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Effects of electron radiation on mono- and di-methyl pendant poly(*p*-phenylene benzobisthiazole) fibers

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The effect of electron radiation on mono- and di-methyl pendant poly(*p*-phenylene benzobisthiazole) polymers (MePBZT and DiMePBZT, respectively) has been investigated. MePBZT is chemically stable (as measured by ^{13}C NMR) upon exposure to 1 Grad electron radiation at room temperature. The irradiation of DiMePBZT at 225°C was also carried out, which was found to have no effect up to a dosage of 850 Mrad. Thus, the additional molecular mobility brought about by heating (225°C) did not enhance the reactivity of DiMePBZT. The compressive and tensile properties of DiMePBZT fiber remained unchanged at lower radiation dosages. At a dosage of 850 Mrad, the tensile properties were found to decrease substantially, which may be attributed to defects observed in these fibers. The defects can be attributed to the effects of electron radiation, rather than prolonged heating at 225°C.

1. Introduction

Crosslinking has produced limited success as a means to improve the compressive strength in rigid-rod polymeric fibers. Moreover, compressive strength improvements due to crosslinking are often associated with a decrease in tensile properties [1–3]. This was found to be the case for thermally crosslinked monomethyl pendent poly(p-phenylene benzobisthiazole (MePBZT) fibers (See Fig. 1 for chemical structure) [4], where heat treatment without tension resulted in crosslinking, but transverse cracks were developed on the fiber surface. This phenomenon was subsequently investigated via atomistic simulations [5]. Results suggested the development of a substantial axial stress if adjacent phenyl moieties in neighboring MePBZT chains link via a covalent bond (i.e., a phenyl-phenyl crosslink). The development of this stress has also been studied using WAXD and thermal analysis [6]. In addition to these phenyl-phenyl type crosslinks [6–8], other types of crosslinks are conceivable in these methyl pendant rigid-rod polymers (e.g., methylene- or ethylene-type crosslinks) [8]. However, the aforementioned axial stress was not predicted by simulation if crosslinking occurred via these linkages [5].

Exposing toluene to high-energy electron radiation [9] has been found to result in the formation of dimethyldibenzyl dimers [10]. Based on this observation, ethylene-type crosslinks could be expected on electron irradiation of methyl pendant PBZT. As a result, exposing MePBZT to high-energy electron radiation was considered a viable approach to forming the desired crosslinks.

The effects of gamma, proton and electron radiation on the properties of various rigid rod polymers have been reported previously [11, 12]. No significant improvement in the compressive strength was noted when tension heat-treated poly(p-phenylene benzobisoxazole) (PBO) fiber was exposed to 31 Grad of proton radiation. However, proton irradiation (17 Grad) was found to improve the recoil compressive strength of epoxy-impregnated PBO fibers from 179 MPa to 442 MPa. The tensile modulus and strength of both PBO and epoxy impregnated PBO fibers were decreased on exposure to proton irradiation. Gamma and electron irradiation of epoxy impregnated PBO fiber resulted in compressive strength values of 331 MPa and 248 MPa, respectively (Note: dosage was not specified).

The irradiation of monomethyl and dimethyl pendant poly(p-phenylene benzobisthiazole) fibers using proton and electron radiation has been reported. Both proton (max dosage 93.7 Grad) and electron (max dosage 30 Mrad) radiation had no effect on the compressive strength, tensile strength or tensile modulus of MePBZT fiber. Similarly, proton radiation of DiMePBZT fiber was found to have no consequence at dosages as high as 93.7 Mrad. Finally, the electron irradiation (dosage not reported) of DiMePBZT fiber has been reported to increase the compressive strength from 435 MPa to 628 MPa [11]. However, a different report concluded that the compressive strength did not significantly increase at dosages as high as 50 Mrad [12].

In all of the aforementioned studies, solubility has been used to determine the presence of crosslinks.

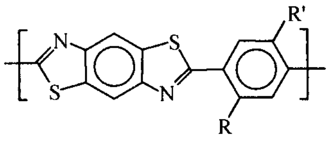

Figure 1 Chemical structure of PBZT (R=R′=H), MePBZT (R=CH_3, R′=H), and DiMePBZT (R=R′=CH_3).

