

Polymer Communication

A preliminary study for fiber spinning of mixed solutions of polyrotaxane and cellulose in a dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system

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Received 20 July 2006; received in revised form 15 September 2006; accepted 24 September 2006

Available online 24 October 2006

Abstract

Polyrotaxane fiber and polyrotaxane/cellulose blend fibers were prepared by wet-spinning of the polyrotaxane or polyrotaxane/cellulose blend solution dissolved in the new solvent system, i.e. dimethylacetamide/lithium chloride (DMAc/LiCl), into methanol and a subsequent annealing. In the resultant polyrotaxane/cellulose fiber, some undissolved rodlike cellulose microcrystals were oriented along with the fiber axis, resulting in formation of nanocomposite-like structure. From tensile measurements, it was found that the Young's modulus and tensile strength of the fibers with polyrotaxane/cellulose ratio of 1:1 and 2:1 were higher than those of the pure cellulose fiber. Although the mechanical properties of the fiber with polyrotaxane/cellulose ratio of 4:1 and the pure polyrotaxane fiber were lower than those of the pure cellulose fiber, these fibers showed significantly large strain at break (up to 90% strain), presumably due to the sliding of the cyclodextrin rings of the polyrotaxane in the fibers.

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Keywords: Polyrotaxane; Fiber spinning; Nanocomposite structure

1. Introduction

Polyrotaxane is a typical supermolecule in which many cyclic molecules are threaded onto a single linear molecule whose end is capped with bulky functional groups to prevent dethreading. A polyrotaxane consisting of poly(ethylene glycol) (PEG) and α -cyclodextrins (α -CD) was first successfully synthesized by several research groups in the 1990s [1–5], and is the most investigated polyrotaxane to date [6–16].

This polyrotaxane is intriguing not only as an object of supramolecular study but also as a precursor of novel soft materials. As well as the preparation and investigation of nano-scale supramolecular materials such as molecular tubes [2b] and insulated molecular wires [7], it has been applied as a component of macroscopic materials with supramolecular networks, such as polyrotaxane gels [6,12–14]. Most of these, however, consist almost completely of polyrotaxane, and there have been few studies of materials prepared using a combination of polyrotaxane and other components [6]. One reason for this is a lack of good solvents for the polyrotaxane; it was initially reported to be soluble only in DMSO and aqueous sodium hydroxide solution, and insoluble in all other solvents [1,2]. This infusibility strongly restricted the application of polyrotaxane in blending, casting and molding techniques. Recently, some of the authors achieved dissolution of the polyrotaxane

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in several new solvent systems, including a dimethylacetamide/lithium salt system [15] and ionic liquids [16]. The discovery of these new solvents for polyrotaxane allows the possibility of a wider variety of polyrotaxane modifications [15], as well as the potential for innovative investigations of polymer blends containing polyrotaxane, because dimethylacetamide/lithium chloride (DMAc/LiCl) is known to dissolve a wide variety of polymers, including cellulose, chitin and polyamide [17]. A DMAc/LiCl solvent has been utilized in polymer blending as a cosolvent for synthetic polymer and natural crystalline polysaccharides [18], and fiber spinning of regenerated cellulose from this solvent has also been investigated [19]. As reported previously, the PEG/CD polyrotaxane was readily dissolved in DMAc/LiCl solvent, presumably due to the interruption of inter- and intramolecular hydrogen bonding between polyrotaxane CD molecules by DMAc/LiCl macro-cation complexation of CD hydroxyls [15a], in a similar process for the dissolution of cellulose [17,18]. The dissolution of the polyrotaxane and the above-mentioned polymers in DMAc/LiCl encouraged us to prepare a blend polymer of the polyrotaxane and cellulose, and to attempt fiber spinning from it. In the present study, fiber spinning from polyrotaxane and cellulose was examined in a first attempt to blend polyrotaxane with another polymer. The fibers obtained were characterized by polarized optical microscopy, X-ray diffractometry and tensile measurements.

2. Experimental

The polyrotaxane, supplied by Advanced Softmaterials Inc. (Tokyo, Japan), consisted of α -CD, poly(ethylene glycol) carboxylic acid (PEG-COOH) and a terminal adamantane moiety, and is essentially the same as the sample prepared in our previous study [10]. According to information from the supplier, the polyrotaxane contained 90–100 CDs in a single molecule, corresponding to an inclusion ratio of ca. 25%. Microcrystalline cellulose (CF11, Whatman, UK) was used as received. Other chemicals were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Dimethylacetamide (DMAc) was kept over dried 4 Å molecular sieves. Anhydrous lithium chloride (LiCl) was dried when necessary at 105 °C for 2 h.

