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3 Preparation of Polyrotaxane Fibers. Part II: Tensile Properties of Polyrotaxane Fibers Treated
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5 with Various Cross-linking Reagents
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10 Abstract
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12 Polyrotaxane fibers prepared with wet spinning of polyrotaxane consisting of
13 poly(ethylene glycol) and cyclodextrins (CDs) were cross-linked with two different
14 cross-linking reagents, i.e., divinyl sulfone (DVS) and ethylene glycol diglycidyl ether
15 (EGDE), to improve tensile properties of the fibers. By cross-linking with DVS, the values for
16 the tenacity at break and the initial modulus were increased with cross-linking time, while the
17 elongation at break was improved only moderately. On the other hand, drastic improvements
18 in elongation at break were observed after EGDE cross-linking, up to 645% of its original
19 length, although the tenacity at break and the initial modulus showed only slight
20 improvements. **After cross-linking, only minor changes** in the degree of crystallinity fibers
21 were observed by wide-angle X-ray scattering (WAXS) measurements.
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39 Keywords: polyrotaxane fibers, cyclodextrins, cross-linking, tensile measurements
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Introduction

In our previous paper [1] on the functional polyrotaxane fibers, we reported a successful preparation of pure polyrotaxane fibers by wet spinning from polyrotaxane dope solution in various polyrotaxane solvents, i.e., dimethylsulfoxide (DMSO), dimethylacetamide (DMAc) containing lithium chloride (LiCl), and dimethylformamide (DMF) containing LiCl. Electron microscopy observations revealed a smooth and crack-free surface texture of the as-spun polyrotaxane fibers. By tensile measurements, the fibers spun from these three solvent systems showed similar levels of initial modulus and tenacity at break, whose values were relatively lower than those of commercial fibers such as polyesters and rayons. The values for elongation at break, however, were extremely high: up to 388% at 50% RH and 972% at 95% RH. The fiber spun from the DMSO dope solution showed a higher value of the elongation at break than the fibers from DMF/LiCl and DMAc/LiCl.

Much attention has been focused on the recent developments in materials science based on supramolecular chemistry, especially those dealing with polyrotaxane molecules [2-4]. Materials consisting of cross-linked polyrotaxane or cross-linked polyrotaxane blends are called “slide-ring materials” [2,3]. The outstanding characteristics of the slide-ring materials are their high degrees of extensibility, swelling and toughness, imparted by the internal free movements of the cross-linked rings in the polyrotaxane. Whereas previous studies on the slide-ring materials mainly dealt with swollen gels to ensure movement of the polyrotaxane rings, our polyrotaxane fibers are typical instances of polyrotaxane materials without solvents, as well as cellulose/polyrotaxane blend fibers [5] and a cross-linked film of a “sliding graft copolymer (SGC),” i.e., a polyrotaxane possessing freely sliding and rotating side chains [6]. The reported high levels of elongation of the polyrotaxane/cellulose fibers [5] and the elastomeric stress-strain behavior of the cross-linked SGC film [6] strongly suggest movements of the cross-linked polyrotaxane rings in these solid materials without solvents.

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3 The results also imply a successful preparation of novel spandex-like fibers exhibiting high
4 levels of elongation at break and elastomeric properties.
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8 Cross-linking treatments of spun fibers are widely used for the preparation of
9 functional fibers and improvements in physical properties of fibers. For example, previous
10 studies showed remarkable improvements in wet and dry mechanical properties of chitosan
11 fibers by cross-linking [7,8]. Poly(vinyl alcohol) fibers cross-linked with boric acid also
12 showed improved strength and Young's modulus [9]. Cross-linking treatments are also
13 applied to the preparation of rayons [10] and ultra-high-molecular weight polyethylene fibers
14 [11] with improved physical properties, as well as finishing of fabrics such as crease-resistant
15 finishing [12]. Recent investigations have utilized novel bio-mimetic cross-linking
16 mechanisms, mediated by the action of enzymes or oxidation reactions [13,14].
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29 Inspired by the above-mentioned reports on cross-linked fibers, we investigated
30 improvements in the physical properties, especially initial modulus, tenacity at break and
31 elongation at break, of polyrotaxane fibers by chemical cross-linking of the as-spun fibers
32 using two different types of cross-linking reagents, i.e. divinyl sulfone (DVS) and ethylene
33 glycol diglycidyl ether (EGDE).
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43 Materials and Methods

