

High Conversion Synthesis of Pyrene End Functionalized Polyrotaxane Based on Poly(ethylene oxide) and α -Cyclodextrins

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We describe the quantitative synthesis of new pyrene labeled cyclodextrin-based polyrotaxane starting from pseudopolyrotaxane of α,ω -dimethacrylate poly(ethylene oxide) (PEO) and α -cyclodextrins (α -CDs). Using a solvent mixture (H_2O /dimethyl sulfoxide (DMSO)), an almost quantitative conversion in polyrotaxane can be achieved using the coupling reaction between methacrylic functions and 1-pyrene butyric acid *N*-hydroxysuccinimide ester. This result is due to the fast blocking reaction of the pseudopolyrotaxane telechelic functions. The polyrotaxanes are characterized by NMR, size exclusion chromatography (SEC), and small-angle neutron scattering (SANS). A rodlike structure of the polyrotaxane is evidenced by SANS, and a persistence length of 70 Å is determined. This result corresponds to an almost completely stretched PEO chain of 1000 $\text{g}\cdot\text{mol}^{-1}$ molecular weight. We furthermore studied the opposite case of low packing density polyrotaxanes that were also silylated to suppress interactions between cyclodextrins. We observed a random coil structure only for silylated low packed polyrotaxane. This result demonstrates that both hydrogen bonding and packing density can explain the rodlike structure of cyclodextrin-based polyrotaxane.

1. Introduction

The polyrotaxanes are supramolecular assemblies in which cyclic molecules are threaded on a linear polymer chain. They presently are the subject of many studies.¹ Supramolecular assemblies of poly(ethylene oxide) (PEO) and cyclodextrins (α -CDs) have in particular been reported by Harada and colleagues.² These samples are simply formed by mixing both components in water, and the cyclic molecules spontaneously thread the linear chain forming hydrophobic interactions,³ and the supramolecular complex precipitates once formed. These complexes are called pseudopolyrotaxane because the cyclodextrins can be dethreaded of the polymer chain when dissolved in a good common solvent. To prevent this phenomenon, reaction of the telechelic functions of the threaded polymer with a bulky group has to be carried out. The reactions that can be used for such blocking must fulfill several conditions such as an inertia of the reactive groups versus the hydroxyl functions of the CD, effective at room temperature, and the involved reactants must be soluble in polar solvent without providing any competitive complexation with the cyclodextrin. Harada and colleagues⁴ first reported the synthesis of cyclodextrin-based polyrotaxane. An α,ω -diamino PEO-based polyrotaxane was reacted with fluorodinitrobenzene. This reaction has been selected due to its efficiency at room temperature; however, reaction with the hydroxyl functions of the CD cannot be dismissed. Ooya and Yui⁵ suggested to use the benzyloxycarbonyl(Z)-L-phenylalanine as a blocking agent to provide degradable supramolecular assemblies. These authors also used FITC for the blocking reaction of an α,ω -diamino PEO–poly(propylene oxide) (PPO)–PEO triblock copolymer/cyclodextrin-based polyrotaxane.⁶ In every case, the reported yields do not exceed 40%.

Polyrotaxanes made out of cyclodextrins and PEO may find numerous applications in material science, that is, polyrotaxanes for drug release via supramolecular dissociation,⁷ hydrogels,⁸ insulated molecular wires,⁹ topological gels,¹⁰ purification process,¹¹ and so forth. The main issue is now to find a process that allows large-scale synthesis of such materials in high conversion. In this work, we report the synthesis of new polyrotaxane labeled with pyrene functions and having two telechelic functions that could be used for subsequent chemistry. The blocking chemistry that we use is based on the coupling of a succinimidyl ester derivative with methacrylic telechelic functions of a PEO chain. The packing density of these supramolecular assemblies is varied, and SANS is carried out on samples having various filling ratios. The importance of hydrogen bonding in the stretching of the assembly is investigated. A preliminary report¹² of the neutron scattering studies of our polyrotaxane structure has been published. Since that time, a single study¹³ has been reported on the subject focused on polyrotaxane with a low CD filling ratio, that is, a low number of cyclic molecules threaded on the PEO chain. Surprisingly, Karino and colleagues¹³ observe that rodlike structure can be achieved without a high CD filling ratio, which requires the presence of hydrogen bonding. We will also investigate this point by synthesizing silylated polyrotaxanes.

2. Experimental Section

Materials. Cyclodextrins (α -CDs) were kindly supplied by Wacker. They were used after drying under vacuum for 16 h at room temperature. α,ω -Dimethacrylate poly(ethylene glycol) ($\bar{M}_n = 1000 \text{ g}\cdot\text{mol}^{-1}$ and $I_p = 1.09$) was purchased from Polysciences, Inc. The average molecular weight of the polymer samples was determined by size exclusion chromatography, and the rate of functionalization $\bar{f} = 2$ was verified by ^1H NMR. Radical initiators, that is, ammonium persulfate (Acros) and azobisisobutyronitrile (AIBN, Merck), were used as received.

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Ultrapure water was achieved with a Quantum Ultrapure Organex Cartridge (QTUM000EX, Millipore), and dimethyl sulfoxide (DMSO) was purchased from Merck and used as received.

