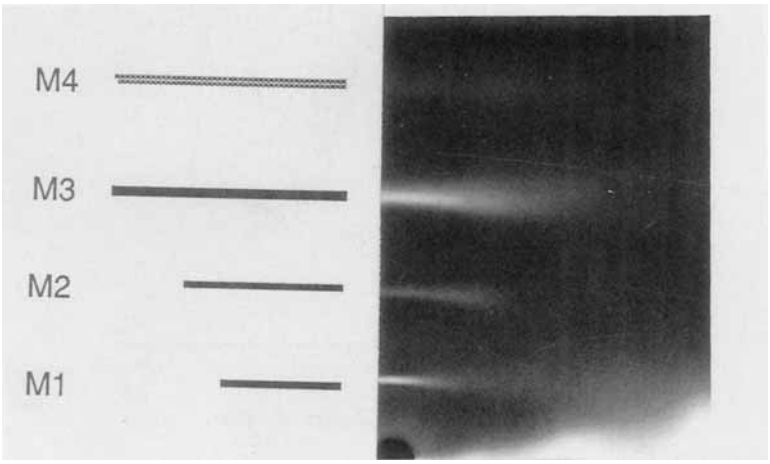


Fig. 3. WAXS print of PBZT coagulated in water, spin/draw = 9.7 [PH9]. Meridional reflections are emphasized.

TABLE I
d-Spacings of Reflections of PBZT Coagulated in Water [PH9]

Reflection	*d* (Å)
E_1	5.60
E_2	3.40
M_1	12.5
M_2	6.13
M_3	4.10

(designated as PH9 and PI9, respectively). Meridional reflections of PI9 are shown in the Statton film and schematic (Fig. 2); Figure 3 is the Statton film and schematic of PH9, with meridional reflections emphasized. The standard equatorial and meridional reflections for PBZT coagulated in water are found in the PH9 fiber and are listed in Table I. Table II lists the meridional and equatorial reflections for the PI9 fiber, the associated d-spacings and, where possible, assigns the reflections seen in the PI9 fiber.

It will be quickly noted that the PI9 fiber does not contain all reflections present in the (standard) PH9 fiber. Also, several new reflections are present. The equatorial spacings of 9.76 and 4.87 Å are unique to the PBZT/iodide fiber and are also present in the wide-angle flat film of PBZT coagulated into iodine/ethanol with a spin/draw of 3. While the standard PBZT E_3 reflection at 3.40 Å is present in PI9 and PI3, the E_2 reflection at 5.60 Å is missing. Furthermore, two meridional reflections, which correspond to *d*-spacings of 15.4 and 10.6 Å, are found in the Statton photograph of PI9 but are not found in the Statton photographs of either PH9 or in PBZT fibers coagulated into 95% ethanol with a spin/draw ratio of 3 (PE3, shown in Fig. 4).

The equatorial spacing of 9.76 Å and the meridional spacing of 15.4 Å have been observed in a number of other molecular complexes involving iodine and an electron donor molecule. It has been found that these reflections are "fingerprints" for the I_3^- and the I_5^- anions, respectively.[11]

Resonance Raman spectroscopy was performed in order to independently confirm the presence of the I_3^- and the I_5^- anions. Both these species appear at

TABLE II
Assignment of Wide-Angle X-Ray Scattering Reflections for PI9

Reflection	*d* (Å)	Assignment
E_1	9.76	I_3^-
E_2	4.87	Unknown
E_3	3.31	PBZT
M_1	15.4	I_5^-
M_2	12.5	PBZT
M_3	10.6	Unknown
M_4	4.70	Unknown
M_5	4.10	PBZT