Cellulose was dissolved in DMAc/LiCl with preheating, as reported previously [17a,20,21], although this method has been reported to cause partial degradation of the cellulose chain. The solvent exchange technique [17d,18c,21], which does not cause degradation, may be used as an alternative. Five grams of cellulose was dispersed in 100 ml of DMAc and heated at 130 °C for 2 h. After the mixture had been cooled to 100 °C, 10 g of LiCl was added to the mixture and further stirred to give a transparent solution, followed by cooling to room temperature; the solution was used directly in the following procedure. Polyrotaxane solution in DMAc/LiCl (8%) solvent, with a polymer content of 10%, was prepared by overnight stirring at room temperature. Although gentle heating up to 60 °C was found to accelerate dissolution (for example, to within several hours), high temperatures (above

80 °C) should be avoided due to the possibility, as previously reported, of decomposition of polysaccharides by activated species generated in DMAc/LiCl [22]. For spinning of the pure polyrotaxane fiber, a solution of 20 wt% polyrotaxane content was prepared, as spinning from a more dilute solution was found to be difficult. For blending with the cellulose solution, a 10 wt% solution was prepared.

Blended solutions of cellulose and polyrotaxane were prepared by vigorously mixing the polyrotaxane and cellulose solutions at various ratios (1:2, 1:1 and 2:1, corresponding to polymer weight ratios of 1:1, 2:1 and 4:1). The mixed solutions were extruded from a syringe equipped with a cut pipette tip into a coagulation bath filled with methanol. The resulting coagulated gel-like fiber was wound around a polypropylene centrifugation tube, followed by drying in an oven at 60 °C.

The morphologies and optical anisotropy of the fibers were observed with a polarized optical microscope (Olympus BX51M). Wide angle X-ray scattering measurements of the fibers were performed using a Rigaku RU-200BH rotating anode X-ray generator equipped with a flat-plate vacuum camera. Ni-filtered Cu K α radiation ($\lambda = 0.1542$ nm) generated at 50 kV and 100 mA was collimated by a pinhole of 0.3 mm diameter. Diffraction images recorded on a Fuji Imaging Plate were converted into 2θ -intensity profiles using Rigaku R-Axis software. Camera length was calibrated using crystalline sodium fluoride. Young's moduli and tensile strengths of the fibers were measured using an RSAIII (TA Instruments) at room temperature. The measurements were performed on a monofilament of each fiber with a span length of ca. 15 ± 1 mm (slightly varied for samples) at a tensile speed of 1/100 of the initial span length per second (i.e. 0.15 mm/s for a sample with initial span length of 15 mm). The effect of these slight variations in span length and tensile speed on the results may be negligible. The cross-sectional areas of the fibers were calculated from the optical microscope images under the assumption that the cross section was elliptical (for the pure polyrotaxane fiber, diameter 70×160 μm) or circular (for the blend fiber, diameter 180 μm). Independent results from 10 pure polyrotaxane fibers and five other fibers were averaged.

3. Results and discussion

With a series of procedures described above, flexible fibers, some of which are shown in Fig. 1, were prepared from a pure cellulose solution, a pure polyrotaxane solution or a mixture of both in DMAc/LiCl (8–9% LiCl concentration) by wet-spinning into methanol followed by annealing at 60 °C. Optical and polarized optical micrographs of the fibers, shown in Fig. 2, show a number of characteristics. The diameter of the pure polyrotaxane fiber is ca. 70×160 μm , and that of the blend fiber is ca. 180 μm . The pure polyrotaxane fiber seemed to have an elliptical cross section, since the width of the fiber observed under an optical microscope changed periodically between 70 and 160 μm by rotating the fiber. The size and shape of the cross-sectional areas presumably depend on that of the scissored pipette tip used in preparation, or softness