However, solubility has been shown to be insufficient as an evidence in determining the presence of crosslinking in these systems [8]. In addition, the aforementioned studies have all been conducted at room temperature. In this paper, we report the effects of electron irradiation, performed at room temperature as well as elevated temperature, on the structure and properties of MePBZT and DiMePBZT fibers.

2. Experimental

2.1. Fiber spinning and heat treatment

Fibers were dry-jet wet spun using polymer solutions ranging from 10 to 12 wt% in polyphosphoric acid. Spinning was conducted at 100°C, and distilled water was used as the coagulant. The intrinsic viscosities of monomethyl pendant PBZT (MePBZT) and dimethyl pendant PBZT (DiMePBZT) were 1.5 and 1.8 m^3/kg, respectively. A single-hole spinneret of diameter 250 μm and an air gap of approximately 150 mm were used for the spinning of both polymers. The spin draw ratios obtainable in the case of MePBZT ranged between 10 and 12. Slightly higher spin draw ratios (about 15) were possible for DiMePBZT. All fibers were soaked in distilled water for approximately one week and subsequently vacuum dried at 100°C overnight.

2.2. Electron irradiation

Room temperature electron irradiation of as-spun MePBZT was performed at Irradiation Industries Inc. (Gaithersburg, MD) using a 2.5 MeV electron beam accelerator. Samples received a dosage of up to 1 Grad in air by passing them under the electron beam several times in a titanium foil sleeve. Dosimetry was performed in such a way that the influence of the foil on dosage was accounted for. The samples received approximately 8 Mrad per pass.

High temperature irradiation of tension heat-treated DiMePBZT fiber samples was performed at NIST (Gaithersburg, MD). The heating chamber was composed of a stainless steel base and walls with an open top. Aluminum foil of approximately 25 μm thickness was used to cover the top of the heating chamber to minimize heat loss due to convection without significantly influencing beam intensity. Dosimeter measurements were made with the foil in place to ascertain effective dosages received by the sample. Temperature was controlled by placing the chamber on a heating plate. In addition, high temperature heating tape was wrapped around the assembly. Based on this heating arrangement, a sample temperature of 225°C was maintained in air and irradiated to 170 Mrad, 425 Mrad, and 850 Mrad dosages. The time to achieve the maximum dosage was about six hours, using an electron beam of 1 MeV. DiMePBZT fiber heat-treated for six hours in air but in the absence of the electron radiation and was taken as the control sample. Both the irradiated and the control samples were unconstrained during heating. An additional sample receiving a dosage of 425 Mrad at 225°C was irradiated at a constrained length.

2.3. Material characterization

Dynamic mechanical properties were determined on a Seiko 210 DMS. Sample lengths of 20 mm were subjected to a dynamic strain amplitude of 10 μm, a test frequency of 1 Hz, and a heating rate of 3°C/min in air.

A diffractometer mounted on Rigaku Rotaflex rotating anode generator was used to obtain all WAXD scans. $\theta/2\theta$ scans were obtained in the transmission