Measurements. *Size exclusion chromatography (SEC)* was performed in dimethylformamide (DMF) with UV ($\lambda = 345$ nm) and refractive index detection. Two preparative columns (WATO25861) were used in series, and the flow rate was 2.0 mL/min but with analytic quantities (3 mg/mL) to limit the diffusion phenomena and adsorption of CD. The reported molecular weights are expressed in PEO equivalents.

^1H NMR spectra were recorded on a Bruker instrument at 300 MHz in dimethyl sulfoxide ($\text{DMSO}-d_6$).

Neutron Scattering Experiments. Small-angle neutron scattering (SANS) measurements were performed at the Laboratoire Léon Brillouin ("ORPHEE" reactor, CEN Saclay) on the "PACE" spectrometer. The scattering vector length (q) ranges from 10^{-3} to 10^{-1} \AA^{-1} . A neutron beam wavelength of 6 Å was used with a sample-to-detector distance of 3.2 m. The samples were used as 2% solution in $\text{DMF}-d_7$ and loaded into Hellma quartz neutron cells with a 2 mm optical path length. The cells were placed in a sample-passing holder, and scattering for each sample was measured for about 4 h at 20 °C. The temperature was controlled to ± 1 °C. The data have been corrected by background subtraction and water normalization as usual. The respective scattering length densities of $\text{DMF}-d_7$, cyclodextrin, and polyrotaxane are 6.33×10^{-6} , 1.77×10^{-6} , and $1.83 \times 10^{-6} \text{ \AA}^{-2}$ using measured values of the CD and polyrotaxane densities of 1.51 and 1.56 g/cm^3 . The polyrotaxane and the cyclodextrin thus have identical contrast factors. Other scattering experiments have been performed using deuterated DMSO as solvent; no significant signal could be measured due to a lower contrast factor and the probable occurrence of proton exchange between the CDs and $\text{DMSO}-d_6$.

Preparation of the Inclusion Compounds: The Pseudopolyrotaxane. *Pseudopolyrotaxane POE/ α CD.* α,ω -Dimethacrylate poly(ethylene glycol) ($M_n = 1000 \text{ g}\cdot\text{mol}^{-1}$) was added to a saturated aqueous solution of CD (14.5 g/L). The reaction was mixed at room temperature for 2 h. According to Harada's findings, the stoichiometries of the ethylene oxide unit and α -CD in the pseudopolyrotaxane were 2:1 ($2n_{\text{OE}} = n_{\alpha\text{-CD}}$); at this stoichiometry, α -CD should be almost closely packed from end to end of the POE dimethacrylate chain. The mixture became turbid, and the complexes were obtained as a white crystalline precipitate. The precipitate was collected by filtration, washed successively with CH_2Cl_2 (POE's solvent) and with ethanol (α -CD's solvent), and dried under vacuum at 60 °C to give the pseudopolyrotaxane. The yield is 80%. ^1H NMR of the complex: POE's peaks: 1.7–1.9 ppm (s, 6H, $\text{CH}_3\text{—C=}$), 3.5–3.6 ppm (s, 80H, $\text{—CH}_2\text{—CH}_2\text{—O}$), 3.6–3.7 ppm (t, 4H, $\text{CH}_2\text{—CH}_2\text{—COO}$), 4.1–4.3 ppm (t, 4H, $\text{CH}_2\text{—COO}$), 5.5–5.7 ppm (s, 2H, —CH=), 5.9–6.1 ppm (s, 2H, —CH=). Cyclodextrin's peaks: 3.5–3.6 ppm (m, 1H, H_4), 3.6–3.7 ppm (m, 1H, H_2), 3.8–3.85 ppm (m, 1H, H_5), 3.85–3.95 ppm (m, 1H, H_6), 3.9–4.0 ppm (m, 1H, H_3), 4.3–4.5 ppm (t, 1H, OH_6), 4.6–4.8 ppm (s, 1H, $\text{H}_1=\text{H}$ anomeric), 5.3–5.6 ppm ($2 \times$ d, 1H, OH_3 and OH_2).

Synthesis of the Polyrotaxane. A powder mixture of 1 g of the pseudopolyrotaxane POE/ α CD, 340 mg of 1-pyrene butyric acid *N*-hydroxysuccinimide ester ($n_{\text{py}} = 5n_{\text{dim}}$), and 700 mg of the initiating molecule (ammonium persulfate, 50% in weight) is added into a reaction flask. The reaction started at room temperature with the addition of 17.5 mL of the proportion of the dimethyl sulfoxide in water (33/6; v/v). The concentration of the system must not be lower than 0.1 g/1.75 mL. Roughly

15 min after the addition of the solvent mixture, the reaction is quenched by dipping the reaction flask in liquid nitrogen followed by freeze-drying. The resulting solid is dissolved in dimethylformamide or dimethyl sulfoxide. It is then precipitated in diethyl ether, filtrated, washed, and dried at 60 °C in a drying chamber. The reported polyrotaxane conversion by SEC measurement is 95% (see below).