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45 *Reagents.* Polyrotaxane consisting of α -cyclodextrins (α -CDs), poly(ethylene glycol) (PEG,
46 weight average molecular weight of 35000) and adamantane end-capping moieties was
47 donated from Advanced Softmaterials, Inc. (Tokyo, Japan) and used without further
48 purification. The used polyrotaxane was essentially identical to the previously reported
49 sample [15], and was characterized in our previous study [1]. Other chemicals were reagent
50 grade from Wako Pure Chemicals, Inc. (Osaka, Japan). Reagents were used as received,
51 except for *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) which were
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3 purified by vacuum distillation and stored over 3A molecular sieves.
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5 *Post-crosslinking treatment of wet-spun polyrotaxane fibers.* Two kinds of
6 cross-linkers, i.e., divinyl sulfone (DVS) and ethylene glycol diglycidyl ether (EGDE), were
7 used for cross-linking treatment of wet-spun polyrotaxane fibers, which were spun from 20
8 wt% polyrotaxane solution in DMSO using a 22-gauge needle and an apparatus described in
9 our previous study [1]. A cross-linking bath containing DVS was prepared by dissolving DVS
10 at 1% (v/v) in 0.01 M aqueous sodium hydroxide solution (0.01 M NaOH aq.) at 4 °C, while
11 EGDE was dissolved at 37 °C in another cross-linking bath of 0.1 M NaOH aq. at various
12 cross-linker concentrations ranging from 1–10% (v/v). The “as-spun” fibers, i.e., fibers dried
13 at 60 °C overnight after coagulation in a methanol bath [1], were soaked in the above
14 cross-linking baths for various durations up to 24 hours. Temperatures for cross-linking were
15 4 °C in the case of DVS cross-linking and at 37 °C in the case of EGDE cross-linking. After
16 the cross-linking treatments, the fibers were washed thoroughly with distilled water, followed
17 by winding onto a centrifugation tube (Nunc, 50 mL) and subsequent air-drying at room
18 temperature. Note that the fibers in the present study never be treated via any drawing process,
19 and therefore they are essentially “undrawn” fibers, although this designation is not
20 specifically described in the following text.
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43 *Characterization of the fibers.* The microscopic morphologies of the spun fibers
44 were observed by a Hitachi S-2380N scanning electron microscope, after Au-Pd ion
45 sputtering for 90 seconds. Tensile measurements of the obtained polyrotaxane fibers were
46 examined essentially in a similar manner to our previous study [1], using a universal testing
47 machine (STA-1150, Orientec Co., Ltd., Tokyo, Japan, a load cell of 10 N, a span length of
48 20 mm, and a tensile rate of 20 mm/min) at 25 °C and 50% RH. Wide-angle X-ray scattering
49 (WAXS) measurements of the fibers were performed as described previously [1]. Briefly, a
50 bundle of about 30 fibers was subjected to measurement using a rotating anode X-ray
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3 generator (Rigaku Rotaflex RU-200BH), with a flat-plate vacuum camera and a Fuji Imaging
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5 Plate and Ni-filtered Cu- K_{α} radiation ($\lambda = 0.1542$ nm) at 150 kV and 40 mA. The camera
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7 length (approximately 52.5 mm) was calibrated with crystalline sodium fluoride.
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10 11 12 Results and Discussion

