Strongly Thixotropic Viscosity Behavior of Dimethylsulfoxide Solution of Polyrotaxane Comprising α-Cyclodextrin and Low Molecular Weight Poly(ethylene glycol)

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ABSTRACT

A strong thixotropic viscosity behavior was observed when polyrotaxane prepared from α-cyclodextrins (CDs) and poly(ethylene glycol) (PEG) with a molecular weight of 2000 was dissolved in dimethylsulfoxide (DMSO). A 10 wt% solution liquefied by vigorous shaking was rapidly gelated by standing — this sol–gel transition was reversible. The time for recovering the viscosity was dependent on the polyrotaxane concentration, i.e., a 10wt% solution regelated within 30 s, whereas several hours were required for the gelation of a 2.5wt% solution. The thixotropic nature of the solution was also confirmed by the clockwise hysteresis curve of the viscosity when the shear rate was increased and decreased. The gel permeation chromatography (GPC) measurement of the polyrotaxane in DMSO exhibited peaks in the high molecular weight region. The peak disappeared after the phenylcarbamoylation of polyrotaxane, suggesting that the peak was due to loose aggregations of polyrotaxane in DMSO. On the other hand, the DMSO solution of polyrotaxane prepared from CD and PEG with a molecular weight of 3350—whose inclusion ratio (51%) is slightly lower than that of PEG2000 polyrotaxane (72%)—neither demonstrated the abovementioned thixotropic viscosity nor the peak corresponding to the aggregations occurring during the GPC measurement. The thixotropic behavior was speculated to be caused by the combined contribution of intermolecular attractive hydrogen bonding and higher rigidity of polyrotaxane prepared from PEG 2000 than that of polyrotaxane prepared from PEG3350, presumably due to the higher inclusion ratio of the former than that of the latter.

Key Word: Polyrotaxane, Thixotropy, intermolecular hydrogen bonding

INTRODUCTION

Polyrotaxane is a typical supramolecular material that possesses linear molecule threading through many cyclic molecules, which can freely slide or rotate over the linear molecule [1–4]. Great advances have been made in the investigation of polyrotaxane since the discovery of the formation of pseudopolyrotaxane by the spontaneous inclusion complexation of cyclodextrins (CDs) and linear polymers by Harada et al. [5–9]. The formation of the inclusion complex with CDs and various linear polymers *via* spontaneous self-assembly was thoroughly investigated by Harada et al. [1, 5, 6], who successfully prepared polyrotaxane by binding bulky end groups (such as dinitrophenyl moieties) to the ends of pseudopolyrotaxane, i.e., the inclusion complex of CDs and PEG [7–9]. A wide variety of attractive concepts have been reported to date after the first finding by Harada, such as the preparation of a "molecular tube" by cross-linking adjacent CDs in single polyrotaxane followed by the dissociation of the included PEG [10], an insulated molecular wire comprising a conducting polymer and a molecular tube [11,12], a drug delivery system using polyrotaxane carrying drugs on the CD moiety [13], multivalent ligand system [14], the construction of an energy transfer system using polyrotaxane with photoluminescent side groups [15, 16], a three-dimensionally cross-linked polyrotaxane network [17–19] and fiber formation by the wet spinning of a blend solution of polyrotaxane and cellulose [20].

Since further applications of polyrotaxane than that mentioned above are anticipated in the future, the fundamental properties of polyrotaxane should be thoroughly characterized. Solution property is one of the most significant characteristics, which is necessary during processing and handling polyrotaxane when used in various applications. Nevertheless, the solution properties of polyrotaxane have been scarcely investigated, probably due to its surprising insolubility in its component solvents (i.e. solvents of PEG and CD) such as water, dimethylformamide (DMF) or pyridine, and solubility only in a limited variety of solvents including dimethylsulfoxide (DMSO) and aqueous sodium hydroxide solutions [7–9], dimethylacetamide (DMAc) containing lithium halide [21, 22], room temperature ionic liquids [23], concentrated aqueous solution of calcium thiocyanate ($Ca(SCN)_2$) [24], and *N*-methylmorpholine-*N*-oxide [24]. Among these systems, DMSO is one of the most popular and the most investigated solvents for polyrotaxane. Aprotic and neutral DMSO readily dissolves PEG/CD polyrotaxane to yield a polyrotaxane solution in which many reactions and/or modifications have been made to date [10, 13–16, 22]. However, many unrevealed properties seem to be potentially buried within this solution system.