Silylation of the Polyrotaxane. Silylation reaction of cyclodextrins was carried out as previously reported.¹⁴ The silylation of polyrotaxane was performed under anhydrous conditions, under an inert atmosphere. A 50 mg portion of polyrotaxane is introduced in a flask where a N_2 flow is maintained for 15 min before adding 1 mL of anhydrous DMF. When the polyrotaxane is totally dissolved, 1.4 mL of *N*-trimethylsilylimidazole (TMSI, Aldrich) is dropped ($n_{\text{TMSI}} = 6n_{\text{OH}}$) at 20 °C under magnetic stirring. After 1 h, the mixture is diluted with 6 mL of chloroform to avoid an eventual precipitation. The reaction is stirred for 1 h under dynamic N_2 and under static N_2 for 8 days. The reaction is stopped by slowly adding 10 mL of water. The organic solution is washed three times with water, and the product is dried. The silylation rate is calculated using ^1H NMR spectroscopy by peak integration of hydrogen bearing by methyl groups of $\text{O—Si}((\text{CH}_3)_3)$ versus the hydrogen of pyrene groups. The silylation rate is 100%.

3. Results and Discussion

Results of the Polyrotaxane Synthesis. The derivatization of α,ω -dimethacrylate PEO was carried out as described in a previous paper.¹⁵ It was previously demonstrated that the reaction of α,ω -dimethacrylate PEO derivatization took place in a solvent mixture of $\text{H}_2\text{O}/\text{DMSO}$ at room temperature and the best conditions for the synthesis of polyrotaxane are described below. In Table 1, the effect of various proportions of H_2O as cosolvent in DMSO is shown. Actually, the conversion of polyrotaxane was very dependent on the H_2O concentration in DMSO. The conversion is defined in this study as the ratio of the weight of polyrotaxane formed to the weight of the initial products, ignoring the excess of the blocking agent 1-pyrene butyric acid *N*-hydroxysuccinimide ester (PyBHS) which is removed by precipitation. To compare the runs, the conversion was discussed. In Table 1, the third column shows the conversion of polyrotaxane obtained from SEC analysis by the ratio of the polyrotaxane peak area to the total peak area of the crude product, assuming the same response of the refractive index detector for all peaks (this assumption can be made, since the crude product is formed by cyclodextrin, either free or complexed in the polyrotaxane). This form of quantification is close to the quantification of polyrotaxane conversion by direct titration of free α -CDs after calibration. This last determination is presented in the fourth column of Table 1. α -CD calibration was previously carried out and permits the ratio of free α -CDs in a given amount of polyrotaxane to be quantified. It can be seen that the two determinations are in good agreement for the highest water concentration. The fifth column of Table 1 shows the M_n values of the polyrotaxanes in PEO equivalence, which does not represent the absolute value but allows the various experiments to be compared. The presence of high molecular weight compound witnesses the presence of stable supramolecular structure. Indeed, pseudopolyrotaxane analyzed through this technique shows a total dethreading of the supramolecular structure. SANS characterization was realized to afford absolute molecular weight values.

As a control, the first experiment (run 1) was carried out in pure DMSO, under homogeneous conditions, with the use of

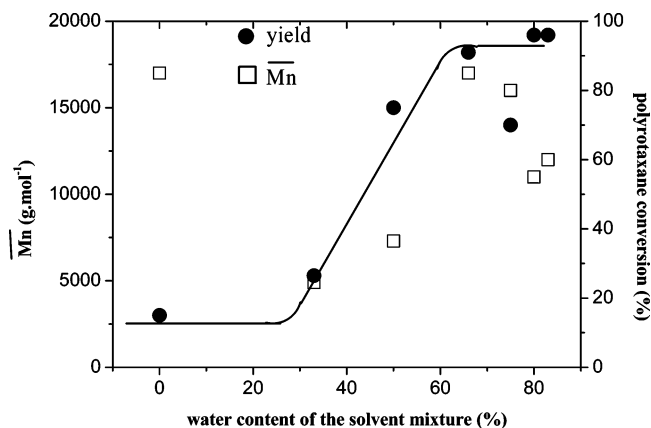
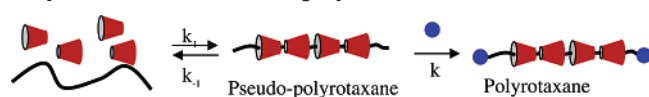
TABLE 1: Effect of Solvent Composition of the Conversion, the \bar{M}_n , and the Polydispersity (I_p)

| run | % H ₂ O | conversion (peak area by refractive detection in SEC) | conversion (from free CDs by refractive detection in SEC) | \bar{M}_n (g·mol ⁻¹) | I_p |
|-----|--------------------|---|---|------------------------------------|-------|
| 1 | 0% | 14% | 15% | 17 000 | 1.1 |
| 2 | 33% | 18.5% | 27% | 4900 | 4.5 |
| 3 | 50% | 43% | 75% | 7300 | 3.5 |
| 4 | 66% | 100% | 91% | 17 000 | 1.2 |
| 5 | 75% | 38% | 70% | 16 000 | 1.7 |
| 6 | 80% | 99% | 96% | 11 000 | 2.7 |
| 7 | 83% | 91% | 96% | 12 000 | 1.9 |

AIBN at 60 °C. A low conversion of 15% demonstrated that working at high temperature under homogeneous conditions leads to a large dethreading of cyclodextrins before derivatization. To avoid dethreading, the medium was enriched in water and the other runs (Table 1) were carried out with ammonium persulfate as initiator at room temperature. The results of runs 2–4 showed a conversion increasing with the water content of the reaction solvent, which was accompanied by an increase of the average number molar mass \bar{M}_n and a decreasing polydispersity index. This trend allows it to be concluded that the CD packing on the polymer chain increases with the polyrotaxane conversion, and this fact will be demonstrated in the neutron scattering section. From 33% weight of water content in the solvent of the reaction, the solution becomes turbid to the eye. To account for these data, the competition between cyclodextrins dethreading and the derivatization reaction must be considered (Scheme 1).

