

New Solvent for Polyrotaxane. III. Dissolution of a Poly(ethylene glycol)/Cyclodextrin Polyrotaxane in a Calcium Thiocyanate Aqueous Solution or *N*-Methylmorpholine-*N*-Oxide Monohydrate

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ABSTRACT: Calcium thiocyanate [Ca(SCN)₂] aqueous solutions above 40 wt % and *N*-methylmorpholine *N*-oxide (NMMO) monohydrate, which are known to dissolve cellulose, were found to be good solvents for a polyrotaxane comprising α -cyclodextrin and poly(ethylene glycol). The polyrotaxane could be dissolved up to 12 and 10 wt % in a 40 wt % Ca(SCN)₂ aqueous solution and NMMO, respectively. These are the first instances of a neutral aqueous solution and a cyclic amine oxide, respectively, that readily dissolve the polyrotaxane. These new good solvents, as well as other solvents of the polyrotaxane, except for dimethyl sulfoxide, are

identical to those of cellulose, indicating that the dissolution mechanism of the polyrotaxane is dominated by intra- and intermolecular hydrogen bonding of the molecule similar to that of cellulose dissolution. The concentrated polyrotaxane solution in a 40 wt % Ca(SCN)₂ aqueous solution showed apparent thixotropy and spontaneous gelation of the solution caused by a gradual increase in its viscosity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2265–2270, 2007

Key words: host-guest systems; inclusion chemistry; solution properties; supramolecular structures; viscosity

INTRODUCTION

Polyrotaxane, comprising α -cyclodextrins (CDs) and poly(ethylene glycol) (PEG), has been one of the most energetically investigated supramolecular materials since it was first prepared by Harada et al.,¹ and it has been applied to a number of research fields. Although the PEG/CD polyrotaxane is being thoroughly investigated from both theoretical and practical viewpoints, as described in several recent reviews,^{2–5} its analysis and investigation are sometimes restricted by a few drawbacks; one of these drawbacks is its considerable infusibility, in general, in solvents other than dimethyl sulfoxide (DMSO) and aqueous sodium hydroxide solutions;¹ therefore, the polyrotaxane should be modified to yield various polyrotaxane derivatives to achieve its dissolution in water or other organic solvents.^{6–9} We recently found other good solvents for the unmodified polyrotaxane, such as a dimethylacetamide (DMAc)/lithium salt system⁶ and ionic liquids.¹⁰ One of the intriguing properties of these two solvent systems is

the dissolution of cellulose, a natural crystalline polysaccharide. A highly crystalline cellulose is known to be insoluble in water and many general solvents because of its stable intra- and intermolecular hydrogen bonds, which are interrupted by solvation or complexation with a combination of solvent molecules in the aforementioned solvent system to achieve cellulose dissolution.^{11–13} Polyrotaxane is also soluble in these solvents and insoluble in other general solvents, being similar to cellulose, and this suggests that the dissolution mechanism of polyrotaxane is also governed by the formation of intra- and intermolecular hydrogen bonding. Therefore, the dissolution of the polyrotaxane in other cellulose solvents is intriguing for the confirmation of a hydrogen-bonding-dominant dissolution mechanism of polyrotaxane as well as the practical uses of the obtained solution, such as the molding of polyrotaxane or the blending of polyrotaxane with another polymer. The creation of aqueous and neutral solvent systems for polyrotaxane must be especially appreciated for their nontoxicity and facile recovery of solvent reagents; for example, the solvent used for the molding of polyrotaxane can be easily recovered and used repeatedly after coagulation in water. In this study, a preliminary examination of polyrotaxane dissolution in two well-known cellulose sol-

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vents—an aqueous calcium thiocyanate [$\text{Ca}(\text{SCN})_2$, i.e., rodan calcium salt] solution^{14–17} and *N*-methylmorpholine *N*-oxide (NMMO) monohydrate^{18,19}—was conducted. A viscometric study was also conducted on the former solution, which revealed a typical thixotropic behavior over an extended duration.