In the present study, we report novel strong thixotropy of the DMSO solution of polyrotaxane prepared from α-CDs and PEG with a low molecular weight (MW = 2000). Thixotropy is a phenomenon in which the viscosity that decreases because of shearing is recovered by letting it stand in the absence of shear; it is a typical structural viscosity behavior induced by changes in the internal structure [25, 26]. While we already reported the thixotropy of a polyrotaxane solution in aqueous $Ca(SCN)_2$ over a long time scale (as long as three days) [24], the thixotropy demonstrated in the present study occurs far more rapidly, i.e., within 30 s. The occurrence of thixotropy for two different polyrotaxanes with different levels of PEG molecular weights and inclusion ratios was characterized by viscometry and gel permeation chromatography (GPC) before and after the modification of polyrotaxane.

EXPERIMENTAL

Materials. PEG-bisamine (PEG-BA), i.e., PEG with terminal primary amino groups with a molecular weight of 3350, was purchased from Aldrich. α-CD was obtained from Nihon Shokuhin Kako Co. Ltd. (Tokyo, Japan) and 1-hydroxybenzotriazole (HOBt) was from Dojindo (Kumamoto, Japan). Adamantaneacetic acid and 1,1'-carbonyldiimidazole (CDI) were purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). The other chemicals were

purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). All the chemicals were of reagent grade and used without any special purification, unless otherwise noted. Anhydrous solvents were stored on 4A molecular sieves, if necessary. PEG-diaminoterminated (PEG-DAT) with a molecular weight of 2000 was prepared according to a previous report [27], i.e., by the activation of the terminal hydroxyl groups of PEG2000 with CDI and the subsequent addition of ethylenediamine.

Synthesis of polyrotaxane. Polyrotaxane was prepared from CD and PEG derivatives (PEG-DAT2000 or PEG-BA3350) according to Harada's method [7, 8] with slight modifications. Briefly, an aqueous solution of PEG-DAT2000 or PEG-BA3350 (1 g in 10 ml water) was slowly added to an aqueous solution of CD (15 g in 170 ml water), followed by overnight stirring. The obtained turbid mixture was directly freeze-dried to yield a mixture of PEG/CD inclusion complex and free CDs almost quantitatively. Then, 4-dinitrofluorobenzene (DNFB, 1.16 g (6.25×10^{-3} mol) when PEG-DAT2000 was used and 1.39 g (1.49×10^{-4} mol) when PEG-BA3350 was used) was added to the obtained white powder (4 g containing 2.50×10^{-4} mol NH_2 when PEG-DAT2000 was used and 1.49×10^{-4} mol-NH_2 when PEG-BA3350 was used), followed by the addition of dry DMF (40 ml) and overnight stirring in an argon atmosphere at room temperature. The yellow precipitate collected by centrifugation was washed with acetone and water (two times, respectively), followed by freeze-drying. The obtained yellow powder was further dissolved in DMSO (40 ml) and precipitated by pouring into vigorously stirred water (450 ml). The washing of the precipitant collected by centrifugation and subsequent freeze-drying yielded polyrotaxane as a yellow powder. The yields were 810 mg (from PEG-DAT2000) and 1.25 g (from PEG-BA3350). Polyrotaxane with terminal adamantane moiety was prepared from CD, PEG-DAT2000, and adamantaneacetic acid according to an earlier report [16], although the total amount of DMF at the end-capping reaction was increased up to 10 ml (yield: 713 mg).