As previously reported about the model reaction,¹⁵ the coupling reaction takes place between the $-\text{CH}_2^\bullet$ type species issued from the PyBHS initiation. In fact, this initiation results from the reaction between PyBHS and radicals obtained by persulfate degradation. According to Scheme 1, the results are explained kinetically assuming that the pseudopolyrotaxane can dissolve and also dissociate in the diluted reaction medium. When the concentration of water increases, dethreading (reaction rate constant of dethreading (k_{-1})) is avoided or largely diminished and the pseudopolyrotaxane can be derivatized by the radical coupling reaction (whose reaction rate constant is k). For polyrotaxane formation, the coupling reaction must occur at a higher rate than the dethreading process. Our results show that a higher water concentration decreases the rate of dethreading, in agreement with the fact that pseudopolyrotaxane spontaneously forms in water and precipitates. Up to 66% of water ($k_{-1} \ll k$), the polydispersity indexes and the conversion are optimized, as shown in Figure 1. The overall result depends on the water content. Nevertheless, when the water concentration is too high, the insolubility of PyBHS in water is responsible for the decreasing rate of the blocking reaction rate, as previously shown.¹⁵ Finally, it is straightforward to assume that the increase of the polydispersity index is due to the increased coupling reaction rate between methacrylate functions.

The influence of the reaction time upon polyrotaxane formation was examined. To achieve this goal, the conditions of run 4 (66% water content) were chosen as the reference reaction, and the reaction conversion was determined at various reaction times (Table 2). It can be seen that the reaction is over within less than 15 min.

SCHEME 1: Sketch of the Blocking Process Leading to Polyrotaxane from Pseudopolyrotaxane**Figure 1.** Influence of the solvent composition on \bar{M}_n and the conversion of polyrotaxane (the line is a guide for the eye).**TABLE 2: Influence of the Reaction Time on \bar{M}_n , I_p , and the Conversion of Polyrotaxane Synthesis**

| run | reaction time (min) | conversion (CDs calibrate by refractive detection in SEC) | \bar{M}_n (g·mol ⁻¹) | I_p |
|-----|---------------------|---|------------------------------------|-------|
| 8 | 15 | 94% | 42 000 | 1.1 |
| 9 | 30 | 100% | 36 000 | 1.1 |
| 10 | 60 | 94% | 33 000 | 1.1 |

TABLE 3: Influence of the Reaction Temperature on \bar{M}_n , I_p , and the Conversion of Polyrotaxane

| run | reaction temperature (°C) | conversion (CDs calibrate by refractive detection in SEC) | \bar{M}_n (g·mol ⁻¹) | I_p |
|-----|---------------------------|---|------------------------------------|-------|
| 4 | 25 | 91% | 17 000 | 1.2 |
| 12 | 30 | 82% | 11 000 | 1.5 |
| 13 | 40 | 96% | 5000 | 1.2 |
| 14 | 60 | 96% | 10 000 | |

Considering that the reaction could be dependent on the competition between pseudopolyrotaxane dethreading and the blocking reaction, both possibly temperature sensitive, the influence of the reaction temperature was investigated. The results are shown in Table 3.

Table 3 shows that the temperature had no influence on the polyrotaxane conversion in this temperature range. It is important to mention that, in the synthesis process, the solvent is added to the reactant to start the blocking reaction. Thus, the reactive medium is placed at the desired temperature. One cannot omit a possible delay for the increase in temperature due to the reaction procedure. However, these surprising results emphasized that polyrotaxane formation is apparently ruled by a high value for the kinetic constant ratio k/k_{-1} .

At this point, as a consequence of the overall behavior of the reaction products in which α -CD is assembled to the PEO dimethacrylate, it was concluded that, following the above procedure, α -CDs are not free, that the ends of PEO dimethacrylate are functionalized as shown by the model experiment,¹⁵ and that the high molar mass obtained demonstrated the existence of polyrotaxane. More detailed characterization was carried out to firmly establish these conclusions.

Physicochemical Characterization. Characterization by ¹H NMR. The spectrum of the polyrotaxane (Figure 2) presents the characteristic peaks of the various constituents such as pyrene (around 8.1 and 8.5 ppm), cyclodextrins (mainly around 3 and 4 ppm), and PEO.