EXPERIMENTAL

The polyrotaxane, supplied by Advanced Softmaterials, Inc. (Tokyo, Japan), was essentially similar to that reported in the previous study;²⁰ it consisted of PEG with a molecular weight of 35000, about 90–100 CDs, and two terminal adamantane moieties in a single molecule. NMMO (50% in water) was obtained from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan), and all other reagents were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the chemicals were reagent-grade and were used without any special purification unless noted otherwise.

The aqueous solutions of $\text{Ca}(\text{SCN})_2$ were prepared by the dissolution of calcium thiocyanate tetrahydrate [$\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$] in deionized water, the water of hydration being considered for the determination of the final salt concentration; for instance, 58.5 g of $\text{Ca}(\text{SCN})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 41.5 g of water to yield 100 g of a 40 wt % $\text{Ca}(\text{SCN})_2$ solution. Solutions with five different $\text{Ca}(\text{SCN})_2$ concentrations—10, 20, 30, 40, and 50 wt %—were prepared at room temperature.

The polyrotaxane was dissolved in a $\text{Ca}(\text{SCN})_2$ solution at a desired concentration in a water bath at 80°C, unless noted otherwise. The dissolution of the polyrotaxane in NMMO was examined with two methods: a direct method and an evaporation method. In the direct method, a solid NMMO monohydrate (49 g) was melted through heating to 100°C followed by the addition of the polyrotaxane (1 g) and propyl gallate as an antioxidant (10 mg, typically 1–2% against polyrotaxane) and stirring at 100°C. In the evaporation method, a mixture of an approximately 50% aqueous solution of NMMO (50 g) and propyl gallate (15 mg) was evaporated up to about 80% (ca. 31 g) with a rotary evaporator at 80°C, and this was followed by the addition of the polyrotaxane (1.5 g); it was further rotated without evaporation. The evaporation of a well-mixed, slurry-like suspension up to a final weight of about 30 g (85–90% NMMO concentration in the solvent) yielded complete dissolution of the polyrotaxane at about 5%.

The polyrotaxane, dissolved in various solvents, including a 40 wt % $\text{Ca}(\text{SCN})_2$ aqueous solution, NMMO, and DMSO, was collected by precipitation with water. One gram of polyrotaxane was dissolved in 49 g of each solvent (2 wt % of the polyrotaxane content) and poured into 450 mL of water with vig-

orous stirring. The collected precipitant was repeatedly washed with water by centrifugation and subsequently freeze-dried. The recovered polyrotaxane was analyzed with proton nuclear magnetic resonance (¹H-NMR) and gel permeation chromatography (GPC). ¹H-NMR spectroscopy in DMSO-*d*₆ was recorded at 400 MHz on a JEOL JNM-AL400 (Tokyo, Japan) at the ambient temperature. Chemical shifts were referenced by tetramethylsilane. GPC measurements were performed on a Tosoh HLC-8220GPC high-performance liquid chromatography system (Tokyo, Japan) using a refractive-index detector equipped with three columns in series: a TSK Super AW-H guard column and two TSK Super AWM-H gel columns (6.0 mm in diameter and 150 mm in length; pore size = 9 μm). DMSO containing 10 mmol/L LiBr was used as the eluent (50°C, 0.5 mL/min). The molecular weights and polydispersity were calculated on the basis of poly(ethylene oxide) standards. The values of the recovery from the solutions were recalculated on the basis of the weight, excluding a very slight amount of decomposition of the starting polyrotaxane (6.5 wt %, detected by GPC measurement), which probably happened during long storage over a year.