The prepared polyrotaxanes were hereafter coded with the abbreviated names of bulky end groups and molecular weights of the PEG axis. For example, polyrotaxane prepared using PEG-DAT2000 and DNFB and that from PEG-DAT2000 and adamantaneacetic acid were called DNFB-PR2000 and APR2000, respectively.
DNFB-PR2000. ^{1}H NMR (δ, ppm in DMSO-*d*6): 8.88 and 8.28 (very weak, aromatic protons), 5.69 (O-2H of CD), 5.53 and 5.44 (O-3H of CD), 4.80 (C-1H of CD), 4.45 (O-6H of CD), 3.75–3.28 (C-2H, C-3H, C-4H, C-5H, C-6H of CD), 3.50 (CH_2 of PEG).
DNFB-PR3350. ^{1}H NMR (δ, ppm in DMSO-*d*6): 8.96, 8.86, 8.28 and 7.25 (aromatic protons), 5.68 (O-2H of CD), 5.50 (O-3H of CD), 4.78 (C-1H of CD), 4.44 (O-6H of CD), 3.73–3.27 (C-2H, C-3H, C-4H, C-5H, C-6H of CD), 3.49 (CH_2 of PEG).
APR2000. ^{1}H NMR (δ, ppm in DMSO-*d*6): 5.67 (O-2H of CD), 5.52 and 5.43 (O-3H of CD), 4.79 (C-1H of CD), 4.43 (O-6H of CD), 3.74–3.28 (C-2H, C-3H, C-4H, C-5H, C-6H of CD), 3.50 (CH_2 of PEG), 1.90 and 1.52 (very weak, H of adamantane).
^{1}H NMR results of APR35000 were reported in our previous paper [28].

Phenylcarbamoylation of polyrotaxane. The phenylcarbamoylation of DNFB-PR2000 was performed according to a previous report [22] with a partial modification of the method. Briefly, dibutyltin dilaurate (DBTDL, 20 μL) and phenylisocyanate (6.43×10^{-1}, 5.40×10^{-3} mol) were added to DNFB-PR2000 (100 mg) dissolved in dry DMSO (10 ml), followed by overnight stirring in an argon atmosphere at room temperature. The obtained orange solution was poured into vigorously stirred diethyl ether (200 ml). The precipitant collected by centrifugation and dried *in vacuo* was dissolved in THF (10 ml) and precipitated again by diethyl ether (200 ml). The collection of the precipitant by centrifugation and subsequent drying *in vacuo* yielded phenylcarbamoylated DNFB-PR2000 as a yellow solid (147 mg). A

small portion of the reaction mixture was diluted with DMSO immediately before the first precipitation and characterized with the GPC measurement as follows.

Measurements. The ^{1}H NMR spectra at 400 MHz were recorded in DMSO-*d*6 or 4% NaOD/D_2O on a JEOL JNM-AL400 spectrometer at room temperature. The chemical shifts were referenced with 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (in the case of NaOD/D_2O) or residual proton in deuterated solvent (in the case of *d*-DMSO, $\delta = 2.50$). The amounts of CDs in a single molecule of DNFB-PR2000 and DNFB-PR3350 were calculated from the ^{1}H NMR spectra after decomposition with 4% NaOD/D_2O solution at room temperature for 7 days according to a previous report [9]. The calculated amounts of the included CDs and the corresponding values of inclusion ratios are summarized in Table 1 along with these values for polyrotaxane prepared from PEG with a molecular weight of 35000 [28]. Our result of inclusion ratio for DNFB-PR3350 and DNFB-PR2000 well agrees with the results by Harada et al. [9]. Although relatively low inclusion ratio for the former, 51%, should be due to some dissociation of CDs during the endcapping reaction, the reason of the lower inclusion ratio of DNFB-PR3350 than that of DNFB-PR2000 is still unclear.