In the polyrotaxane spectrum (black line), we can see that the usual peak of PEO at 3.4–3.5 ppm in DMSO-*d*₆ is shifted upfield compared with the case of the pseudopolyrotaxane (red line). The good correlation of the chemical shift between PEO

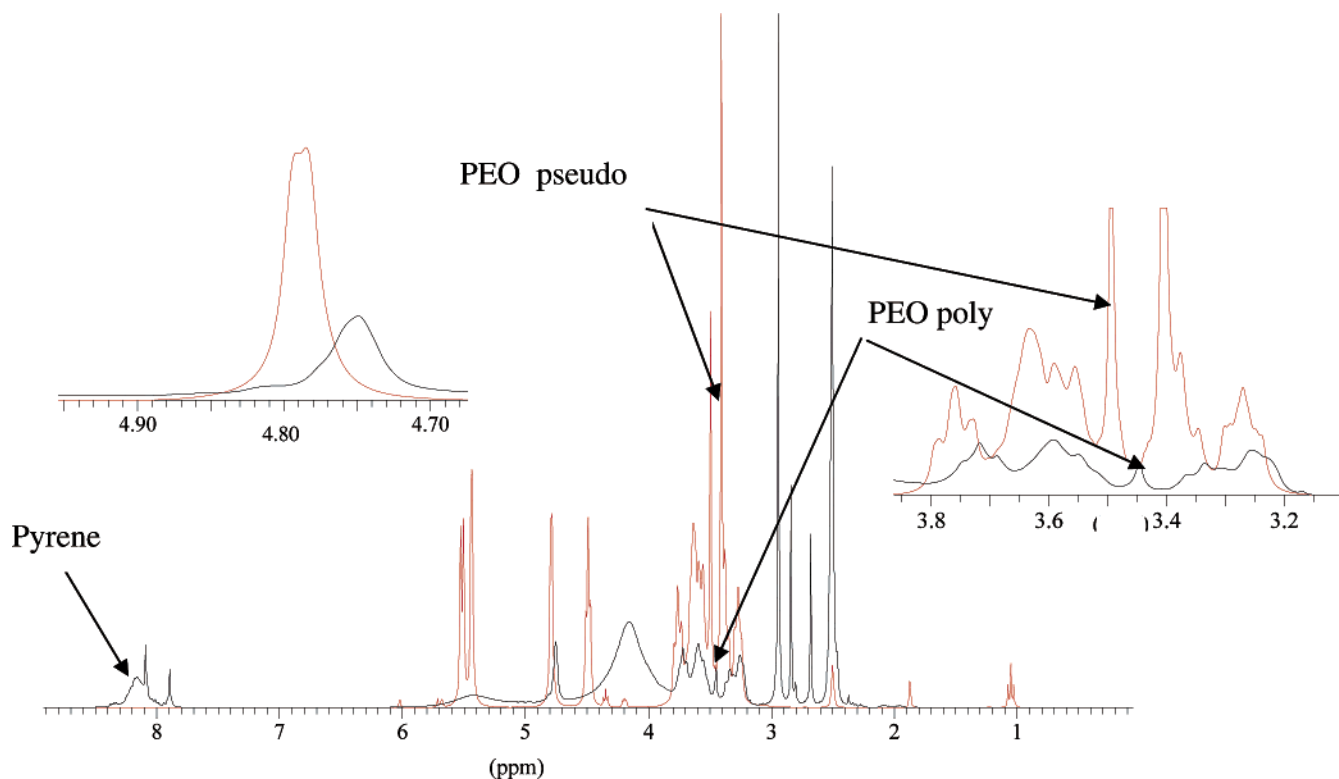


Figure 2. ^1H NMR spectra of a polyrotaxane (black) and the corresponding pseudopolyrotaxane (red) in $\text{DMSO}-d_6$ (2.5 ppm in both spectra).

