# The First Fullerene-Terminated Soluble Poly(azomethine) Rotaxane

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**Introduction.** Poly(azomethine)s (PAMs) with aromatic backbones are attractive conducting polymers.[1] However, their insolubility in common organic solvents limits their processability and characterization. Over the past 25 years different methods have been adopted toward processable poly(azomethine)s by incorporating nonconjugating linkages into the main chain,[2] through copolymerization,[3] by attaching functional groups or flexible chains as branches onto the main chain,[4] or by a combination of both.[5] In most cases, the polymers were still insoluble, and hence the problems of processability and characterization remain unresolved. Modifying the conjugated chain by solubilizing groups disturbs the electron delocalization and affects the interesting properties of this conducting polymer. Recently, the concept of polymerization in the cyclodextrin cavity has been introduced[6] and also applied to the synthesis of PAMs, leading to soluble rotaxanes.[7]

We attempted to solubilize **1** (Scheme 1) according to this concept by condensing $\beta$-cyclodextrin (CD) inclusion complexes of *p*-phenylenediamine (PD) and terephthalaldehyde (TD) but failed to get any soluble product. However, the polycondensation in the presence of a 3 M excess of CD and using $C_{60}$ as the end-capping agent led to the high molecular mass soluble polyrotaxane **5**.

**Experimental Section. a. Synthesis of the Pseudopolyrotaxane.** Equimolar quantities of **2** (0.343 g, 0.3 mmol) and **3** (0.381 g, 0.3 mmol) were dissolved in 25 mL of DMF; a solution of CD (1.135 g, 1.0 mmol) in 25 mL of DMF was added, followed by $CaCl_2$ (0.02 g, 0.18 mmol), and stirred at room temperature for 24 h under nitrogen in complete protection from light. DMF was removed in the rotary evaporator, 50 mL of water was added, the insoluble solid was filtered off, and the residue was washed thoroughly in 100 mL of water, leading to the pseudorotaxane **4** (yield 0.104 g, 14.3%). The filtrate was purified in an ultrafiltration (UF) setup[8,9] using a membrane with a molar mass cutoff of 2 kg mol$^{-1}$ and washing through deionized water at pH 7. Thus, an excess of CD as well as of $CaCl_2$ was removed. The retentate was freeze-dried and oven-dried at 65 °C, leading to a product very similar to **4**.

**b. Synthesis of the Polyrotaxane.** To ensure $C_{60}$ as an effective end-capping agent, it is necessary that there are reactive end groups in **4**. To this end, the reaction between **2** and **3** was carried out as detailed above. After the reaction was over, *p*-xylylenediamine (0.005 g, 0.036 mmol) in 10 mL of DMF was added and stirred for 2 h. $C_{60}$ (0.01 g, 0.014 mmol) dissolved in 10 mL of toluene was added in one lot, and stirring continued for 48 h. After solvent evaporation 50 mL of water was added to the product; the insoluble material was filtered off and washed with a large excess of water. The residue was then dissolved in DMF and filtered, and after workup the filtrate led to the polyrotaxane **5** (yield 0.087 g, 11.8%). The water-soluble component was purified in the ultrafiltration system, which also led to the rotaxane (labeled **5a** for comparison; yield 0.423 g, 57.2%).

**c. Measurements.** The molecular masses were determined by size exclusion chromatography (SEC) accomplished on a Waters SEC system equipped with three columns and a refractive index detector. Polystyrene standards were used for calibration using THF at a flow rate of 1.0 mL min$^{-1}$. Fourier transform infrared (FTIR) spectra were taken at room temperature using a Perkin-Elmer System 2000 under nitrogen in KBr pellets. $^1$H NMR spectra were recorded at 300 MHz and proton-decoupled $^{13}$C NMR at 75 MHz using a JEOL JNM-LA300WB instrument and DMSO-$d_6$ as the solvent. Thermogravimetric analyses (TGA, TA-2050) were recorded under a nitrogen atmosphere at a heating rate of 10 °C min$^{-1}$. The UV−vis spectra in DMF solution were taken in a Perkin-Elmer Lambda 12 series spectrophotometer. The potentiostat/galvanostat for the cyclic voltammetry was Autolab PGSTAT 30 of Ecochemie. A solution of tetrabutylammonium hexafluorophosphate solution (0.1 M) in acetonitrile was used as the electrolyte. Pt−Pt−Ag were used as working, counter, and reference electrodes, respectively. The samples for measurement were solution-casted from DMF onto the working Pt electrode. Luminescence studies were carried out using Spectra Pro monochromator/spectrograph models 150i and 300i (Acton Research) and a xenon lamp LPS 251 SR (Spectral Energy).