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14 *Cross-linking treatment of the polyrotaxane fibers.* The two types of cross-linking
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16 reagents used in this study, i.e., DVS and EGDE, were selected for post-crosslinking
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18 treatment of the polyrotaxane fibers. These reagents are known to cross-link two hydroxyl
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20 groups in a dilute alkaline solution, and are used for the preparation of a wide variety of
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22 functional materials *via* cross-linking, such as polysaccharide-based gels [16–19],
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24 chitosan/silk blend membrane [20], porous silk fibroin gels [21] and polyrotaxane gels
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26 [22–24].
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32 Since the fibers are expected to become insoluble in solvents after the cross-linking
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34 treatment, solubility of the treated fibers in DMSO, a good solvent for the starting
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36 polyrotaxane and therefore for the untreated fiber, was **examined**. Under the cross-linking
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38 conditions described in the Materials and Methods section, treatment using the DVS bath for
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40 more than 1 hour gave a cross-linked fiber insoluble in DMSO. The treatment with the EGDE
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42 bath for 1 hour at an EGDE concentration of 10% also gave an insoluble fiber, whereas
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44 treatment for 1 hour at EGDE concentrations of 1% and 5% resulted in the dissolution of the
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46 obtained fiber. Thus, except for the latter two treatments, these results clearly indicated the
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48 successful formation of the cross-linked polyrotaxane fibers, which may be useful in good
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50 solvents of polyrotaxane, such as DMSO and aqueous NaOH [25–27].
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54 *Morphology of the cross-linked fibers.* All of the obtained cross-linked fibers exhibited a
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56 semi-transparent and smooth surface texture, and were thus almost identical to the untreated
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58 (uncrosslinked) fibers [1]. Scanning electron micrographs of these fibers also show a smooth
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3 surface texture at the microscopic level without any cracks (Figure 1). Prolonging the
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5 cross-linking time does not seem to alter the surface smoothness of the treated fibers. Values
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7 of the fiber diameters measured from micrographs are summarized in Tables 1 and 2. It should
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9 be noted that all the cross-linked fibers had diameter values less than those of untreated fibers,
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11 probably due to very slow dissolution of the fiber during the cross-linking treatment. Aqueous
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13 NaOH is known to be a good solvent for polyrotaxane [25-27]. Although our preliminary
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15 qualitative experiments showed no dissolution of the polyrotaxane used in NaOH aq. (below
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17 0.1 M), trace dissolution of the polyrotaxane fibers into the cross-linking baths, which contain
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19 0.01–0.1 M NaOH, might be possible. Values of the fiber diameter for the fibers treated in the
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21 EGDE bath are lower than those of the fibers treated in the DVS bath, probably due to a
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23 slightly higher rate of dissolution in the former than in the latter, which is dependent on the
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25 concentrations of alkali (0.1 M and 0.01 M, respectively). Other possibilities responsible for
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27 the decrease in fiber diameter might be a decrease in free volume or an increase in the degree
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29 of crystallinity of the fibers.
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36 *Physical properties of the cross-linked fibers.* Figure 2 shows typical stress-elongation
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38 curves for the cross-linked polyrotaxane fibers. The calculated values of tenacity at break,
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40 initial modulus and elongation at break are also summarized in Tables 1 and 2.
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43 As shown in Table 1, the values of the initial modulus were improved after
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45 cross-linking treatment with DVS. The values of the tenacity at break also increased by DVS
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47 cross-linking, and plateaued after 12 hours of treatment at about 1.6 times the value for the
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49 untreated fiber. The values of the elongation at break of the DVS-treated fibers are all higher
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51 than that for the untreated fiber, although the values gradually decreased at cross-linking times
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53 above 6 hours. On the other hand, the fibers treated with EGDE showed a remarkable
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55 improvement in elongation. Namely, the values of elongation at break increased with
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57 cross-linking treatment time, reaching a value 1.6 times higher than that of the untreated fiber
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3 for up to 6 hours of cross-linking treatment, after which the values plateaued. By EGDE