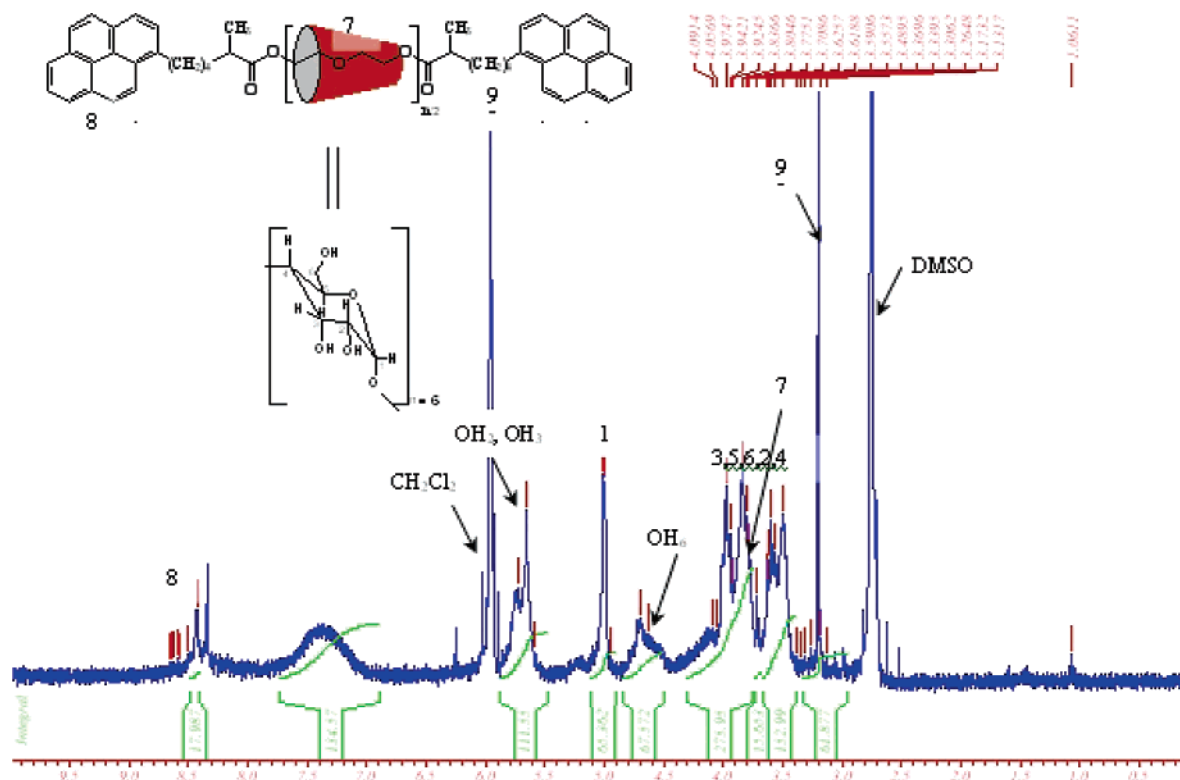


Figure 3. ^1H NMR spectra of a polyrotaxane (run 4) in $\text{DMSO}-d_6$.

and pseudopolyrotaxane translates into a dethreading of the molecular assembly when diluted in DMSO for analysis purposes. When the polyrotaxane spectrum is compared with that of pseudopolyrotaxane, the PEO signals are very different. In DMSO solution of pseudopolyrotaxane, the dethreading of the supramolecular assembly allows a neat characterization of the PEO signal. However, in the case of the polyrotaxane, the blocking groups avoid dethreading and the PEO signal is much

lowered. The inclusion complex formation leads to the shift of the anomeric hydrogen of the glucopyranose unit around -0.1 and -0.2 ppm¹⁶ (see above in the inserted spectrum placed on the left). The same phenomenon is also characteristic of H_3 , H_5 , H_6 , H_2 , and H_4 , as presented in the inserted spectrum on the right side of Figure 2. Thus, this NMR characterization can be considered as an indirect proof of the presence of polyrotaxane. The disappearance of the PEO signal was also noticed

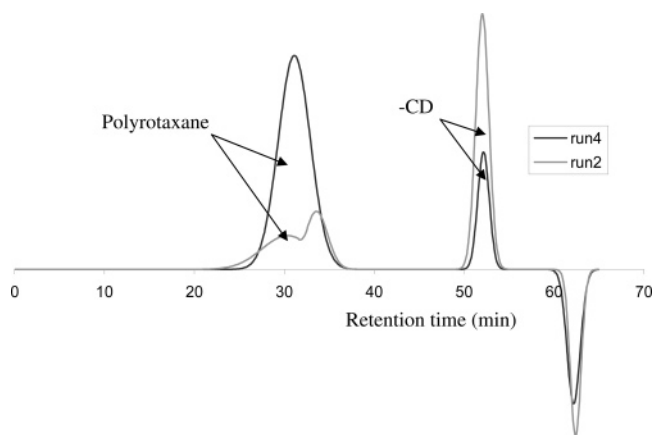


Figure 4. SEC chromatograms of runs 2 and 4 obtained by refractometric detection.

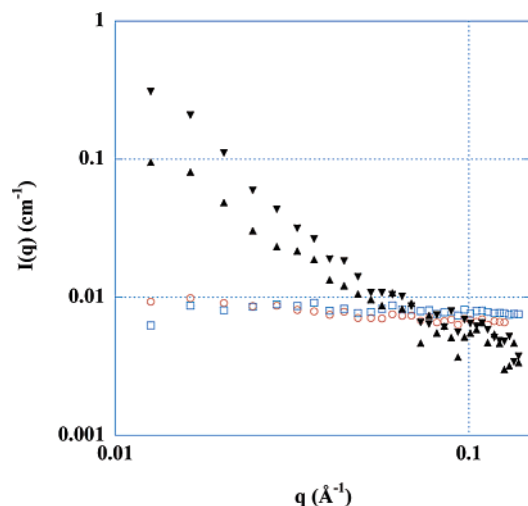


Figure 5. Neutron scattering intensity versus scattering vector for three different samples on a logarithmic scale: (▲) polyrotaxane 1% in DMF; (▼) polyrotaxane 2% in DMF; (○) pseudopolyrotaxane 2% in DMF; (□) α -cyclodextrine 2% in DMF.

by Ueno et al.,¹⁷ and it can be attributed to restricted mobility of the polymer chain inside the molecular tube formed by the cyclodextrin rings.