The rheological measurement of the polyrotaxane solution in a 40 wt % $\text{Ca}(\text{SCN})_2$ aqueous solution (with a polyrotaxane concentration of 12 wt %) was carried out at 30°C with a rotational rheometer (Rheosol-G5000, UBM Co., Ltd., Kyoto, Japan) equipped with a coaxial cylindrical fixture (with an inner diameter of 23 mm, a height of 30 mm and a gap of 1 mm). To prevent the sample from drying, its surface was covered with a slight amount of liquid paraffin. For the thixotropy measurements, the shear rate was increased from 0 to 136 s⁻¹ (0–100 rpm) over 90 s, and this was immediately followed by a decrease from 136 to 0 s⁻¹ over another 90 s.

RESULTS AND DISCUSSION

Both a 40 wt % $\text{Ca}(\text{SCN})_2$ aqueous solution and NMMO monohydrate were found to readily dissolve the PEG/CD polyrotaxane, yielding colorless and transparent, light-brown solutions, respectively, as shown in Figure 1. The polyrotaxane that dissolved in both solvents could be recovered by precipitation with water in a considerable amount and showed molecular weights almost identical to those of the starting polyrotaxane, as shown in Table I. The ¹H-NMR spectra of these collected polyrotaxanes were completely identical to that of the starting polyrotaxane (data not shown). From these observations, the two solvents were found to be good solvents of the unmodified polyrotaxane without degradation. The $\text{Ca}(\text{SCN})_2$ aqueous solution is the first example of a

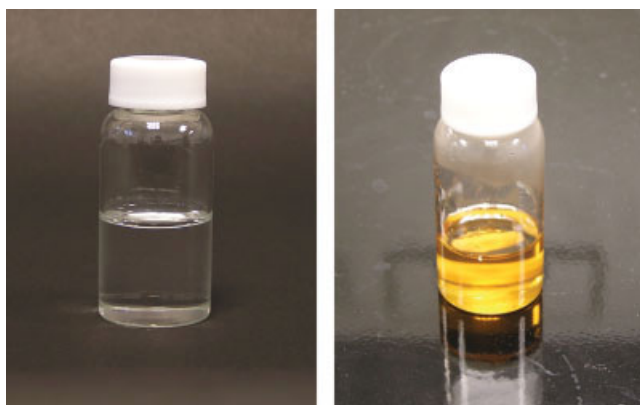


Figure 1 Polyrotaxane solutions in a 40 wt % aqueous $\text{Ca}(\text{SCN})_2$ solution (left) and NMMO monohydrate (right). The polyrotaxane content was 2 wt % for both solutions. The $\text{Ca}(\text{SCN})_2$ solution was photographed at room temperature, whereas the solution in NMMO was photographed immediately after dissolution above 80°C . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

neutral aqueous solvent, and the NMMO monohydrate is the first amine oxide solvent for polyrotaxane. The former solution was stable at room temperature, although the standing of the solution for an extended period (i.e., a month) resulted in an insignificant amount of precipitation. A solution with a polyrotaxane content up to 12 wt % could be prepared with this solvent. The latter solution solidified at room temperature because the melting point of the NMMO monohydrate was reported to be 72°C .¹⁸ Dissolution in NMMO could be achieved by either the direct method or evaporation method, as described in the Experimental section; however, the latter method is preferred for dissolving a relatively high polyrotaxane concentration—as high as 5–10 wt %. Similar to the previous study on NMMO dissolution,²¹ a significant browning was observed, especially above 90°C , presumably because of the oxidation of the solute

and/or the solvent at a high temperature. The slightly lower recovery from the NMMO solution than those from DMSO and $\text{Ca}(\text{SCN})_2$ solutions also implies possible oxidative decomposition in the former solution. This may be effectively suppressed by the addition of propyl gallate as an antioxidant. A more careful and inert dissolution, such as the one under N_2 , would be more suitable.