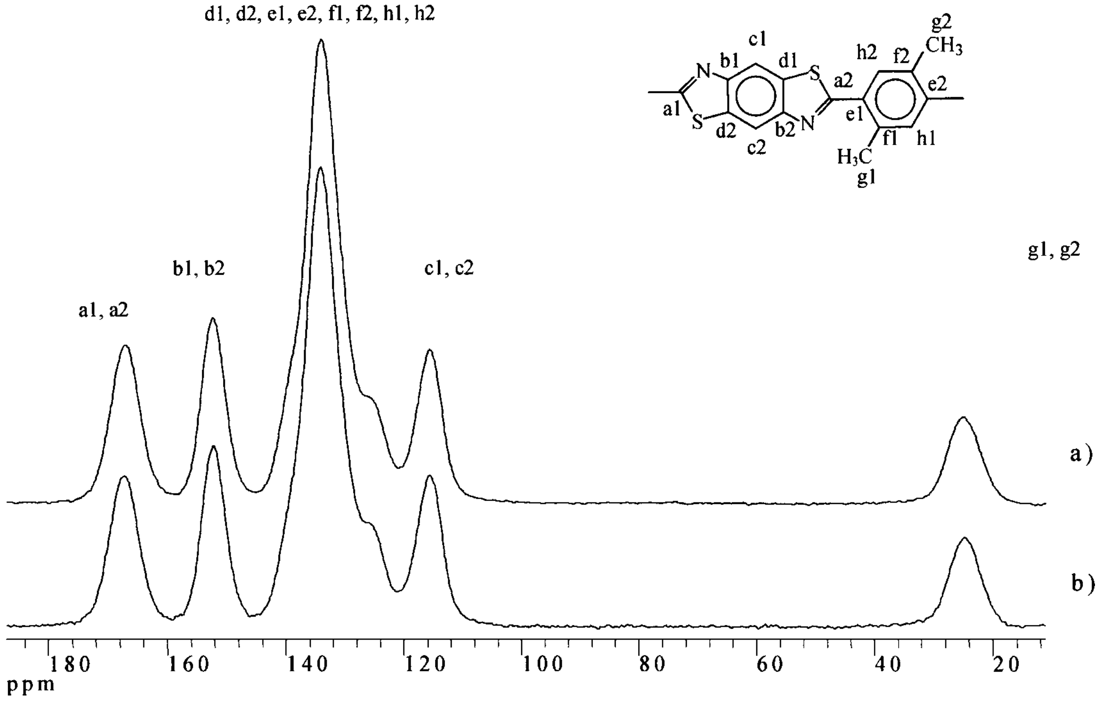

Figure 2 Solid-state ^{13}C NMR of as-spun (a) unirradiated MePBZT and (b) MePBZT fiber after 1 Grad dosage at room temperature.

mode using pinhole collimation. Cu K_α radiation was used in all experiments, with the x-ray generator being operated at 45 kV and 100 mA. The K_β component of the incident beam was minimized using a standard nickel filter. The smallest detector window, 1 mm × 1 mm, was used in an attempt to maximize resolution. The peak apex was used in calculating peak positions.

Solid-state ^{13}C NMR spectra were obtained on MePBZT and DiMePBZT following a procedure detailed elsewhere [8]. Single filament tensile testing was carried out on an Instron Universal Tester (Model 5567), at 25.4 mm gage length [4]. For each sample fifteen specimens were tested. Compressive strength was measured using the recoil compression test [13, 14]. Three to four stress levels were used for each sample, with ten specimens being tested at each stress level. Each fiber halve was assumed to be an independent specimen. The stress at which 50% of the fiber halves exhibited compressive failure was taken as the fiber compressive strength. Fiber loop strength was measured using the Elastica loop test [14]. For the Elastica test, approximately ten specimens were used in measuring the compressive strength, with approximately six data points collected for each specimen. The torsional modulus was measured using a torsion pendulum [15]. Five specimens were used for each measurement, collecting at least four data points (i.e., the measured amplitude and period of oscillation) for each specimen. For the torsional test, multiple diameter measurements were made on each specimen, as the calculation of torsional modulus is strongly dependent on fiber diameter.

3. Results and discussion

The solid-state ^{13}C NMR spectra on unirradiated, as-spun MePBZT and as-spun MePBZT exposed to 1 Grad electron irradiation at room temperature are given in Fig. 2. The lack of change in the NMR spectrum suggests that no structural change took place upon irradiation. Specifically, a shift of the methyl-pendant carbon resonance (ca. 23 ppm) to the methylene region of the spectrum (ca. 38 ppm) was absent, which would be expected if methylene type crosslinks had formed [8]. Moreover, the irradiated sample was soluble in methane sulfonic acid, which confirmed the absence of crosslinking. Spectra$^{\text{TM}}$ 1000 fiber, also irradiated side-by-side (1 Grad at room temperature), showed significant discoloration and appeared degraded.