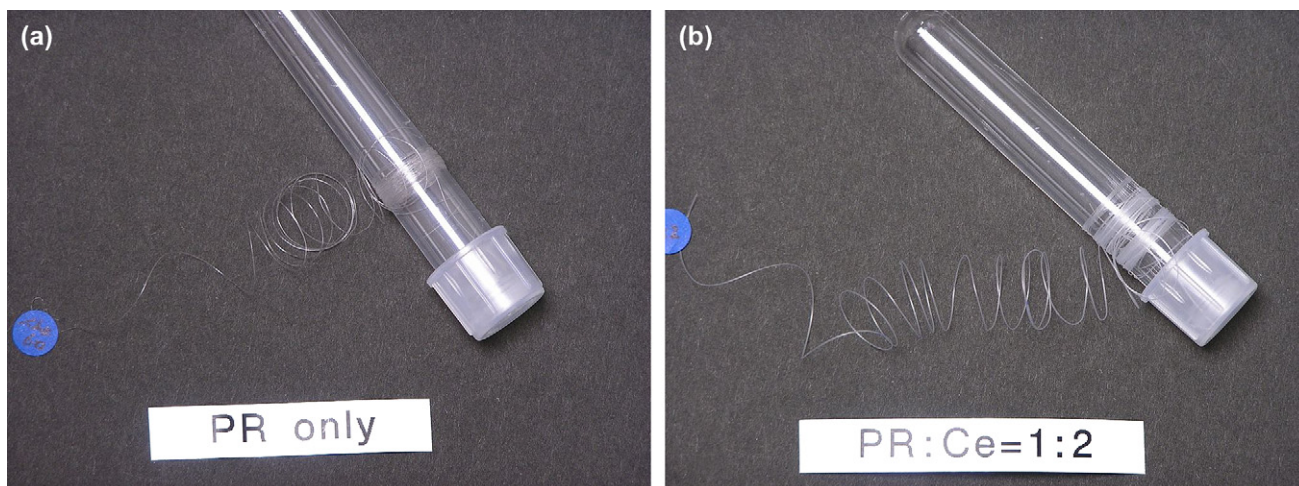


Fig. 1. Appearances of: (a) pure polyrotaxane fiber and (b) polyrotaxane/cellulose hybrid fiber (solution mixing ratio of 1:2, polymer weight ratio of 1:1). Note that the ratio described in the photograph are the volume ratios of the both solutions, not the polymer weight ratios.

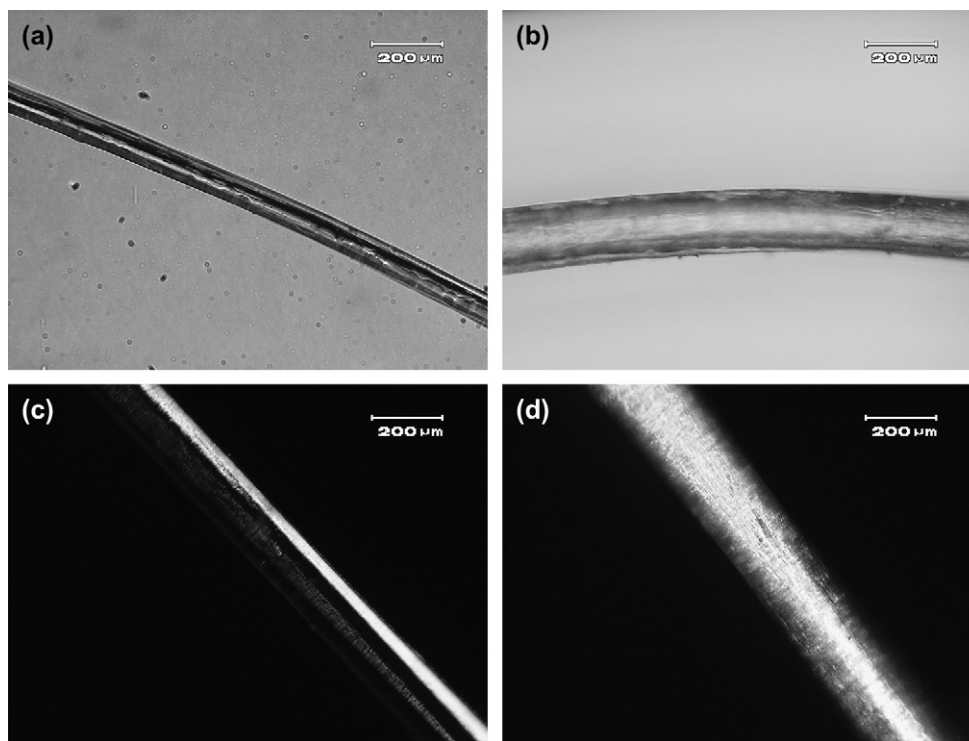


Fig. 2. Optical micrographs of: (a) pure polyrotaxane fiber and (b) polyrotaxane/cellulose hybrid fiber (polymer weight ratio of 1:1), and polarized optical micrographs of (c) pure cellulose fiber (part of the fiber shows birefringence) and (d) polyrotaxane/cellulose hybrid fiber (polymer weight ratio of 1:1). All scale bars are 200 μm . Although the pure polyrotaxane fiber (a) has an elliptical cross section (see the text), only a micrograph from one direction is presented.