A $\text{Ca}(\text{SCN})_2$ aqueous solution and NMMO monohydrate are also good solvents of cellulose, a natural crystalline polysaccharide. The former was previously examined for the preparation of cellulose gel beads¹⁴ and the gel spinning of a regenerated cellulose fiber,¹⁷ and the latter was applied to the wet spinning of a regenerated cellulose fiber termed Lyocell.²¹ Interestingly, the previously reported good solvents of the polyrotaxane other than DMSO and aqueous sodium hydroxide solutions, i.e. a DMAc/lithium chloride system,⁶ ionic liquids¹⁰ and the solvents used in this study, were all reported to dissolve cellulose by the interruption of the intra- and intermolecular hydrogen bonds of cellulose due to solvation or complexation.^{10–19,22} As reported earlier,^{6,10} the dissolution mechanism of the polyrotaxane, based on a similar interruption of hydrogen bonding, was evidently confirmed by the dissolution in the aforementioned solvents. The dissolution of the polyrotaxane and that of cellulose, however, show several noticeable distinctions in the conditions. For instance, the dissolution of cellulose in a $\text{Ca}(\text{SCN})_2$ aqueous solution requires a high $\text{Ca}(\text{SCN})_2$ concentration, such as 55–60 wt %, and heating up to 100 – 140°C ,^{14–17} whereas the dissolution of the polyrotaxane in the solvent can be achieved above a 40% $\text{Ca}(\text{SCN})_2$ concentration and above 65°C , as explained hereafter. Similar differences in the dissolution conditions were also observed for the previous solvents. Polyrotaxane could be easily dissolved in 0.1–1M aqueous NaOH,^{1,20} whereas cellulose should be pretreated by steam explosion and acid hydroly-

TABLE I
Recovery and Molecular Weights of the Polyrotaxane Dissolved in Various Solvents

Solvent	Recovery from a 2 wt % solution (wt %)	Molecular weight of the recovered polyrotaxane ^a	
		M_w	M_w/M_n
Before dissolution ^b	—	1.14×10^5	1.35
40 wt % $\text{Ca}(\text{SCN})_2$ ^c	94	1.21×10^5	1.31
NMMO ^d	84	1.27×10^5	1.31
DMSO ^e	93	1.20×10^5	1.43

^a Determined by GPC. M_w = weight-average molecular weight; M_n = number-average molecular weight.

^b Starting, undissolved polyrotaxane.

^c Dissolved at 80°C for 3 h.

^d Dissolved at 95°C for 3 h with 10 mg of propyl gallate by the direct method (see the text for details).

^e Dissolved at room temperature.

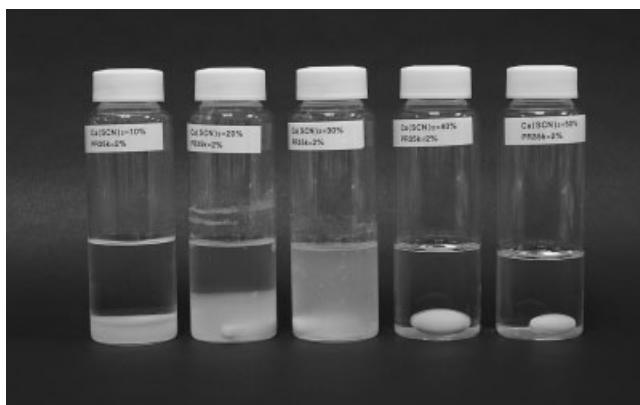


Figure 2 Appearance of the polyrotaxane solutions prepared in aqueous solutions with various $\text{Ca}(\text{SCN})_2$ concentrations. The $\text{Ca}(\text{SCN})_2$ concentrations in the solvents were 10, 20, 30, 40, and 50 wt %, from the left to right. The weight ratio of the polyrotaxane to the solvent was 1 : 49 for all the samples, corresponding to a polyrotaxane content of 2%. The used stirring bars were left in the bottles to show the clarity of the samples.