**Results and Discussion.** The feasibility of the polycondensation in the CD cavity would depend on the stability of the inclusion complexes. For the CD/TD complexation, there was a change in absorbance ($\Delta A$) observed at $\lambda_{\max} = 307$ nm in DMF at 25 °C with increasing CD concentration, that led to evaluating the stability constant $K_{11}$ of the 1:1 inclusion complex by nonlinear regression analysis of eq 1, using eq 2 iteratively:[10]

$$\Delta A = \frac{S_t K_{11} \Delta\epsilon_{11}[L]}{1 + K_{11}[L]} \tag{1}$$

$$[L]^2 = (L_t - S_t - 1/K_{11})[L] + L_t/K_{11} \tag{2}$$

where $S_t$ is the total molar concentration of the substrate (guest), $L_t$ the total molar concentration of the ligand (CD), and L the free ligand concentration (CD without guest in its cavity). The $K_{11}$ values of **2** and **3** were 744.2 ± 317.6 and 863.4 ± 216.2 M$^{-1}$, respectively. Most of the reported $K_{11}$ values of 1,4-disubstituted benzenes with $\beta$-CD fall in the range ~40−1000, exceeding 1000 M$^{-1}$ only for large substituents like iodine and *n*-propyl or *n*-butyl groups. Although both of the

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**Scheme 1. Synthesis of the Poly(azomethine) Rotaxane with [60]Fullerene as the End-Capping Agent**

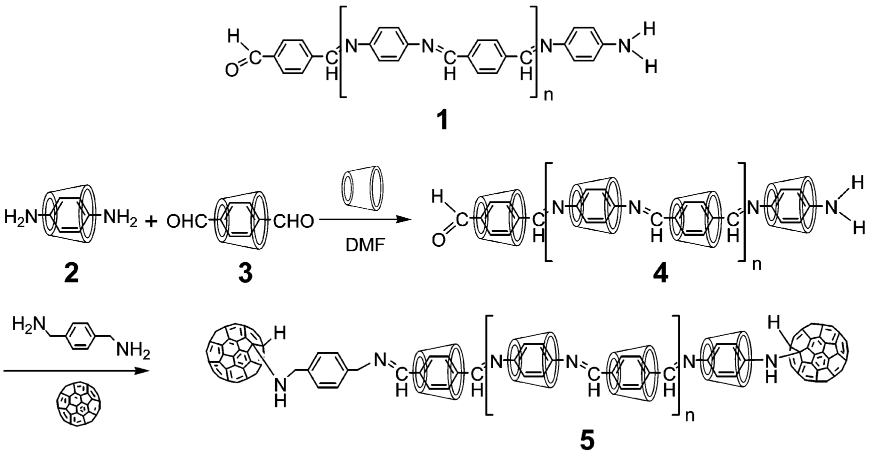

**Table 1. Condensation of Inclusion Complexes Yielding Poly(azomethine)s with Pseudorotaxane and Rotaxane Architecture.**

| sample | CD/PD, mmol | CD/TD, mmol | yield of polymer, % | molecular weight $M_n$ | $M_w$ | $M_n/M_w$ |
|---|---|---|---|---|---|---|
| **4** | 0.3 | 0.3 | 14.3 | 49 704 | 66 427 | 1.33 |
| **5** | 0.3 | 0.3 | 11.8 | 79 151 | 169 730 | 2.14 |
| **5a** | | | 57.2 | 82 423 | 243 377 | 2.95 |

monomers form stable complexes, the reaction probably did not occur in the macrocyclic cavity. Since the dynamic equilibrium involves the complex, the host, and guest, the growing polymer chains may be formed in or outside the CD cavity; or if formed in the cavity, they can slip out and may not thread back.