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5 treatment, however, the values of the initial modulus were slightly decreased by cross-linking
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7 over 1 hour, and the values of the tenacity at break were almost unchanged.
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10 Cross-linking treatments of fibers usually improve the physical properties of fibers,
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12 such as tenacity and modulus [9–11]. In addition, materials consisting of cross-linked
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14 polyrotaxanes (slide-ring materials) are known to be strengthened thanks to the so-called
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16 “pully effect,” i.e., a relaxation of internal stress by optimized movements of the cross-linked
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18 rings in the polyrotaxane [2,3]. The improvements in initial modulus and tenacity at break of
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20 the DVS-treated fibers can be explained with this mechanism. On the other hand, levels of
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22 elongation of the EGDE-treated fibers are quite higher than those of the DVS-treated fibers
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24 and those of the untreated fibers, showing an elongation comparable to polyurethane fibers [1].
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26 A high level of extensibility imparted by the internal sliding of cross-linked rings is another
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28 outstanding characteristic of the slide-ring materials, i.e., cross-linked polyrotaxane materials
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30 [2,3]. Therefore, the two types of fibers, treated with DVS and EGDE, respectively, were
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32 found to exhibit the two distinct advantages of slide-ring materials.
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38 Although the reason for the difference in the behaviors of these two **cross-linked**
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40 fibers is still unclear, such a difference may be affected by various properties of the
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42 cross-linking reagent, including molecular flexibility and rate of reactivity. **The latter is likely**
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44 to have a marked influence on the properties of the treated fibers, since it alters the degree of
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46 cross-linking. However, precise measurements of the degree of cross-linking of these fibers
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48 are quite difficult to make. The added cross-linkers might either be unused or remain with one
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50 hand open (i.e., does not bind two polyrotaxane chains). **An estimation of the degree of**
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52 **cross-linking may be possible by analyses of the cross-linked fibers, namely scission of the**
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54 **end-capping moiety of the polyrotaxane, dissociation of all CD molecules including**
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56 **cross-linked and uncrosslinked ones, and subsequent size exclusion chromatography or mass**
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3 **spectrometry**. The polyrotaxane used in the present study, however, is difficult to break at its
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5 bulky end moieties, which are linked to the axis molecule *via* stable amide linkages [15].
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7 Although cross-linking densities of common cross-linked materials such as gels and rubbers
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9 can be estimated by dynamic mechanical measurements, this method is thought to be
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11 inapplicable to slide-ring materials possessing mobile cross-links [28]. Although the precise
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13 cross-linking density in the present cross-linked fibers **should** be qualitatively elucidated in
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15 future investigations, the cross-linking treatment of the polyrotaxane fibers was found to give
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17 fibers with improved tenacity, modulus or elongation properties.
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22 *Wide-angle X-ray scattering (WAXS) measurements of the fibers after cross-linking treatment.*
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25 WAXS results of the polyrotaxane fibers prepared in the present study, including
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27 uncrosslinked, DVS-treated and EGDE-treated ones, indicated almost the same **levels of**
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29 crystallinity. Typical 2θ -intensity profiles of the three fibers, i.e., the uncrosslinked fiber, the
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31 fiber treated with DVS for 24 hours and the fiber treated with EGDE for 24 hours, are shown
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33 in Figure 3, in which all samples show no drastic **difference** in crystal form and degree of
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35 crystallinity. All exhibited profiles including crystalline peaks characteristic for crystalline
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37 polyrotaxane [1]. **WAXS profiles for the cross-linked fibers (Figures 3(b) and 3(c)) seem to be**
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39 **slightly sharper than that for the uncross-linked fiber (Figure 3(a)), although its quantitative**
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41 **degree could not be estimated. The slight increase in the degree of crystallinity after**
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43 **cross-linking treatment may correspond to the decrease in fiber diameters, as stated above.**
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45 **However, the** result suggests that the cross-linking procedures employed in the present study
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47 have **only a minor** effect on the crystallinity of the spun polyrotaxane fibers.
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55 Conclusion