sis to break its intramolecular hydrogen bonding for dissolution in 7–9% aqueous NaOH.²² Another instance is the dissolution of polyrotaxane in DMAc/LiBr,⁶ which was reported to be incapable of dissolving cellulose because of its inability to eliminate the hydrogen bonding of cellulose by macrocationization.¹² In light of all these observations, the conditions necessary for the dissolution of cellulose in the aforementioned solvents seem to be more severe than those for the dissolution of the polyrotaxane. The results suggest that the hydrogen-bond formation in the solid polyrotaxane is weaker than that in cellulose crystals. Although it is required to elucidate the reason for this phenomenon in future investigations, one of the speculations is the freedom in the formation and disruption of hydrogen bonding in bulk polyrotaxane caused by the sliding and/or rotation of CD molecules, preventing the formation of a stable, three-dimensional hydrogen-bond network observed in the cellulose crystals. Moreover, the potential difference between the numbers and/or geometrical arrangements of inter- and intramolecular hydrogen bonding in the polyrotaxane and those in cellulose should be considered.

Additional detailed investigations of the dissolution conditions for polyrotaxane in aqueous $\text{Ca}(\text{SCN})_2$ solutions were conducted. The solvents with salt concentrations varying from 10 to 50 wt % were prepared in which the dissolution of the polyrotaxane was examined at 80°C. As shown in Figure 2, the aqueous solutions with a $\text{Ca}(\text{SCN})_2$ concentration of 40 and 50 wt % readily dissolved the polyrotaxane almost within 15 min, and transparent solutions were obtained, whereas the solutions with a $\text{Ca}(\text{SCN})_2$ concentration of 10 and 20 wt % showed

apparently no trace of dissolution even with an hour of stirring, giving a precipitated polyrotaxane. At a $\text{Ca}(\text{SCN})_2$ concentration of 30 wt %, the added polyrotaxane seemed to swell, and the entire mixture turned into a nonsedimenting, slurry-like suspension, although complete dissolution did not occur. This nonsedimenting mixture in 30 wt % $\text{Ca}(\text{SCN})_2$ lost its fluidity and formed a physical gel within a day at room temperature. The temperature necessary for dissolution in 40 wt % $\text{Ca}(\text{SCN})_2$ was also investigated with a polyrotaxane concentration of 2% by a gradual increase in the temperature. Although no apparent change was observed up to 60°C, the mixture became a viscous dispersion above this temperature and became a clear solution at 65°C by continued stirring. In the case of cellulose dissolution in a $\text{Ca}(\text{SCN})_2$ aqueous solution,¹⁵ the breaking of hydrogen bonding is reported to be endothermic, whereas the complex formation of $\text{Ca}(\text{SCN})_2$ with hydroxyl groups is exothermic. Because the latter occurs even at room temperature over a long period,¹⁵ the heating is considered to be necessary for the endothermic hydrogen bond breaking. The conditions for polyrotaxane dissolution were therefore concluded to be follows: a temperature above 65°C in a solution with a $\text{Ca}(\text{SCN})_2$ concentration of more than 40 wt %. These conditions are milder than those necessary for the dissolution of cellulose, as mentioned previously.

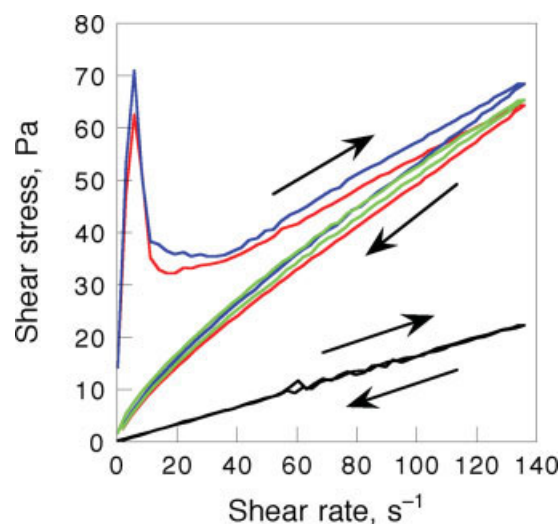


Figure 3 Thixotropic hysteresis loops shown by a polyrotaxane/40 wt % $\text{Ca}(\text{SCN})_2$ solution with a polyrotaxane content of 12 wt %. The first shearing was applied after 3 days of quiet storage of the solution in the rheometer (red). The second shearing (blue) was applied 4 days after the first shearing and was immediately followed by the third shearing of the polyrotaxane/DMSO solution with the same polyrotaxane content, performed after it stood for 3 days, is also displayed (black). All the measurements were performed at 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Figure 4 Nonflowing polyrotaxane/40 wt % $\text{Ca}(\text{SCN})_2$ solution gelled for 3 days at room temperature.