In general, increasing temperature enhances the effects of irradiation [16]. This is due to the increased molecular mobility at higher temperature, which can increase the probability for radicals to come in close proximity to one another and react. As one might expect, given the molecular structure of rigid-rod polymers, molecular mobility is relatively limited. Therefore, a radical generated within these polymers may be expected to exhibit a higher degree of stability than the same radical on a flexible polymer having more significant chain motion. Ribbon-like motions are thought to take place within these rigid-rod systems to some extent in both solution and the solid-state [6, 17, 18]. However, it is still debated whether certain motions occur in the crystalline or noncrystalline regions [19] or whether one can discriminate between the two in these systems.

The dynamic mechanical behavior of PBZT, MePBZT, and DiMePBZT is given in Fig. 3. Molecular motions, as observed by tan δ peak positions, occur at 400°C, 250°C, and 225°C, respectively in each of the three systems. It is reasonable to suspect the transitions in MePBZT and DiMePBZT involve comparatively similar motions. However, the transition at 400°C in PBZT may originate from a different type of motion. Moreover, the transitions in MePBZT and DiMePBZT may be due to the presence of the methyl groups. Based on the results of the dynamic mechanical tests suggesting enhanced molecular mobility in either system at 225°C, irradiation studies were conducted at

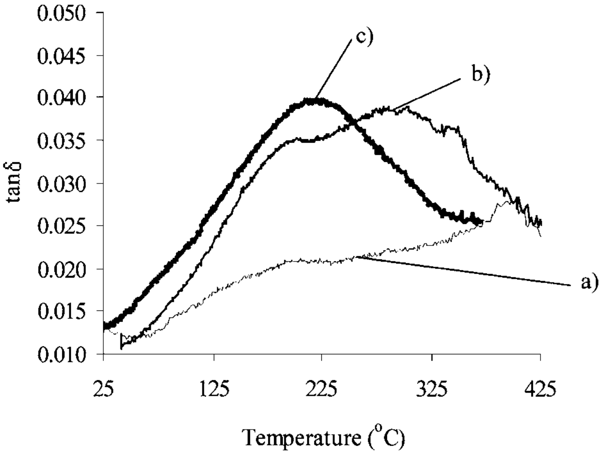

Figure 3 Tan δ vs. temperature for (a) PBZT, (b) MePBZT, and (c) DiMePBZT. All fibers were tension heat-treated at 350°C.

TABLE I Mechanical properties of DiMePBZT fiber before and after irradiation

DiMePBZT Fiber	σ_T (GPa)	(±)	E_T (GPa)	(±)	ε (%)	(±)	σ_c^{recoil} (GPa)	σ_c^{loop} (GPa)	G (GPa)	(±)
HT[a]	1.8	(0.4)	100	(16)	2.0	(0.3)	0.30	~0.46	1.51	(0.18)
Control[b]	1.6	(0.2)	92.6	(8.5)	1.5	(0.1)	0.35	0.56	1.52	(0.20)
170 Mrad	1.5	(0.2)	103	(12)	1.6	(0.2)	0.44	0.65	1.57	(0.11)
425 Mrad	1.3	(0.5)	96.8	(14)	1.6	(0.4)	0.40	0.63	1.41	(0.18)
425 Mrad (Constant length)	1.0	(0.3)	84.3	(13)	1.3	(0.3)	0.39			
850 Mrad	0.6	(0.1)	64.0	(9.4)	1.1	(0.3)	0.34	0.55	1.48	(0.09)

[a] HT - DiMePBZT fiber heat-treated under tension at 350°C for 10 minutes under nitrogen.

[b] Control – HT fiber annealed at 225°C for six hours in air.

170 Mrad to 850 Mrad – HT fiber exposed to electron radiation to indicated dosage at 225°C in air. Fiber length was free to relax unless specified otherwise.