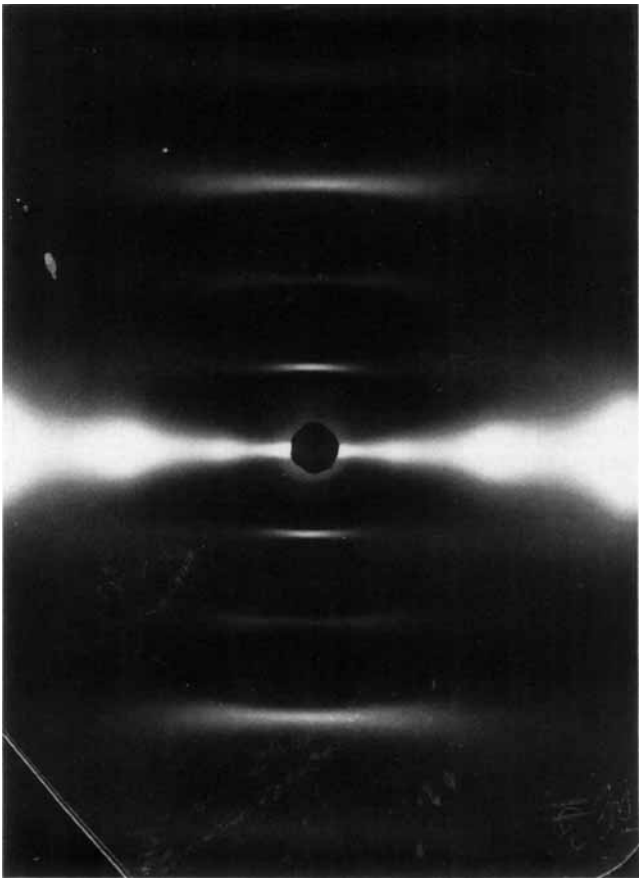


Fig. 4. WAXS print of PBZT coagulated in ethanol, spin/draw = 3 [PE3].

characteristic wave numbers that have been well documented in the literature.[12,13] The I_3^- anion generally appears at 109–113 cm^{-1} and the I_5^- anion at 160 cm^{-1}. Spectra of all fibers that were coagulated in iodine/ethanol contained absorbance bands at both locations, showing that these fibers contained both the I_3^- and I_5^- anions.

Iodine complexation can also affect the mechanical properties of these as-spun fibers; the amount of iodine present in the fiber may be an important factor. Table III lists mechanical properties, average diameter, weight percent iodine (as obtained through chemical microanalysis), and the densities for PBZT fibers coagulated into water, 95% ethanol, and iodine/ethanol. The most striking results are those for tensile strength and shear modulus for PBZT coagulated in iodine/ethanol, having a spin/draw of 3 (PI3). When compared to the control fiber, PE3, there seems to be an improvement in the strength of the microfibrils in the direction of the chain axis as well as perpendicular to it. The shear modulus is a measure of lateral cohesiveness between chains and has been shown to be related to the compressive strength of rigid-rod fibers.[9]

TABLE III
Mechanical Properties of PBZT Coagulated in Water, Ethanol and Iodine/Ethanol Solutions

	PI3	PE3	PI9	PH9
Coagulant	Iodine/ ethanol	Ethanol	Iodine/ ethanol	Water
Spin/draw	3	3	9.7	9.7
Diameter (μm)	77 ± 1	48 ± 2	68 ± 2	48 ± 2
Tensile modulus (E) (GPa)	170 ± 7	230 ± 50	150 ± 50	140 ± 50
Tensile strength (σ_b) (GPa)	2.2 ± 0.1	1.8 ± 0.1	1.5 ± 0.1	1.6 ± 0.1
Shear modulus (G) (GPa)	1.14 ± 0.04	0.630 ± 0.02	0.610 ± 0.05	0.600 ± 0.06
Wt % iodine	19.5	0	40.0	0
Density (g/cm^3)	1.84	1.50	—	—

PBZT fiber that was impregnated with iodine in an iodine/ethanol solution exhibited the same deep purple color as the iodine-coagulated fiber (PBZT is normally bright red). But in contrast to the properties of PBZT fiber coagulated into iodine/ethanol, the iodine-impregnated fiber showed no differences in its wide-angle X-ray scattering pattern (see Figs. 5 and 6). Table IV lists the mechanical properties for the iodine-impregnated and control fibers; there is no difference in the tensile or shear modulus.

Heat treatment of PI9 and PH9 fibers was carried out in order to determine how strongly the iodine anions complexed with the PBZT molecules. For both PH9 and PI9 fibers, there was no change in average fiber diameter after heat treatment. Chemical microanalysis showed that as-spun PI9 contained 40% iodine species by weight while the heat-treated fiber contained 29% iodine species; the heat-treated fiber retained almost 75% of the original weight percent iodine species, even at temperatures far above the sublimation point of iodine.

CONCLUSIONS

These results have shown that the composition of the coagulation bath can measurably affect both the structural and mechanical properties of a fiber spun from an anisotropic solution of a lyotropic polymer and raises the possibility of tailoring fiber properties through judicious choice of coagulants. It is important to realize that coagulation into iodine/ethanol solution can greatly change both structural and mechanical properties of the PBZT fiber, while impregnation of a water-coagulated PBZT fiber with iodine/ethanol solution apparently has no effect on either structural or mechanical properties.