It should be noted that other dissolution conditions may be suitable for polyrotaxanes with different inclusion ratios as well as dissolution in NMMO.

The solution in a 40 wt % $\text{Ca}(\text{SCN})_2$ solvent with a relatively high polyrotaxane content (typically over 10%) exhibited another intriguing phenomenon, namely, a spontaneous increase in the viscosity and gelation on standing. During this gelation behavior, the solution showed apparent thixotropy over an extended period; that is, its viscosity gradually decreased under continuous shearing but almost recovered its initial viscosity by being allowed to stand without shearing, as shown in Figure 3 by viscometric measurements with a rotational cylindrical rheometer. For each measurement, the shear rate was linearly increased from 0 to 136 s^{-1} over 90 s, and this was followed by a linear decrease from 136 to 0 s^{-1} over another 90 s. After 3 days of quiet storage in the sample cell of the rheometer, the viscosity of the polyrotaxane/40 wt % $\text{Ca}(\text{SCN})_2$ solution (with a polyrotaxane content of 12 wt %) showed considerable hysteresis during the up and down scanning; that is, the plot showed a typical clockwise hysteresis loop (red line in Fig. 3), which was observed again after standing for a long time (4 days; blue line in Fig. 3) but disappeared immediately after the previous shearing (green line in Fig. 3). These behaviors, which are typical for a thixotropic flow,^{23,24} were not observed for the polyrotaxane/DMSO solution at the same polyrotaxane concentration even after standing for 3 days (black line in Fig. 3). Although thixotropy is frequently observed for a structure-containing liquid such as a suspension,^{23–25} there are few reports on the thixotropy of a solution, particularly a polymer solution, to the best of our knowledge. On standing for 2–3 days at room temperature, as shown in Figure 4, the concentrated

polyrotaxane/40 wt % $\text{Ca}(\text{SCN})_2$ solution sometimes formed a stable and nonflowing physical gel, which could be converted into a fluid only after extremely vigorous shaking. A gelation of cellulose dissolved in the same solvent was also reported,¹⁷ suggesting certain associative interactions between glucosic moieties in the solvent. Both the aforementioned increase in the viscosity and the thixotropy were considered to be caused by the intermolecular attractive force. The gelation of the polyrotaxane solution was thermoreversible, being similar to that for the cellulose solution;¹⁷ that is, the formed gel shown in Figure 4 was liquefied again at 80°C , and this was followed by a second gelation when it was allowed to stand for another 2–3 days at room temperature.

In addition to the solvents for polyrotaxane that were previously reported, the two new solvents reported in this study are expected to extend the range of the investigation and applications of polyrotaxane. An aqueous $\text{Ca}(\text{SCN})_2$ solution seems to provide a considerable advantage—a low degradation tendency—because of its neutrality. NMMO is an industrially attractive solvent system because it already enables a closed system with complete recovery of the solvent.²¹ The two solvents also lead to the anticipation of further study on polyrotaxane, such as a study on polyrotaxane blending similar to our previous report,²⁶ because they are also good solvents for other natural polymers such as cellulose,^{14–17} chitin,²⁷ and silk fibroin.²⁸

The viscosity measurements were performed with help from Shibayama Laboratory, Institute of Solid State Physics, University of Tokyo. The gel permeation chromatography measurements were performed with help from Advanced Softmaterials, Inc. (Tokyo, Japan).

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