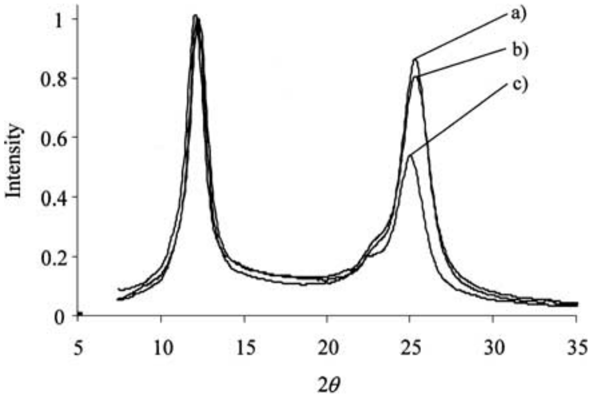

Figure 4 Equatorial WAXD patterns of (a) DiMePBZT control, (b) DiMePBZT fiber after 425 Mrad radiation at 225°C, and (c) DiMePBZT fiber after 850 Mrad radiation at 225°C. Note decrease in relative intensity of (1 0 0) diffraction at ca. 25 degrees 2θ.

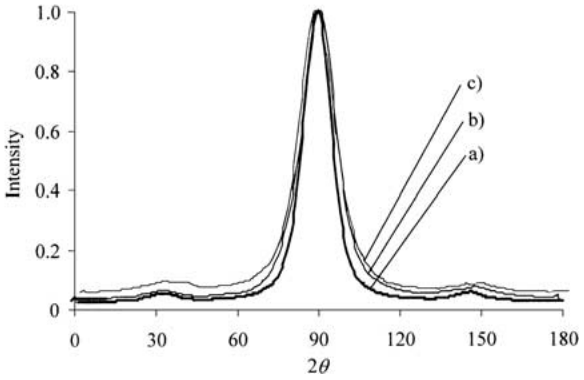

Figure 5 Azimuthal WAXD patterns of (a) DiMePBZT control, (b) DiMePBZT fiber after 425 Mrad radiation at 225°C, and (c) DiMePBZT fiber after 850 Mrad radiation at 225°C.

this temperature. Moreover, given the comparatively low transition temperature in DiMePBZT, the increased concentration of methyl pendants, and the apparent stability of MePBZT at room temperature up to 1 Grad radiation dosage, DiMePBZT was selected for the high-temperature irradiation work.

For the elevated temperature irradiation studies, DiMePBZT fiber was tension heat-treated under nitrogen for 10 minutes at 350°C. This temperature was chosen so as to develop as much crystalline perfection and order as possible, without inducing thermal crosslinking [7]. However, similar to previous observations made on MePBZT fibers [8], tension heat-treatment resulted in the DiMePBZT fibers becoming insoluble in methane sulfonic acid. This, in turn, made solubility studies ineffectual as a means to determine the presence of crosslinks in this work.

The mechanical properties of tension heat-treated DiMePBZT fiber are given in Table I. Fibers irradiated to 850 Mrad electron dosage were held at 225°C for approximately six hours. A control sample was produced by heating the previously tension heat-treated fibers to 225°C for six hours in air without tension or radiation. The mechanical properties of the control sample are also reported in Table I. Annealing DiMePBZT fiber at 225°C did not significantly affect the compressive strength or the torsional modulus. However, the tensile properties were found to decrease. The data in Table I suggests the effect of electron radiation on the mechanical properties of DiMePBZT fiber can, in general, be characterized as benign or detrimental. At high dosage (850 Mrad), a decrease in tensile strength and modulus