The GPC measurements were performed using a TOSOH HLC-8220GPC high-performance liquid chromatography system using a RI detector equipped with three columns in series: a TSKguardcolumn Super AW-H and a pair of TSKgelSuper AWM-H (diameter of 6.0 mm; length, 150 mm; and pore size, 9 μm). DMSO containing 10 mmol/L LiBr was used as the eluent (50 °C at 0.5 ml/min). The polyrotaxane concentrations in all the GPC samples were adjusted to 0.25% w/v.

The rheological measurement of the polyrotaxane solution in DMSO was carried out at 30 °C using a rotational rheometer (Rheosol-G5000, UBM Co., Ltd., Kyoto) equipped with a coaxial cylindrical fixture (inner diameter of 23 mm; height, 30 mm; and gap, 1 mm). To prevent the sample from absorbing moisture, its surface was covered with a slight amount of liquid paraffin. For the thixotropy measurement, the shear rate was increased from 0 to 136 s^{-1} (0–100 rpm) over 90 s, immediately followed by a decrease from 136 to 0 s^{-1} over another 90 s.

RESULTS AND DISCUSSION

A yellow semitransparent solution of DNFB-PR2000 in DMSO, which was initially a viscous fluid, at a polyrotaxane concentration of 10wt% became nonflowing after letting it stand for several minutes, as shown in Figure 1. The solution once gelated was liquefied again by vigorous shaking, followed by very rapid regelation within ca. 30 s (a movie of the rapid gelation is shown in the Supporting Information). At room temperature, the observed sol-gel transition was completely reversible and repeatable; that is, a concentrated solution of DNFB-PR2000 in DMSO exhibited an apparent thixotropy. We tried to investigated the effect of temperature on the thixotropic behavior, but a detailed examination was difficult due to the formation of the irreversible aggregation on heating up to 70 ˚C. In a previous report [24], we already reported a relatively slow thixotropic behavior of the polyrotaxane solution in 40wt% $Ca(SCN)_2$ aqueous solution over three days, whereas the DNFB-PR2000/DMSO solution used in the present study showed far more rapid thixotropy than that in the $Ca(SCN)_2$ system. [24].

As shown in Figure 1, the gelation of the DNFB-PR2000 solution was observed for a wide range of polyrotaxane concentrations—2.5–10wt%. The apparent time for the recovery of viscosity was strongly dependent on the polyrotaxane concentration; that is, well-shaken solutions with polyrotaxane concentrations of 10wt% and 5wt% became nonflowing after 30 s and 30 min of standing, respectively, and even a dilute solution with a polyrotaxane

concentration of 2.5wt% gelated after overnight standing. The APR2000 solution in DMSO at a polyrotaxane concentration of 10wt% was similarly gelated, suggesting no effect of the terminal bulky moiety.

Figure 2(a) shows the viscometric result for the DNFB-PR/DMSO 5wt% solution. Although the plot was rumpled due to the relatively low torque for the equipment, the viscosity curves with ascending and descending shear rates showed a clockwise hysteresis, which is a typical indication of thixotropic viscosity [25, 26]. The second measurement after 1 h of quiet standing in a rheometer also showed similar hysteresis (Figure 2(b)), whereas the third measurement performed just after the second measurement indicated a relatively low degree of thixotropy (Figure 2(c)), presumably due to the incomplete recovery of viscosity. The measured viscosity value in the second run seem to be slightly higher than that in the first run, but it might contain slight fluctuation of the measured values, probably due to both unsteady formation of the aggregated structure and the measured torque relatively weak for the used apparatus (rheometer). The results showed that the thixotropic nature of the DNFB-PR2000/DMSO solution was confirmed by viscometry, although the phenomenon was intrinsic to polyrotaxane prepared from PEG2000; namely, the 5wt% solution of DNFB-PR3350 neither showed an apparent sol-gel transition (as shown in Figure 1) nor hysteresis during the viscosity measurement (as shown in Fig. 2(d)). Moreover, viscosity of DNFB-PR3350/DMSO solution was extremely lower than that of DNFB-PR2000/DMSO solution even at the same polyrotaxane concentration, as shown in Figure 2 (d). The DMSO solution of APR35000, i.e., adamantane-capped polyrotaxane prepared from PEG35000, was not thixotropic but completely Newtonian, as in our earlier report [24].