of the fibers just after extrusion into methanol; namely, the pure polyrotaxane fiber which was relatively soft gel-like at the extrusion might be pressed during winding to form an elliptical cross section, whereas the fibers blended with cellulose were rapidly coagulated in the methanol bath and unchanged morphologically by winding. The surface texture is smooth, without any apparent phase separation; and there is a certain degree of optical anisotropy, which is enhanced by extrusion. In the spinning process, the choice of dissolution medium and coagulation bath seemed to be essential, since

other combinations such as DMSO and water did not show good spinnability, resulting in a bulky precipitation of polyrotaxane.

Wide angle X-ray scattering (WAXS) fiber diagrams of several fibers are shown in Fig. 3, together with the corresponding 2θ –intensity profiles. The diffraction pattern of the pure polyrotaxane fiber showed several peaks at 5.3° , 12.8° , 19.7° and 22.4° , corresponding to the (100), (110), (210) and (300) planes of crystalline polyrotaxane [23]. No specific orientation of the polyrotaxane crystals was shown by diffraction. The

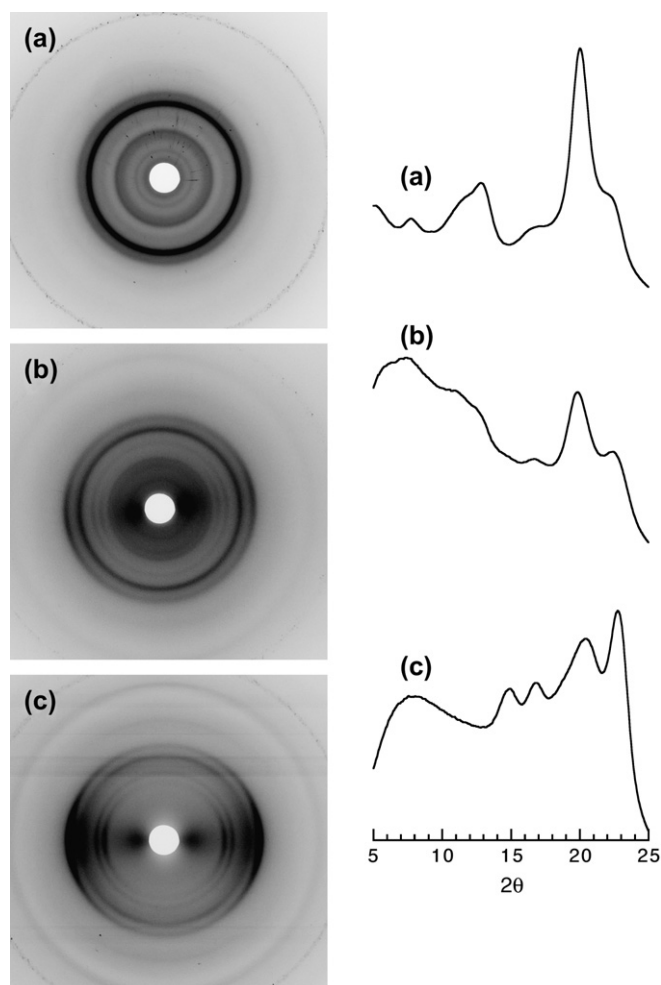


Fig. 3. (Left) X-ray fiber diagrams of: (a) pure polyrotaxane fibers, (b) polyrotaxane/cellulose hybrid fibers (polymer weight ratio of 1:1) and (c) pure cellulose fibers. (Right) 2θ -I profiles of: (a) pure polyrotaxane fibers, (b) polyrotaxane/cellulose hybrid fibers (polymer weight ratio of 1:1) and (c) pure cellulose fibers.