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57 The cross-linking treatments of polyrotaxane fibers with two types of cross-linkers,
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59 namely DVS and EGDE, successfully produced cross-linked fibers that were insoluble in
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3 DMSO. The DVS-treated fibers showed improved tenacity and modulus instead of decrease
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5 in elongation, whereas the EGDE-treated fibers showed an increased degree of elongation up
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7 to 645% and only minor improvements in tenacity and modulus. The degree of crystallinity of
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9 all the fibers did not change after all cross-linking treatments. These results indicate that the
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11 cross-linker can be selected to fulfill the desired purpose, i.e., whether physical properties or
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13 degree of elongation need to be improved. Another approach to polyrotaxane fiber treatment,
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15 i.e., improvement of physical properties by drawing of polyrotaxane fibers, is currently being
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17 undertaken underway in our laboratories.
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Table 1: Properties of the polyrotaxane fibers cross-linked with DVS

Time of treatment, hours	Diameters, μm	Fineness, tex	Tenacity at break, cN/dtex	Initial modulus, cN/dtex	Elongation at break, %
0 (untreated)	139	180	0.23 ± 0.02	14.6 ± 0.8	388 ± 112
1	120	147	0.33 ± 0.01	17.8 ± 1.0	443 ± 21
6	117	150	0.47 ± 0.02	19.0 ± 1.0	554 ± 55
12	123	155	0.51 ± 0.02	20.6 ± 0.8	455 ± 22
24	116	157	0.52 ± 0.02	19.1 ± 1.0	386 ± 47

Table 2: Properties of the polyrotaxane fibers cross-linked with EGDE

Time of treatment, hours	Diameters, μm	Fineness, tex	Tenacity at break, cN/dtex	Initial modulus, cN/dtex	Elongation at break, %
0 (untreated)	139	180	0.23 ± 0.02	14.6 ± 0.8	388 ± 112
1	110	103	0.33 ± 0.02	15.3 ± 1.1	556 ± 64
6	106	108	0.35 ± 0.02	11.1 ± 1.1	628 ± 70
12	107	110	0.34 ± 0.02	8.6 ± 0.9	645 ± 31
24	110	112	0.34 ± 0.03	6.0 ± 1.2	600 ± 67

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3 Figure Captions:
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8 Figure 1: Scanning electron micrographs of (a) an untreated (uncrosslinked) polyrotaxane
9 fiber, (b) a fiber treated with DVS for 6 hours, (c) a fiber treated with DVS for 12 hours, (d) a
10 fiber treated with DVS for 24 hours, (e) a fiber treated with EGDE for 6 hours, (f) a fiber
11 treated with EGDE for 12 hours, (g) a fiber treated with EGDE for 24 hours, and (h) a
12 cross-sectional view of the fiber treated with DVS for 24 hours. Scale bars are 100 μm .
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24 Figure 2: Typical tenacity versus elongation curves of the polyrotaxane fibers cross-linked
25 with DVS (a) and EGDE (b). Closed circles, uncrosslinked fiber; open circles, cross-linked
26 for 1 h; closed triangles, cross-linked for 6 h; open triangles, cross-linked for 12 h; and
27 crosses, cross-linked for 24 h.
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34 Figure 3: Wide-angle X-ray scattering profiles of (a) uncrosslinked fibers, (b) fibers
35 cross-linked with DVS for 24 hours and (c) fibers cross-linked with EGDE for 24 hours.
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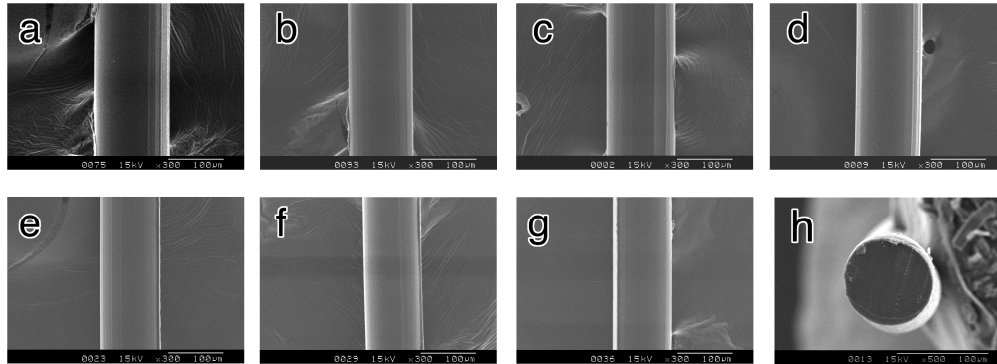