It has been considered that thixotropy is induced by the formation of a structure in a solution or a colloidal system by an attractive interaction of the solute or particles [25, 26]. The thixotropy in the present system, therefore, suggests the occurrence of an attractive interaction between the polyrotaxane molecules and the formation of loose aggregates, although strong precipitation does not occur. The formation of the aggregated structure was also observed by the GPC measurement. Figure 3(a) and 3(b) shows the GPC profiles of DNFB-PR2000 and APR2000 in DMSO with 0.01 M LiBr, respectively. In addition to a large peak corresponding to single polyrotaxane molecules (10.8 min), two small peaks were observed at earlier elution times (8.42 min and 9.70 min). The peaks were reproducibly observed in repeated measurements, although their size and elution times showed small variations. The corresponding high molecular weight compound, however, does not seem to be formed, since the preparation of DNFB-PR2000 and APR2000 only includes the end-capping of the pseudopolyrotaxane terminals by monofunctional end-cappers (DNFB or adamantaneacetic acid) and never perform cross-linking. It was also confirmed that DNFB-PR3350, prepared by exactly the same method as that for DNFB-PR2000, showed no high molecular weight fraction, as shown in Figure 3(c). These GPC results suggest that DNFB-PR2000 and APR2000 form loose aggregates in DMSO, even after the filtration of a very dilute solution with a concentration of 0.25wt%, whereas no aggregation occurs for the DNFB-PR3350/DMSO system, indicating the absence of thixotropy.

For a further characterization of the high molecular weight fractions, DNFB-PR2000 was subjected to phenylcarbamoylation, i.e., the addition of phenylcarbamoyl groups on the CD hydroxyls. The addition of phenylisocyanate to polyrotaxane was performed at room temperature in DMSO, which is fundamentally based on our previous results [22]. The sample mixture was diluted before purification and characterized by GPC under the same conditions (profile shown in Figure 3(d)); here, the high molecular weight fractions disappeared. The profile showed peaks corresponding to phenylcarbamoylated polyrotaxane, DBTDL used as a catalyst, dimerized phenylisocyanate, and phenylisocyanate.

The GPC measurements performed after purification with diethyl ether showed only one peak corresponding to phenylcarbamoylated polyrotaxane (Figure 3(e)). Similar to that in the determination of the molecular weight of polysaccharides [29, 30], phenylcarbamoylation does not affect the molecular weight distribution of the original sample. Furthermore, the present phenylcarbamoylation reaction was performed at room temperature in DMSO, and almost no decomposition was considered to occur. These results suggest that loose aggregates of the unmodified DNFB-PR2000—not an essentially high molecular weight component—were observed in the form of earlier elution peaks by GPC measurements; further, the aggregates were well dispersed after phenylcarbamoylation, resulting in the disappearance of peaks at earlier elution times. A solution of phenylcarbamoylated DNFB-PR2000 in DMSO at a concentration of 10wt% was a less viscous fluid and showed no apparent thixotropy, corresponding to the abovementioned changes in the GPC results. Information on molecular weight values obtained by GPC analysis was summarized in Table 2.