The PBZT fiber has been shown[14,15] to be composed of a microfibrillar network; each microfibril is 70–100 Å in diameter. While these microfibrils are both physically entwined and connected via Y-shaped junctions, there is a significant void volume in the macroscopic fiber. Although further investigation

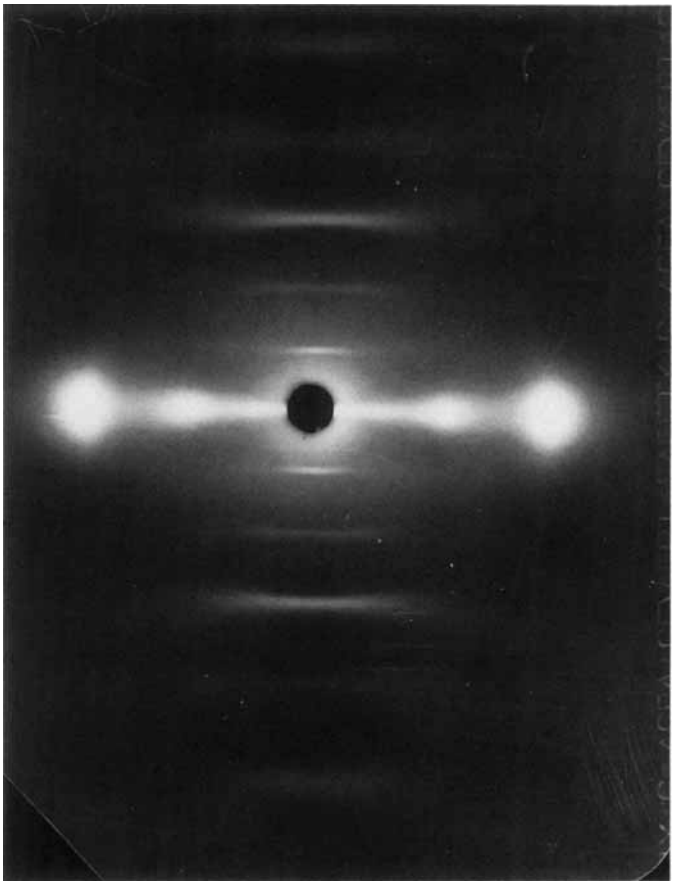


Fig. 5. WAXS print of PBZT coagulated in water, as-spun, spin/draw = 8.

of the chemical and physical interactions of the iodide species with the microfibrillar network and the PBZT molecule are necessary to fully understand the structure of the alloyed PBZT/iodide fiber, one possible model for the iodine/PBZT composite fiber is shown in Figure 7. The heat treatment results suggest that some of the iodide anions are located between microfibrils, while WAXS results verify that others are located within the microfibrils, strongly complexed to individual PBZT chains. In this figure, the I_3^- and I_5^- anions are purposely aligned perpendicular and parallel to the fiber/chain axis because of their respective equatorial and meridional locations in the WAXS studies. The actual ratio of I_3^- to I_5^- is unknown at this time.

This model would also help to explain the increased tensile and shear properties found in the as-spun (no heat or tension drying) PI3 fiber. This fiber had a shear modulus of 1.14 GPa (almost double that of PE3) and a breaking strength of 2.2 GPa; these values are the highest seen in this laboratory for as-spun fibers of either equivalent spin/draw or diameter. We note that the shear modulus appears to be sensitive to the amount of iodine present in the fiber.

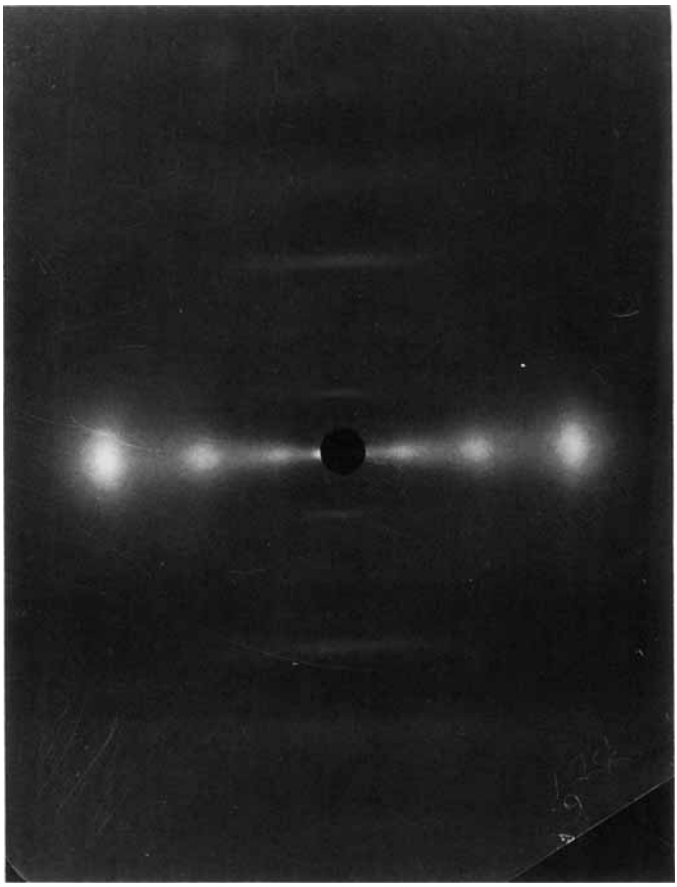


Fig. 6. WAXS print of PBZT coagulated in water, then subsequently impregnated with a 20% iodine/ethanol solution and allowed to air-dry after 1 week [PBZT*I].