Figure 1: Scanning electron micrographs of (a) an untreated (uncrosslinked) polyrotaxane fiber, (b) a fiber treated with DVS for 6 hours, (c) a fiber treated with DVS for 12 hours, (d) a fiber treated with DVS for 24 hours, (e) a fiber treated with EGDE for 6 hours, (f) a fiber treated with EGDE for 12 hours, (g) a fiber treated with EGDE for 24 hours, and (h) a cross-sectional view of the fiber treated with DVS for 24 hours. Scale bars are 100 μm .
158x57mm (576 x 576 DPI)

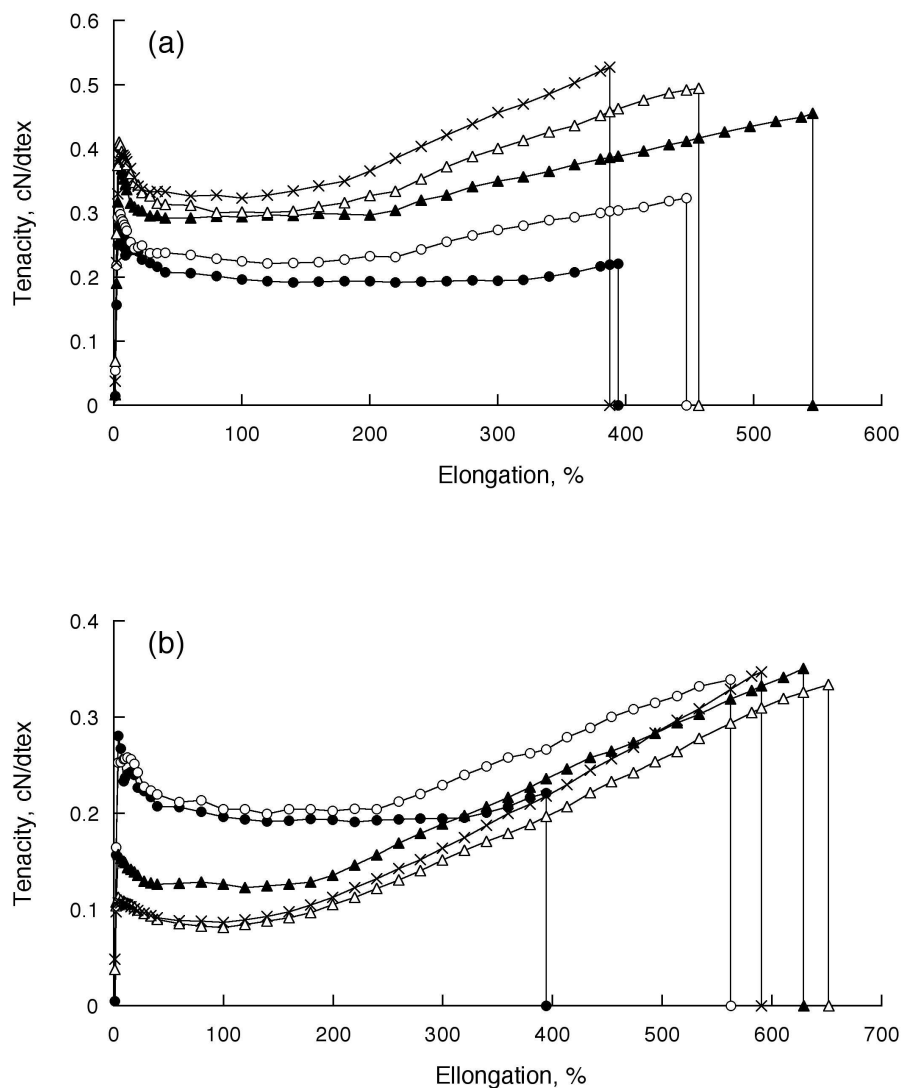