Figure 3 shows the ^1H NMR spectrum of run 4 (Table 1). To determine the average number of cyclodextrins per PEO chain, we selected the well isolated signals of the pyrene end groups of the threaded polymer and the anomeric proton of the cyclodextrins. For run 4, the integration ratio is 10, and the average molar ratio of EO units/CD is 2.2, close to the theoretical value suggested by Harada et al.²

Characterization by SEC. In the case of the formation of a stable supramolecular assembly, species of large molecular weight are expected. Pseudopolyrotaxanes were first analyzed with SEC using usual concentrations, and a total dethreading of the molecular assemblies is observed, witnessed by the presence of one peak on the chromatogram, attributed to free CD and free PEO. Figure 4 shows chromatograms of polyrotaxanes that exhibit a new signal corresponding to large-molecular-weight species as well as the signal corresponding to free cyclodextrins. The ratio of the two populations is related to the conversion of polyrotaxane synthesis. Indeed, this conversion was determined using two methods that lead to similar results: titration of free cyclodextrins using a calibration of the signal and relative surface ratio of peaks corresponding to the polyrotaxane and the free cyclodextrins.

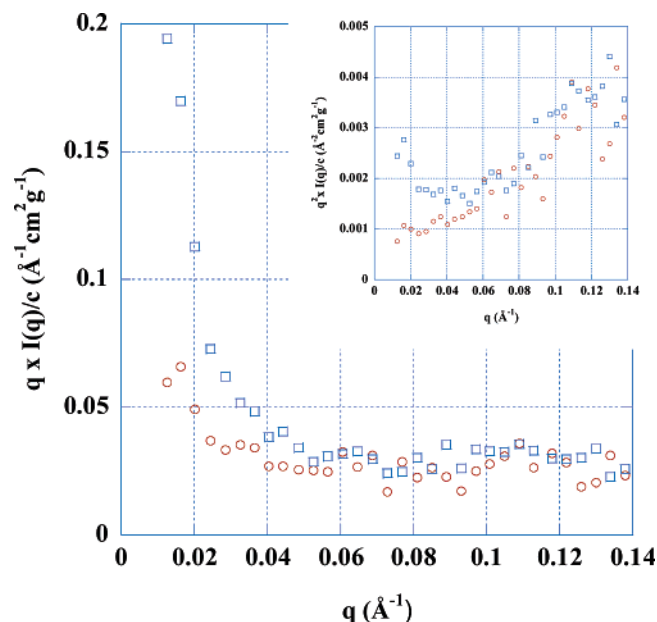


Figure 6. $q^2 I(q)/c$ versus q for polyrotaxanes at two different concentrations exhibiting a rodlike asymptotic behavior: (□) polyrotaxane 2% in DMF; (○) polyrotaxane 1% in DMF. Inset: curve of $q^2 I(q) = f(q)$.

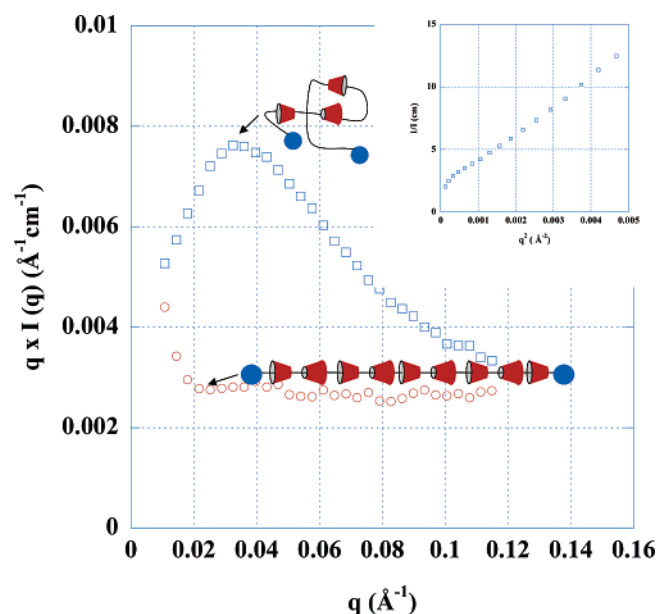


Figure 7. Scattering intensity in the representation $q^2 I(q)$ versus q for two persilylated polyrotaxanes bearing a different number of CDs (□, run 15; ○, run 17) at 2% in acetone- d_6 as represented.

Characterization by Small-Angle Neutron Scattering. As previously reported,¹² the threading of the α -CD by PEO after the coupling reaction can be evidenced by SANS measurements. Figure 5 shows the scattering intensity ($I(q)$) versus the scattering vector (q) for free cyclodextrin, pseudopolyrotaxane, and polyrotaxane on a logarithmic scale. Moreover, the behaviors of pure α -CD and pseudopolyrotaxane, at the same concentration, are identical in DMF. Thus, these results show that pseudopolyrotaxane is dethreaded. On the other hand, the scattering intensity of polyrotaxane is high at low q , as expected for large-molar-mass species.