We tried several alternatives, for example, stirring mixtures of CD and **1** for days or reacting the monomers in the presence of an equimolar concentration of CD, but we did not succeed in getting soluble products. However, a breakthrough came when the inclusion complexes **2** and **3** were reacted in the presence of a large excess of CD. A high CD concentration meant a good probability that the polycondensation reactions could take place inside the microvessel in view of the dynamics of the host−guest equilibrium. The growing polymer chains, if dethreaded, had a greater probability of getting back into the CD macrocycles. We optimized the procedure and were able to isolate a good yield of high molecular mass pseudorotaxane (**4**) using a 3 M excess of CD that was soluble in polar organic solvents. The excess CD could be recovered and reused in subsequent reaction runs. During purification by membrane filtration, dethreading of the pseudorotaxane could not be avoided. To solve this problem, we used $C_{60}$ as the end-capping agent for the first time for a polyrotaxane. That amines can undergo an addition reaction with [60]fullerene is known[11,12] and has been reported for *p*-phenylenediamine recently.[13] The unreactive carbonyl ends were converted to reactive amino termini by treating **4** with *p*-xylylenediamine which led to the rotaxane **5** in high yields.

A comparison of the molar masses of **4** and **5** (Table 1) clearly showed that addition of $C_{60}$ led to higher molar masses, which could be due to (a) an increase in CD content and/or (b) a $C_{60}$-induced cross-linking. The low molar mass of **4** was obviously due to dethreading. For **5** there was a significant increase in $M_n$, and so was the molecular mass distribution (MWD). The portion of the polyrotaxane recovered from the filtrate (**5a**) even had a larger MWD. This indicates that the various short- and long-chain poly(azomethine)s could be retained in the CD cavity due to $C_{60}$ end-capping.

In the FTIR spectra, the specific absorption peaks characteristic of CD in **4** were seen at 3348 ($\nu_{O-H}$, H-bonded), 2923 ($\nu_{C-H}$), 1079, and 1029 cm$^{-1}$ ($\nu_{C-O-C}$), whereas those for **5** were registered at 3377, 2925, 1080, and 1030 cm$^{-1}$, respectively. The absorption at 1617 cm$^{-1}$ was due to the C═N stretching vibration, the same position as for **1**.[4a] The absorption at 1699 cm$^{-1}$ in **4** is due to the carbonyl end groups,[2] which were absent in **5**. The characteristic $C_{60}$ absorption in **5** was prominent at 526 cm$^{-1}$.

The $^1$H NMR spectra of **5** show azomethine protons in the range 8.6−8.8 ppm. The phenylene protons of the diamine and the dialdehyde units were observed as multiplets in the region 7.3−7.4 and 7.9−8.1 ppm, respectively.[2] For **4**, the aromatic proton resonances and the aldimine protons were registered at nearly similar positions as in **5**. In **4** there were peaks at 10.1 ppm region due to the terminal aldehyde protons, which were entirely absent in **5**. Other peaks for both **4** and **5** in the range 3.3−3.65 are due to the CD protons. The peaks in the range 5.6−5.7 are protons on O−H of C2 and C3 carbons of CD. The proton NMR of pure CD showed a shift of the H-3 protons in **4** or **5** by 0.1 ppm to higher field, which has been considered as characteristic of inclusion complexation.[14]

A comparison of the area of azomethine proton and CD proton peaks indicated for every azomethine proton 56.75 CD protons for **4** and 71.65 CD protons for **5**. Molecular modeling calculations showed that there could be one CD ring per azomethine link. This means that for every azomethine proton there should be 70 CD protons (a molecule of $\beta$-CD contains 70 protons). Consequently, the $^1$H NMR data indicate that the polyrotaxane **5** has a structure with one CD ring for each azomethine link; i.e., the molecule is completely covered by the CD rings. The pseudopolyrotaxane **4** has some segments devoid of any macrocycle rings. In the $^{13}$C NMR of **5**, apart from the six CD carbons (59.8−101.9 ppm), the azomethine carbons appeared as two peaks at 170.7 and 171.5 ppm. The $C_{60}$ carbon resonances were weak and seen as a number of small peaks in the 141 ppm region.

In the TG analyses (Figure 1), the parent polymer **1** starts losing weight at 451 °C. On the other hand, both **4** and **5** rapidly lose weight at temperatures as low as 253 and 261 °C, respectively, due to the loss of CD rings.

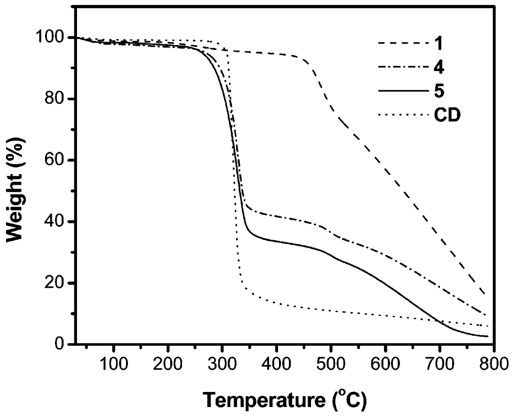

**Figure 1.** Thermogravimetric analysis comparison showing the presence of thermally stable poly(azomethine) chains in both the pseudopolyrotaxae (**4**) and the polyrotaxane (**5**).