WAXS results for the pure cellulose fiber showed a mixed profile of two crystal forms of cellulose, namely “native” cellulose I and “regenerated” cellulose II. Strong crystalline peaks at 14.8° , 16.8° and 22.6° correspond to the (110), $(1\bar{1}0)$, and (200) planes of cellulose I crystals [24], while a broad crystalline peak at around 19.8° is due to $(1\bar{1}0)$ plane of cellulose II crystals [24]. The X-ray profile of the polyrotaxane/cellulose = 1:1 fiber consisted of all of the above peaks in an overlapping arrangement, although it was obscured by the low degree of crystallinity.

The cellulose regenerated from DMAc/LiCl solutions after complete dissolution has been reported to form the cellulose II crystal form [18], so the present results suggest that the dissolution of cellulose was somewhat incomplete: the starting cellulose solution in the DMAc/LiCl system probably contained a certain amount of undissolved native cellulose crystallites, so-called “cellulose microcrystals”, with a size of ca. 10×150 nm [25]. Previous reports have demonstrated that complete dissolution of native cellulose in DMAc/LiCl is attained only after strongly dedicated efforts [17,18].

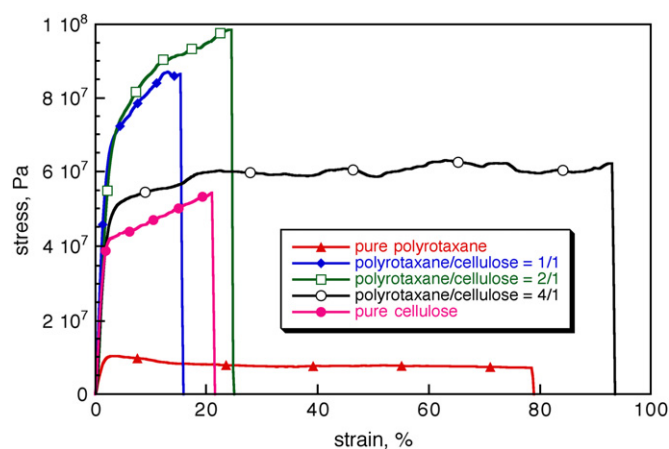


Fig. 4. Typical stress–strain curves of the fibers.

Dissolution of cellulose at molecular level requires lengthy stirring—sometimes up to a month—in solvent, and even then the remaining undissolved cellulose particles must be removed by filtration [18]. Even at low concentrations—less than 1% cellulose content—light scattering studies suggested the presence of aggregated structures in the solvent [17d]. The aggregation of cellulose molecules may be unavoidable at the high concentrations required in the present study. Although the dissolution procedure employed here is useful for the preparation of concentrated cellulose solutions, which are used for preparing materials such as fibers or hydrogel films [20], the fibers obtained in the present study are not so-called “miscible polymer blends”, and are not appropriate for estimation of molecular level blending or molecular miscibility.

The partial infusibility of cellulose in the present sample, however, is responsible for another characteristic feature of the spun fibers. The X-ray diffractograms in Fig. 3 clearly show the orientation of the rodlike cellulose microcrystals by the local distribution of cellulose I crystal diffractions around the equator. The results indicate that in the fiber, the oriented rodlike cellulose microcrystals are covered with a mixed matrix of crystalline cellulose II and polyrotaxane, forming a nanocomposite-like structure. An analogous “all-cellulose” nanocomposite [26] was prepared via a method similar to ours, i.e. partial dissolution of native microcrystalline cellulose in DMAc/LiCl solvent, followed by molding. The formation of a nanocomposite structure, which is retained in the polyrotaxane/cellulose blend fiber, seems to contribute to the strength of the blend fiber: the rodlike cellulose microcrystals, already effectively utilized in other nanocomposite systems [27], are expected to have a high Young’s modulus (ca. 130–150 GPa [28]) and high tensile strength (in the order of 10 GPa [26,29]).

Typical stress–strain curves of the fibers are shown in Fig. 4, and the Young’s modulus and tensile strength calculated from the curves are listed on Table 1 with standard deviation. Since only the sample profiles with the highest elongations are plotted in Fig. 4, the Young’s modulus and the stress at break slightly deviate from the averaged values in

Table 1
Polymer composition (polymer weight ratio) and average mechanical properties (Young's modulus, tensile strength and elongation at break) of the fibers