To investigate the internal structure of the polyrotaxane, we have studied the asymptotic behavior of the scattered intensity. The examined samples have a well-defined asymptotic behavior

TABLE 4: Silylation of Various Types of Polyrotaxane Purified by Preparative SEC

| run | polyrotaxane native issue to run | [polyrotaxane] (mol·L ⁻¹) | [TMSI] (mol·L ⁻¹) | <i>n</i> _{TMSI} / <i>n</i> _{OH} | reaction time (h) | number of persilylated CDs evaluated by ¹ H NMR |
|-----|-------------------------------------|--|----------------------------------|---|----------------------|---|
| 15 | 2 | 5 × 10 ⁻³ | 9.58 | 12 | 192 | 3 |
| 16 | 3 | 5 × 10 ⁻³ | 9.58 | 12 | 192 | 6 |
| 17 | 10 | 5 × 10 ⁻³ | 9.58 | 12 | 192 | 9 |

that is exhibited in Figure 6 where we show that the normalized quantity $q \cdot I(q)/c$ (c being the concentration) reaches a well-defined limit at large scattering vectors: this is typical of a rodlike local behavior, which is expected from a polymer rigidified by the threaded α -CD.

The scattering intensity deviates from the asymptotic $1/q$ behavior at the smallest scattering angle without reaching a well-defined Guinier regime. This corresponds to flexible, possibly slightly aggregated large-scale structures, whose radius of gyration is too large to be measured in the present experiment. However, the deviation from the rodlike behavior can be used to estimate the size of the observed rodlike structure. The crossover between the two regimes corresponds to a scale of 70 (± 10) Å, which implies that the original PEO chains are almost completely stretched.

The hydroxyl functions of the cyclodextrins of the polyrotaxane were silylated to avoid hydrogen bonding between CDs. The reaction time was adjusted to allow the complete modification of CD sterically strained on the polyrotaxane: the much longer reaction time than that for free CD can be attributed to hydrogen bonding between cyclodextrins and to the steric hindrance of the hydroxyl functions in the polyrotaxane. Full silylation was witnessed by ¹H NMR characterization, that is, the disappearance of the hydroxyl function signal accompanied by the appearance of a new signal corresponding to the trimethyl silyl functions. The number of persilylated cyclodextrins per PEO chain was again evaluated by the ¹H NMR integration signal ratio of pyrene end groups to trimethylsilyl functions and reported in Table 4.

SANS measurements were then facilitated by the increase of the contrast factor when the acetone-*d*₆ was used as solvent of the silylated structures. We compare in Figure 7 the scattering intensity in representation $q \cdot I(q)$ versus q of two polyrotaxanes with different cyclodextrin packing ratios. We observed two strikingly different behaviors. The sample with the highest packing density exhibits a perfect rodlike behavior with a well-defined asymptotic decay of the scattering intensity. On the other hand, the sample with a low CD content shows a random coil behavior. This explicitly shows that the CD density along the PEO chain controls the rigidity of the assembly.

This derivatization of polyrotaxanes allows us to discriminate the responsible origin of the rodlike structure of cyclodextrin-based polyrotaxane that we first evidenced.¹² As discussed by Shibayama and colleagues,¹³ a close packed structure of cyclodextrins on the polymer chain allows an energy release due to hydrogen bonding between cyclodextrins. This observation is consistent with theory concerning such supramolecular assembly synthesis. However, the synthesis of highly packed cyclodextrin-based polyrotaxane leads to extended structures not dependent upon hydrogen bond formation. These new results open some interesting liquid crystal applications involving modified densely packed polyrotaxanes.

Figure 7 shows that silylated cyclodextrin-based polyrotaxanes with a low packing ratio are in the Guinier domain. Thus, the scattering intensity is described by the relation:

$$I(q) = \frac{I_0}{\left(1 + q^2 \left(\frac{R_g^2}{3}\right)\right)}$$

where I_0 represents the scattering intensity when the scattering vector tends to 0 and R_g is the radius of gyration. A plot of the reciprocal scattering intensity versus q^2 leads to a radius of gyration of 53 Å and an I_0 value of 0.930 for this sample. Neutron scattering intensity versus scattering vector was recorded for persilylated cyclodextrin in acetone-*d*₆ (2%), and an I_0 value of 0.124 was determined (data not shown). Assuming that the I_0 value of the polyrotaxane is proportional to the number of cyclodextrins on the polymer chain, we calculate a ratio of CD/ethylene oxide dimers close to 0.70. Considering a molecular weight of a persilylated cyclodextrin of 2269 g·mol⁻¹, the \bar{M}_n value of the polyrotaxane is close to 17 000 g·mol⁻¹.

4. Conclusion

α,ω -Pyrene labeled α -cyclodextrin-based polyrotaxanes were obtained in high conversion. The heterogeneous medium with high coupling kinetics was found to be responsible for such a control of the polyrotaxane conversion. We demonstrate that increasing the heterogeneity of the reaction medium allows a higher packing density of the cyclodextrins on the polymer chain. The various synthesized polyrotaxanes were used to discriminate the responsible phenomena of the rodlike structure of these supramolecular assemblies, evidenced by SANS. At low CD packing on the polymer chain, the hydrogen bondings between cyclodextrins lead to an extended structure of the polyrotaxane. When the CD packing increases, geometrical restrictions lead to the same rodlike structure. Silylation of cyclodextrins was then found to be an efficient tool to control cyclodextrin interactions on the polymer chain that govern the conformation of the polyrotaxanes in solution. The rodlike structure of our supramolecular assemblies will be used for further applications.

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References and Notes

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