This model also accounts for the stability of the fibers under vacuum and in air.

We plan to extend this new processing concept to other lyotropic, fiber-forming polymers, both within and outside the PBZT family. Our investigations

TABLE IV
Mechanical Properties of As-Spun PBZT [AS-PBZT] and PBZT Impregnated with Iodine [PBZT*I]

	AS-PBZT	PBZT*I
Spin/draw ratio	8.0	8.0
Average diameter (μm)	74.1 ± 12.7	65.0 ± 11
Tensile modulus, E (GPa)	150 ± 9	102 ± 18
Tensile strength, σ_b (GPa)	1.6 ± 0.1	1.6 ± 0.2
Shear modulus, G (GPa)	0.575 ± 0.038	0.580 ± 0.019

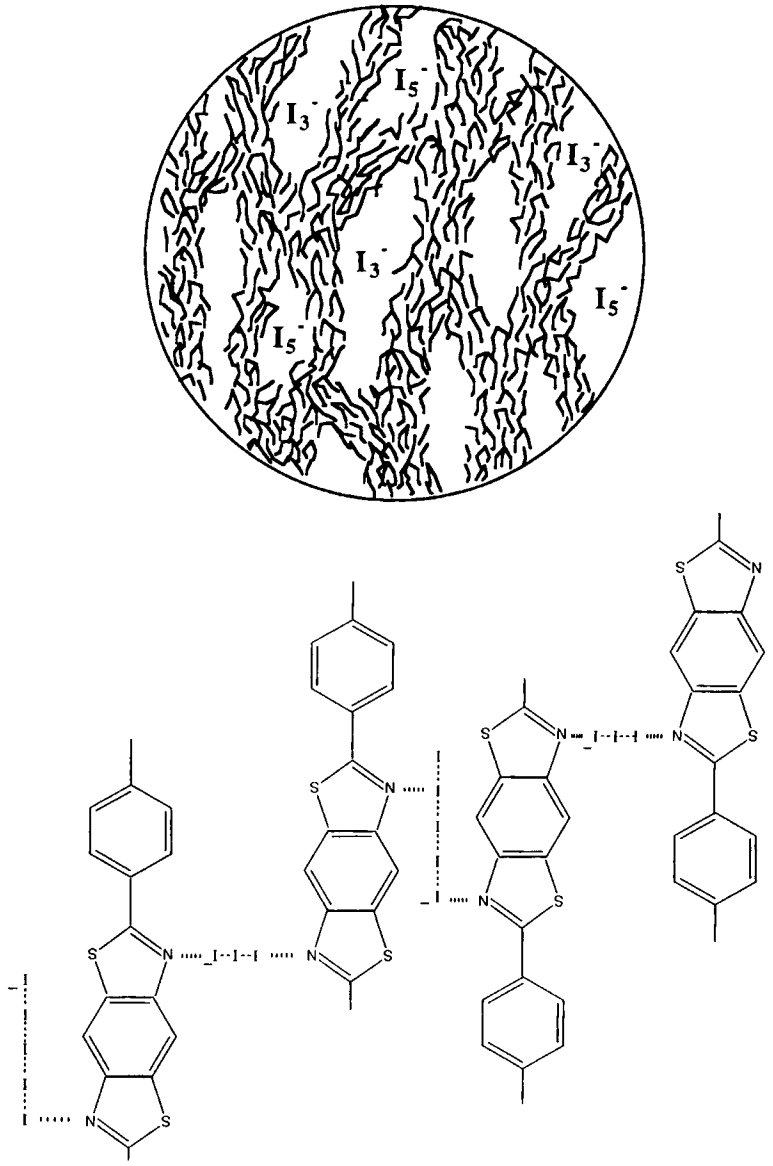


Fig. 7. A possible model for the location of the iodide anions within the PBZT fiber. (A) Iodide anions located between the microfibrillar network within a fiber. (B) Iodide anions located between individual PBZT chains that make up a microfibril.

will center on the effects of coagulant on the structure and mechanical properties, particularly compressive strength and shear modulus.

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