Two different mechanisms for the aggregation of DNFB-PR2000 (or APR2000) described above are suggested. One is the hydrophobic interaction between channel-like (tubularly) arranged CDs in individual polyrotaxanes, which was suggested as a reason for the physical gelation of PEG/CD inclusion complex in water by Li et al. [31]. The other is the attractive interaction dominated by hydrogen bonding between the channel-like CD arrangements, which induces the strong infusibility of the unmodified polyrotaxanes in general solvents [21–24]. The former hydrophobic attraction does not seem to happen in DMSO solvents, whereas the effect of the latter is conceivable since the thixotropy and aggregation during the GPC measurements disappeared after blocking the hydroxyl groups of DNFB-PR2000 by phenylcarbamoylation. Some studies suggested the formation of hydrogen bonding in DMSO [32–34], while most of them have investigated intramolecular hydrogen bonding. As one of the studies suggested [34], upfield and downfield shifts should be observed for the resonances of H-donor and H-acceptor protons incorporated in hydrogen bonding, respectively. However, changes in the chemical shift values of OH groups were observed with all polyrotaxanes as compared to those of free CDs (see Experimental section and ref. [35] for details), regardless of the presence or absence of thixotropy, probably due to the simultaneous occurrence of intramolecular hydrogen bonding within a single polyrotaxane molecule because of the sliding of CDs. Therefore, it seems difficult to observe only the intermolecular hydrogen bonding from the ^{1}H NMR results.

Further, more explanation is required for the reason why thixtropy is unique to polyrtotaxanes prepared from PEG2000 (DNFB-PR2000 and APR2000) and absent for the other ones (DNFB-PR3350 and APR35000). Although convincing evidence is still insufficient, we speculate that thixotropy is induced by the rigidity of a single polyrotaxane molecule in addition to the intermolecular hydrogen bonding between polyrotaxanes. As shown in Table 1, 72% of the PEG chains is covered by CDs in DNFB-PR2000 and probably also in APR2000, whereas the inclusion ratios of DNFB-PR3350 and APR35000 are 52% and 25–30%, respectively. Since the polyrotaxane molecules with a high inclusion of CDs are known to become rigid [36, 37], DNFB-PR2000 and APR2000 molecules possess the most rigid molecular conformation and relatively large excluded volume among the samples in the present study, resulting in the facile formation of a three-dimensional network when contacted *via* intermolecular hydrogen bonding in DMSO. A more detailed investigation on the persistence lengths of these polyrotaxanes (for example, with static light scattering measurements) might be performed, although it seems to be problematical due to the abovementioned aggregation only below a polyrotaxane concentration of 1% and gelation at a concentration of 2.5%.

In conclusion, the thixotropic viscosity behavior was observed only for the DMSO solution of polyrotaxane prepared from PEG2000 due to the combined effect of intermolecular hydrogen bonding and rigid molecular conformation resulting from a high inclusion ratio. The observed phenomenon is significant theoretically since it implies the formation of hydrogen bonding in the DMSO system as well as practically since the time scale of the viscosity behavior can be controlled over a wide range (from 30 s to several hours) only by means of the polyrotaxane concentration. On the other hand, researchers employing this material should take special care when they conduct measurements using this solvent system, such as NMR, GPC, or light scattering measurements.

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Supporting Information Available. A movie of rapid gelation of the 10wt% solution of DNFB-PR2000 in DMSO (Quicktime Movie) is available as a Supporting Information.

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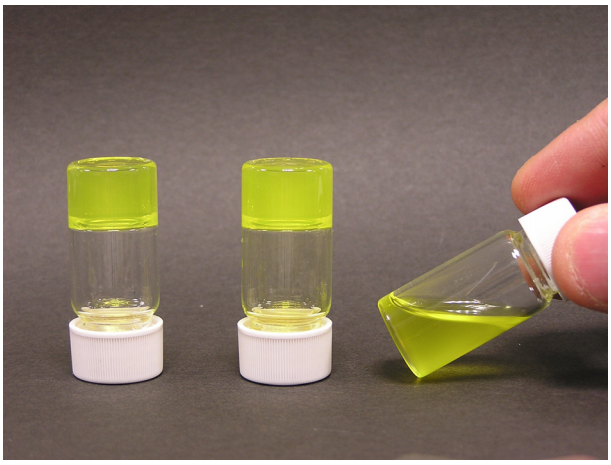
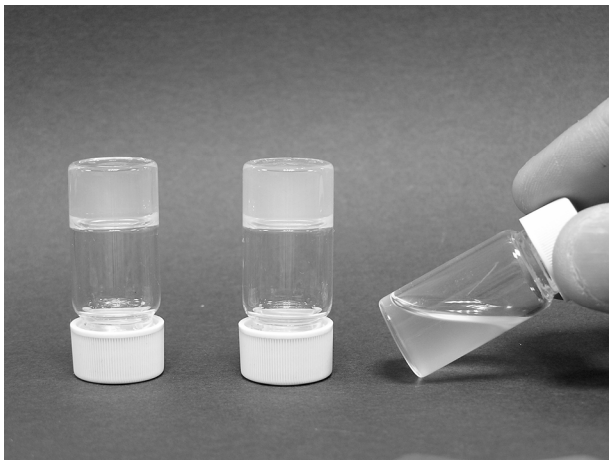