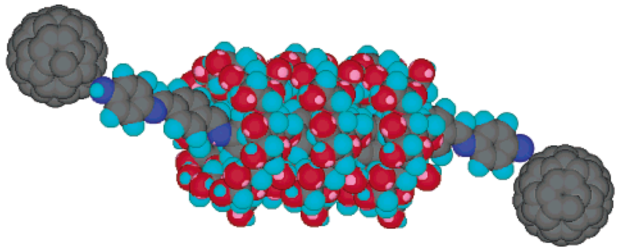

**Figure 2.** Molecular model (MM2 energy-minimized) of a short segment of the macromolecule **5**.

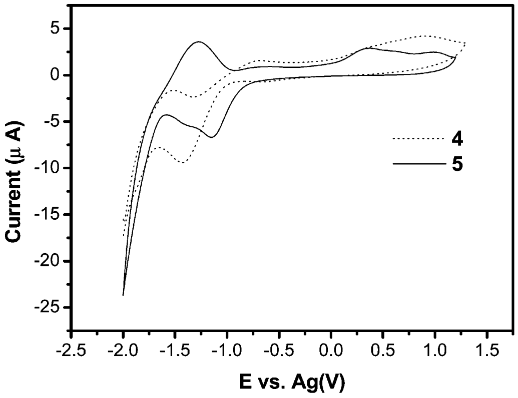

**Figure 3.** Cyclovoltammogram of both the pseudopolyrotaxane (**4**) and the polyrotaxane (**5**), indicating quasi-reversible reduction and irreversible oxidation cycles.

At 350 °C pure CD lost 83% of its original weight, whereas at this temperature, mass loss for **4** and **5** was 55.7% and 63.3%, respectively. The excess mass retained by **4** and **5** at 350 °C is due to the thermally stable poly(azomethine) chains. Beyond this temperature the decomposition pattern is very similar to that of **1**. The lower retained mass for **5** beyond 350 °C indicates a higher CD content compared to **4**. Thus, the higher molar mass of **5** is not due to cross-linking; rather, it is due to a higher CD content. A visualization of a short segment of the macromolecule is given in Figure 2.

The UV–vis absorption maxima of **4** and **5** in DMF occurred at 418 and 426 nm, respectively.[4] The absorption peak at 339 nm in **5** is the typical fullerene absorption, which is absent in **4**.[15] The photoluminescence emission spectrum of sample **5** dissolved in DMF showed a maximum at 550 nm, close to values reported in the literature.[4b] From the UV–vis absorption edge, the optical gap $E_g^{opt}$ for **4** and **5** was found to be 2.34 and 2.41 eV, respectively. The cyclovoltammograms (Figure 3) are typical of poly(azomethine)s with quasi-reversible reduction and irreversible oxidation cycles. Analysis of the data for **4** led to an ionization potential of 3.18 eV (LUMO) and an electron affinity of 5.54 eV (HOMO), yielding a band gap $E_g^{el}$ of 2.36 eV. Similarly, the LUMO and HOMO energy levels of **5** were 3.35 and 5.0 eV, respectively, leading to the $E_g^{el}$ value of 1.65 eV, in close agreement with reported value for **1**.[4a] In the CV measurements there is a decrease of $E_g^{el}$ value in **5** compared to that of **4**, whereas there was little change in the $E_g^{opt}$ value, which may be due to the solvent effect. Further, $C_{60}$ apparently does not increase the conjugation length, as the $\pi$-bonds in $C_{60}$ are not conjugated, but lowering of $E_g^{el}$ could be due to $C_{60}$ acting as a self-doping agent for the polyrotaxane. Further investigations involving conductivity and electroluminescence studies are underway.

**Conclusions.** Solubilizing a para-linked, all-aromatic, high molar mass poly(azomethine) without making any structural changes is possible in the microvessel of a cyclodextrin using the "supramolecular masking concept" by maintaining a high concentration of the macrocycle. $C_{60}$ can be used as an end-capping as well as a self-dopant for the polyrotaxane.

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