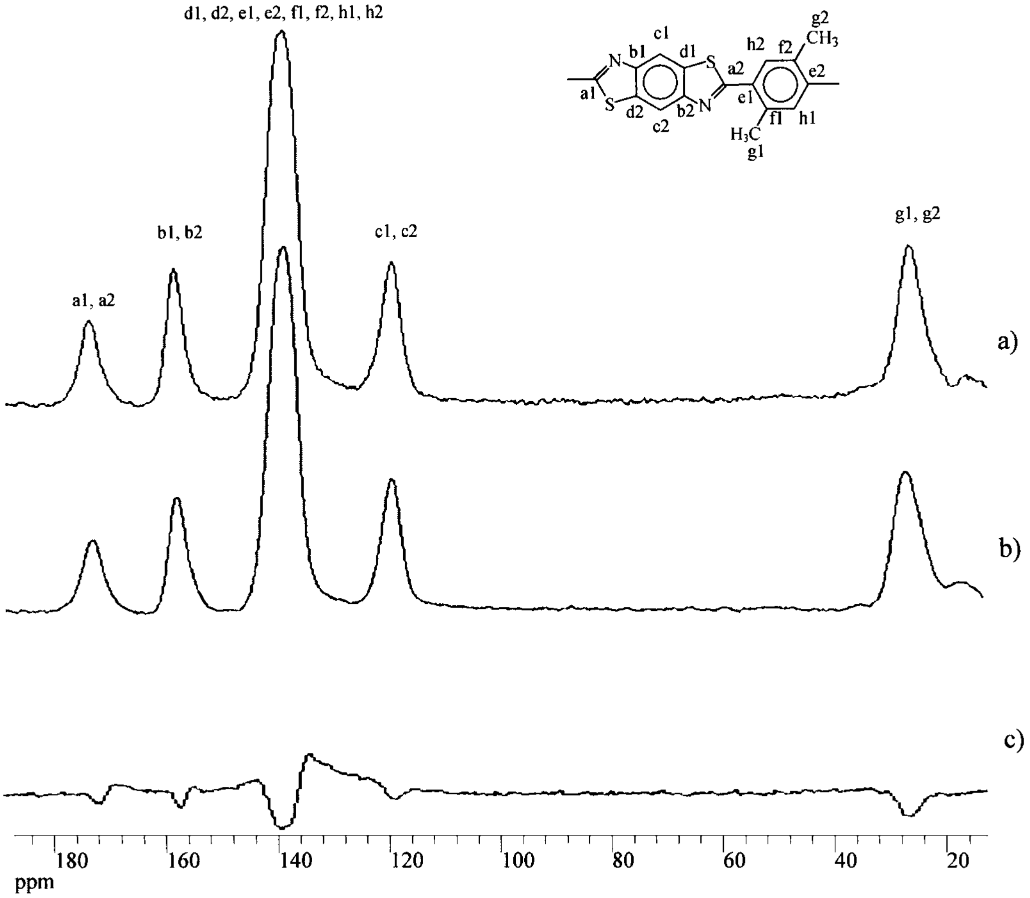

Figure 6 Solid-state ^{13}C NMR spectra of DiMePBZT fibers (a) unirradiated (control), (b) after 850 Mrad dosage, and (c) the difference (a-b) spectrum. Electron irradiation carried out at 225°C, in the absence of tension.

is quite apparent. The drop in tensile strength may be attributed to radiation-induced defects while the decreased tensile modulus can be attributed to changes in orientation. Both observations will be discussed further in subsequent paragraphs. The recoil compressive strength of the fibers receiving a dosage of 850 Mrad was similar to that of the control fiber, while at 170 and 425 Mrad electron radiation dosage the compressive strength was found to be moderately higher. A similar trend was noted by the Elastica loop test. These differences in compressive strength may be ascribed to variances in morphology, which can result from heating and irradiation or the batch heat-treatment of bundles of fibers.

The effect of irradiation on structure is apparent in the WAXD patterns of these fibers presented in Figs 4 and 5. Most notable in Fig. 4 is the decrease in intensity of the (1 0 0) diffraction peak as a function of irradiation, suggesting changes within the crystalline phase. Broadening of the (1 0 0) azimuthal full-width-at-half-maximum, from 12.5° in the control to 15° after 850 Mrad irradiation, indicates some misorientation resulting from irradiation and is consistent with the decrease in modulus.

Solid-state ^{13}C NMR spectra of DiMePBZT fibers before and after irradiation at 225°C are presented in Fig. 6. The absence of a shift corresponding to carbon in CH_2 suggests near complete lack of crosslinking via methylene or ethylene bridge. Therefore it is not surprising that no significant changes in compressive strength or torsional modulus were observed.

A transition from a fibrillar to nonfibrillar morphology on thermal crosslinking of MePBZT [4] and crosslinkable PPTA [20] fibers has been observed and attributed to crosslinking and chain scission, respectively. DiMePBZT fibers irradiated at 225°C were found to exhibit a fibrillar morphology (Fig. 7). Also shown in Fig. 7 is the characteristic kink band, formed during the recoil compressive failure of highly oriented fibers.