Figure 1. Appearance of polyrotaxane solutions in DMSO. From the left to right, DNFB-PR2000 at 5wt% concentration, DNFB-PR2000 at 2.5wt% concentration, and DNFB-PR3350 at 5wt% concentration.



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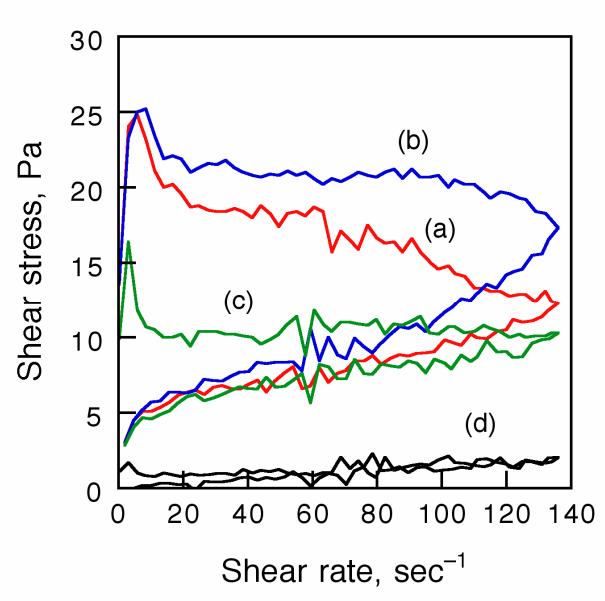

Figure 2. Viscosity curves of the DNFB-PR2000 solution in DMSO at 5wt% concentration (a–c) and the DNFB-PR3350 solution in DMSO at 5wt% concentration (d). (a) First measurement, (b) second measurement performed 1 h after the first measurement, (c) third measurement performed just after the second measurement and (d) first measurement after leaving 1 h in a rheometer.