Samples	Polymer weight ratio (polyrotaxane/cellulose)	Young's modulus, Pa	Tensile strength, Pa	Elongation at break, %
Pure cellulose fiber	0:1	$3.41 \pm 0.99 \times 10^9$	$6.65 \pm 1.54 \times 10^7$	14.2 ± 6.2
Blend fiber 1:1	1:1	$5.01 \pm 0.57 \times 10^9$	$9.50 \pm 1.02 \times 10^7$	12.6 ± 2.1
Blend fiber 2:1	2:1	$4.23 \pm 0.42 \times 10^9$	$8.44 \pm 0.81 \times 10^7$	20.5 ± 3.4
Blend fiber 4:1	4:1	$2.92 \pm 0.67 \times 10^9$	$5.53 \pm 0.85 \times 10^7$	34.1 ± 34.2
Pure polyrotaxane fiber	1:0	$7.08 \pm 0.30 \times 10^8$	$1.16 \pm 0.10 \times 10^7$ ($9.18 \pm 1.66 \times 10^6$) ^a	39.8 ± 33.8

All mechanical data are accompanied by standard deviation.

^a The yield stress is expressed as the tensile strength of the pure polyrotaxane fiber since it was higher than the stress at break. The average stress at break is described in the parenthesis (see text).

Table 1. It should be noted that the mechanical properties of our pure cellulose fiber were found to be significantly lower than those reported for the conventional regenerated cellulose fibers or films [19,26], contrary to our anticipation of reinforcement by the formation of nanocomposite structures, as stated above. Since a reasonable explanation for this observation is not given yet, we discuss hereafter only the relative changes in mechanical properties given by the addition of the polyrotaxane, and do not mention the comparison of the absolute values. It may be also speculated that the “all-cellulose” nanocomposite [26] might contain a larger amount of cellulose microcrystals than the reported values estimated by X-ray diffractions (24–59%) due to the shorter dissolution time during preparation (5 min), and it might contribute to the mechanical strength higher than that of our cellulose fibers.

While the pure polyrotaxane fiber was weakest, it showed a highly intriguing tensile profile, as shown in Fig. 4: the stress showed a yield point at its initial state, followed by a long elongation with slow relaxation and slight decrease in stress, after which the fiber broke. The values of elongation at break for the pure polyrotaxane fiber were distributed within a wide range (7–80%) and were apparently poorly reproducible, while other mechanical properties such as Young's modulus, maximum strength and stress at break were almost reproducible. Both the maximum stress and the stress at break are listed in Table 1. The blend fibers with polyrotaxane/cellulose weight ratios of 1:1 and 2:1 showed higher moduli and strength than those of pure cellulose fiber, while these properties had lower values in the fiber with a polyrotaxane/cellulose weight ratio of 4:1. These results show that the Young's modulus and tensile strength of polyrotaxane/cellulose blend fibers are greater in fibers with weight ratios within a limited range. Although the causes of these mechanical behaviors will be elucidated in future detailed investigations, it is likely that the CD rings, interacting with hydroxyl groups in the cellulose anhydroglucose unit via hydrogen bonding, may slide along with the PEG chain in the blend fiber during drawing, resulting in a larger elongation than that of the pure cellulose fiber. While the increase in ductility of the cellulose by blending with PEG, which was well described in the previous study [30], may be assumed one of the reasons of our findings of the large elongation, the extraordinarily large strain more than 90% does not seem to be explained only by the contribution of PEG blending. Indeed, as shown in Fig. 4 and Table 1,

the pure polyrotaxane fiber and the fiber with a polyrotaxane/cellulose ratio of 4:1 showed particularly high elongation values at break, although they were widely distributed for different samples (7–80% and 4–93%, respectively).

In the present study, we demonstrated the first preparation of composite fibers consisting of PEG/CD polyrotaxane and another polymer. Although positive drawing was not applied during fiber formation, the obtained fiber showed optical anisotropy, which indicates orientation of the polymer and/or cellulose crystallites along the fiber axis. Larger values for physical properties such as Young's modulus are expected when the drawing process is applied during spinning, which should result in a greater degree of polymer orientation. Since the polyrotaxane molecule is likely to have relatively high rigidity in solution [13], a greater degree of polymer chain orientation may be attained via so-called liquid crystal spinning [31] if the concentrated solution of polyrotaxane forms a liquid crystal. Based on the wide variety of novel functionalities possessed by polyrotaxane, we expect to observe further useful properties of these blend fibers in forthcoming investigations.

Acknowledgment

Prof. Shigenori Kuga and Prof. Masahisa Wada (The University of Tokyo) are greatly acknowledged for their help with X-ray diffractometric measurements.

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