Optical micrographs of fibers before and after irradiation (850 Mrad) at 225°C are given in Fig. 8.

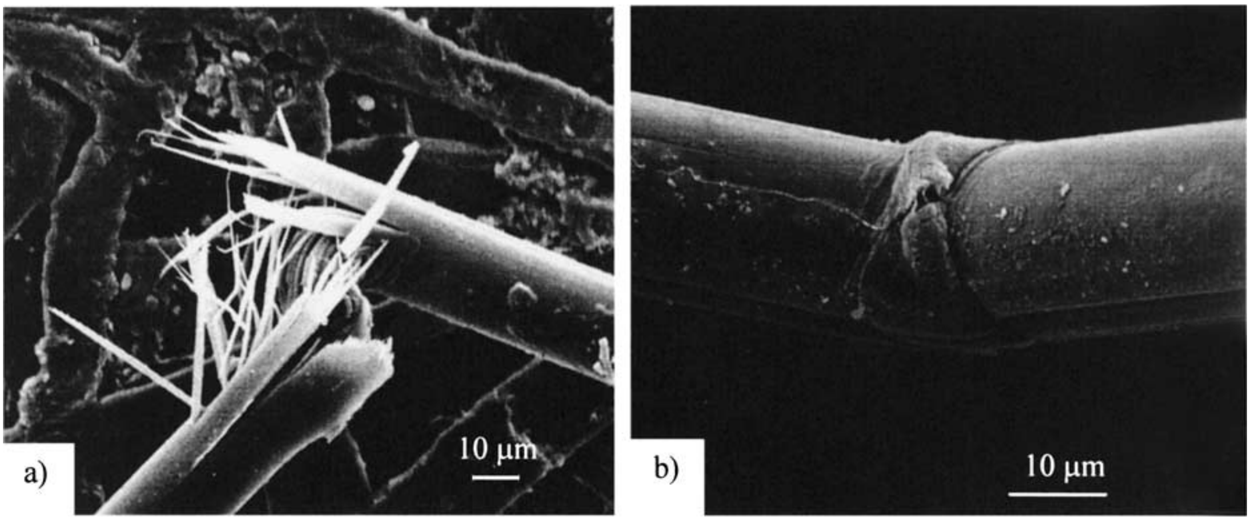

Figure 7 Scanning electron micrographs of DiMePBZT fiber exposed to 850 Mrad electron dosage at 255°C showing the (a) fibrillar structure and (b) recoil compression failure.