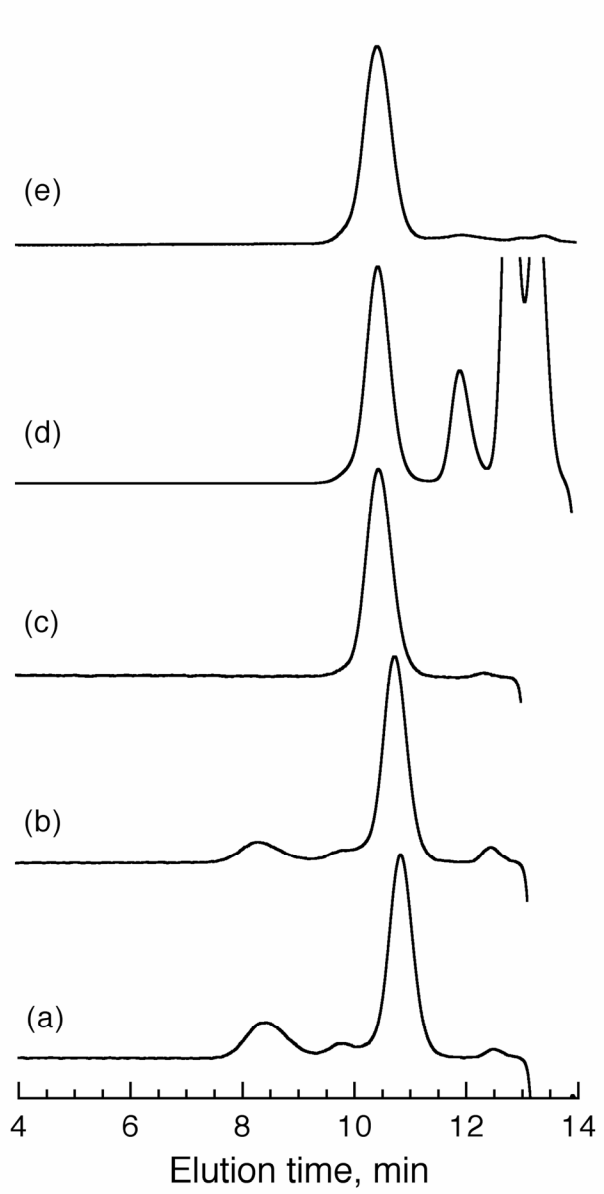

Figure 3. GPC profiles of (a) DNFB-PR2000, (b) APR2000, (c) DNFB-PR3350, (d) triphenylcarbamoylated DNFB-PR2000 sampled before purification, and (e) purified triphenylcarbamoylated DNFB-PR2000 (see the text for details).

Table 1. Amount of CDs in single polyrotaxane and corresponding inclusion ratios of various polyrotaxane samples.

Samples	Used PEG	Averaged number of CDs in single polyrotaxane	Inclusion ratio, % [a]
DNFB-PR2000	PEG-DAT2000	15.9 [b]	72

DNFB-PR3350	PEG-BA3350	19.5 [b]	51
APR2000	PEG-DAT2000	Not determined [c]	Not determined [c]
APR35000	PEG-COOH35000 [d]	90–100 [e]	25–30

[a] Calculated based on the values of the possible maximum amounts of CDs with the hypothesis that one CD molecule occupies two ethylene glycol units of PEG and the maximum amount of CDs. See refs. 5–9 for details.

[b] Calculated from the peak integration in the ^{1}H NMR spectra of the sample decomposed after hydrolysis with 4% NaOD/D_2O at room temperature for 7 days. See the text for details.

[c] The values could not be determined since the sample could not be hydrolyzed with 4% NaOD/D_2O.

[d] PEG with a molecular weight of 35000 and two terminal carboxyl groups. See ref. 28 for details.

e Calculated from the peak integration in the ^{1}H NMR spectra of the sample without hydrolysis with 4% NaOD/D_2O. See ref. 28 for details.

Table 2 Molecular weight results calculated from GPC measurements.

Entry in Figure 3	Sample	Weight average molecular weight, M_w [a]	polydispersity, M_w/M_n	Content of the corresponding fraction
a	DNFB-PR2000	$7.12–8.79 \times 10^5$	1.44–1.64 [b]	Aggregated polyrotaxanes
		$5.69–5.85 \times 10^4$	1.04–1.05 [b]	Aggregated polyrotaxanes
		$1.01–1.19 \times 10^4$	1.12–1.15 [b]	Single Polyrotaxane
b	APR2000	8.06×10^5	1.45	Aggregated polyrotaxanes
		5.61×10^4	1.09	Aggregated polyrotaxanes
		1.10×10^4	1.11	Single Polyrotaxane
c	DNFB-PR3350	1.81×10^4	1.18	Single Polyrotaxane
d	Phenylcarbamoylated DNFB-PR2000 before purification	1.88×10^4	1.15	Single (dispersed) phenylcarbamoylated polyroptaxane
		1.62×10^3	1.07	Dibutyltin dilaurate (DBTDL)
		3.38×10^2	1.05	Dimerized phenylisocyanate
		1.15×10^2	1.05	Free phenylisocyanate
e	Phenylcarbamoylated DNFB-PR2000 after purification	1.81×10^4	1.15	Single (dispersed) phenylcarbamoylated polyroptaxane

[a] Calculated from GPC measurements based on PEG standards.

[b] Ranges of the values within three repeated measurements are shown.