Figure 2. Typical tenacity versus elongation curves of the polyrotaxane fibers cross-linked with DVS (a) and EGDE (b). In both plots, closed circle; uncrosslinked fiber, open circle; cross-linked for 1 h, closed triangle; cross-linked for 6 h, open triangle, cross-linked for 12 h and cross; cross-linked for 24 h.

144x179mm (400 x 400 DPI)

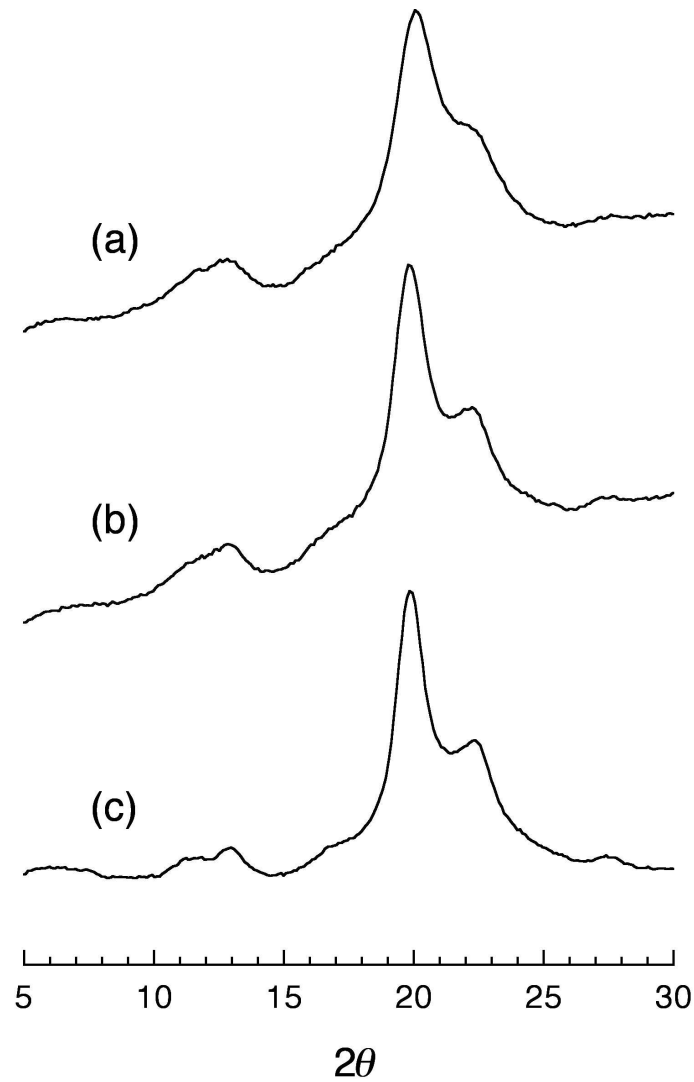


Figure 3. Wide-angle X-ray scattering profiles of (a) uncrosslinked fibers, (b) fibers cross-linked with DVS for 24 hours and (c) fibers cross-linked with EGDE for 24 hours.
119x185mm (360 x 360 DPI)