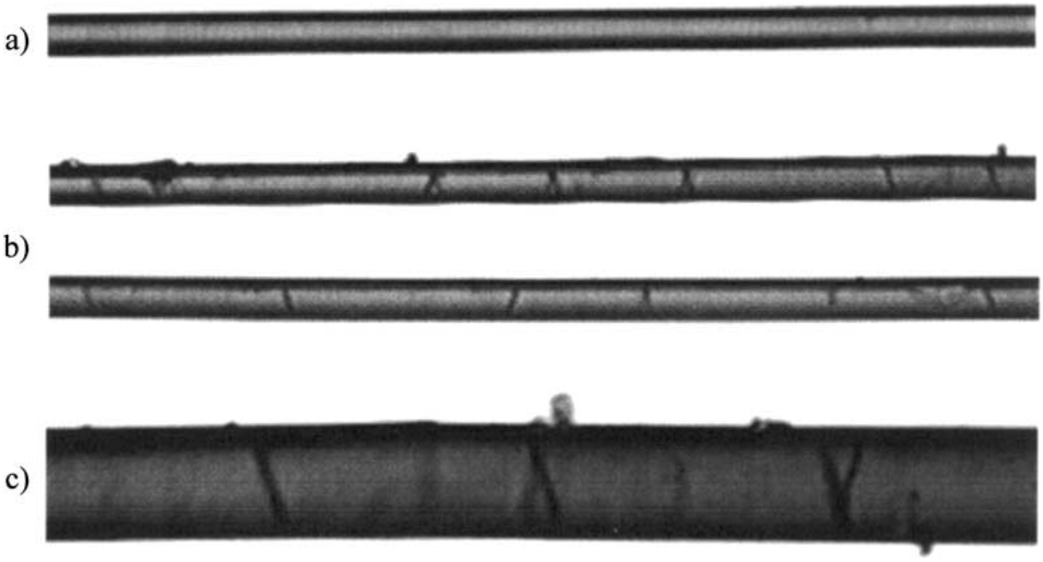

Figure 8 Optical micrographs of (a) unirradiated control DiMePBZT fiber, (b) DiMePBZT fiber exposed to 850 Mrad dosage at 225°C showing internal defects, and (c) enlarged image of internal defects. Fiber diameter is approximately 25 μm in all images.

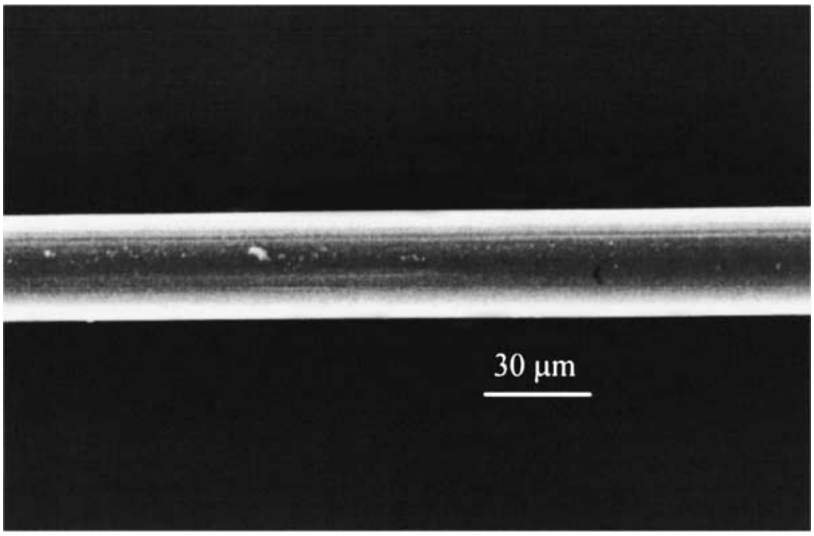

Figure 9 SEM image of the surface of DiMePBZT fibers after receiving 850 Mrad electron radiation at 225°C. Fiber shown is the same as that presented in Fig. 8b and c.

Unirradiated fibers exhibited no visible defects in the optical microscope (Fig. 8a), while irradiated fibers showed significant defects (See Fig. 8b and c). Defects initiated during handling can manifest themselves as kink bands, or other externally obvious modes of failure. However, scanning electron microscope images, shown in Fig. 9, show no defects or kink bands on the irradiated fiber surface. This suggests that the internal defects in DiMePBZT fiber result from heating in combination with electron irradiation (850 Mrad at 225°C) and not from fiber mishandling or heating alone.

4. Conclusions

As-spun, methyl-pendant poly(*p*-phenylene benzobisthiazole) (MePBZT) fiber was exposed to 1 Grad electron radiation at room temperature. Exposure to this high electron radiation dosage resulted in no chemical changes as evidenced by solid state ^{13}C NMR. The irradiated sample was soluble in methane sulfonic acid, suggesting absence of crosslinking. Since high temperature can increase the effect of radiation, electron irradiation studies were conducted on tension heat-treated, dimethyl pendant PBZT (DiMePBZT) fibers at 225°C. ^{13}C solid state NMR spectra of irradiated DiMePBZT (850 Mrad at 225°C) showed no significant evidence of crosslinking via CH_2 groups. The compressive and tensile properties of DiMePBZT fiber remained mostly unchanged at lower radiation levels, while at higher radiation dosages the tensile properties decreased substantially. The compressive strength was left unaffected. Internal defects, originating during heating and irradiation, were observed in irradiated DiMePBZT fiber.

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