Cyclic Polyelectrolyte: Synthesis of Cyclic Poly(acrylic acid) and Cyclic Potassium Polyacrylate

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Introduction

Cyclic polymers are of interest for special properties in solid, solution, and melt states. The earlier reports involving properties of cyclic polymers were mainly theoretical studies. The living polymerization techniques opened the door to the preparations of various well-defined cyclic polymers with narrow molecular weight distribution to understand correlations between observable physical properties and the chain structure. A number of studies on the hydrodynamic,[1−4] rheological,[5−9] thermal,[10−12] and optical[13] properties of cyclic polymers have been reported.

We are interested in cyclic polyelectrolyte. It is known that the viscosity of a linear polyelectrolyte solution depends on the conformation of the molecules, which in turn is affected by intramolecular electrostatic interactions between charged segments located along the polymer backbone.[14,15] However, interactions in systems of charged polyelectrolytes are still far from being understood.[16,17] The study on the solution property of cyclic polyelectrolyte is of interest since the chain expansion of a cyclic polyelectrolyte with relatively low molecular weight is restricted due to the presence of topological restraint. To the best of our knowledge, cyclic polyelectrolytes have not been reported. In this paper we report novel preparations of well-defined cyclic poly(acrylic acid) and cyclic potassium polyacrylate with relatively short chain length.

Experimental Section

Instrumentation. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with JEOL EX-270 nuclear magnetic resonance spectrometer using tetramethylsilane (TMS) as an internal standard. Gel permeation chromatography (GPC) was carried out with a set of Tosoh TSK-gel G2500H and G3000H columns using tetrahydrofuran (THF) and standard polystyrenes as an eluent and references, respectively. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI−TOF MS) was performed using a Voyager DE-PRO spectrometer using *trans*-3-indoleacrylic acid and sodium iodide as a matrix and cationization reagent, respectively.

1-Phenyl-1-[4-(2,2,5,5-tetramethyl[1,2,5]azadisilolidinyl)-phenyl]ethylene (1). Into a solution of 1-(4-aminophenyl)-1-phenylethylene[18] (2.6 g, 13 mmol) in 20 mL of THF was added dropwise 16 mL (26 mmol) of a 1.6 M solution of butyllithium in hexane at −78 °C. After 1 h, a solution of 1,2-bis(chlorodimethylsilylethane) (2.8 g, 13 mmol) in 20 mL of THF was added. The mixture was allowed to warm to room temperature, poured into water, and extracted with ether. The organic layer was dried and placed under reduced pressure to remove the solvent. The residue was passed through an alumina column (neutral, activity I) using hexane as an eluent. The first band was collected and purified by sublimation to give 2.4 g (55%) of **1** as white needles; mp 67.5−68.5 °C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.4−7.3 (m, 5H), 7.18 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.42 (s,1H), 5.29 (s, 1H), 0.88 (s, 4H), 0.25 (s, 12H). ^{13}C NMR ($CDCl_3$, δ, ppm): 149.7, 147.6, 141.9, 132.7, 128.7, 128.5, 128.0, 127.5, 122.1, 112.2, 8.5, 0.0. Anal. Calcd for $C_{20}H_{27}NSi_2$: C, 71.15; H, 8.06; N, 4.15. Found: C, 71.38; H, 8.05; N, 4.20.

α-Amino, ω-Carboxyl Heterodifunctional Poly(*tert*-butyl acrylate) (2). In a typical example, into a solution LiCl (0.68 g, 16 mmol) and 1-phenyl-1-[4-(2,2,5,5-tetramethyl[1,2,5]-azadisilolidinyl)phenyl]ethylene (**1**) (0.87 g, 2.6 mmol) in 100 mL of THF was added 1.5 mL (2.4 mmol) of a 1.6 M solution of butyllithium in hexane at room temperature, resulting into a deep red color. After the reaction mixture was cooled to −78 °C, *tert*-butyl acrylate (3.7 g, 29 mmol) in 20 mL of THF was added dropwise. The color of the mixture changed to light yellow during the addition of the monomer. After stirring 15 min, succinic anhydride (0.44 g, 4.4 mmol) in 10 mL of THF was added to the living poly(*tert*-butyl acrylate) solution, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was poured into aqueous hydrochloric acid and extracted with diisopropyl ether (IPE). The organic layer was washed with water, dried with anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using IPE as an eluent. After the first band was collected to remove excess 1-(4-aminophenyl)-1-phenylethylene, the eluent was changed to ethyl acetate. The second band was collected and freeze-dried to give 2.4 g (54%) of heterodifunctional poly(*tert*-butyl acrylate) (**2**) as an off-white powder. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.3−6.5 (m, phenyls), 2.7−1.2 (m, CH and CH_2), 1.4 (s, *tert*-butyl), 0.75 (m, CH_3). GPC analysis: M_n = 3990 (M_w/M_n = 1.17) as determined using polystyrene standards. MALDI−TOF MS analysis: M_n = 2980 (M_w/M_n = 1.06).

Cyclic Poly(*tert*-butyl acrylate) (3). In a typical example, into a solution of triethylamine (0.1 g, 1.0 mmol) and 1-methyl-2-chloropyridinium iodide (0.13 g, 0.5 mmol) in 800 mL of dichloromethane was added linear precursor **2** (M_n = 2980) (0.60 g, 0.2 mmol) dissolved in 200 mL of dichloromethane over a period of 10 h under reflux with vigorous stirring. After the mixture was concentrated to ca. 200 mL, it was washed with diluted aqueous hydrochloric acid, dried over anhydrous magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was charged on a silica gel column using chloroform as an eluent. After the first band eluted, the eluent was changed to ethyl acetate. The second band was collected and freeze-dried to give 0.39 g (65%) of **3** as an off-white powder. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.6−7.0 (m, phenyls), 2.7−1.3 (m, CH and CH_2), 1.4 (s, *tert*-butyl), 0.75 (m, CH_3). GPC analysis: M_n = 3580 (M_w/M_n = 1.23) as determined using polystyrene standards. MALDI−TOF MS analysis: M_n = 2960 (M_w/M_n = 1.07).

Cyclic Poly(acrylic acid) (4). In a typical example, a solution of cyclic poly(*tert*-butyl acrylate) (M_n = 2960) (0.30 g, 0.10 mmol) in 15 mL of formic acid was stirred at 60 °C for 20 h. The reaction mixture was placed under reduced pressure to remove the volatile materials. The residue was dissolved in a small amount of THF and poured into excess hexane to precipitate 0.18 g (98%) of cyclic poly(acrylic acid) (**4**) as a white powder. ^{1}H NMR (DMSO-d_6, δ, ppm): 12.5−12 (broad, CO_2H), 7.5−6.8 (m, phenyls), 2.6−1.2 (m, CH and CH_2), 0.8 (m, CH_3). IR (KBr disk, cm^{-1}): 1710 ($\nu_{C=O}$).

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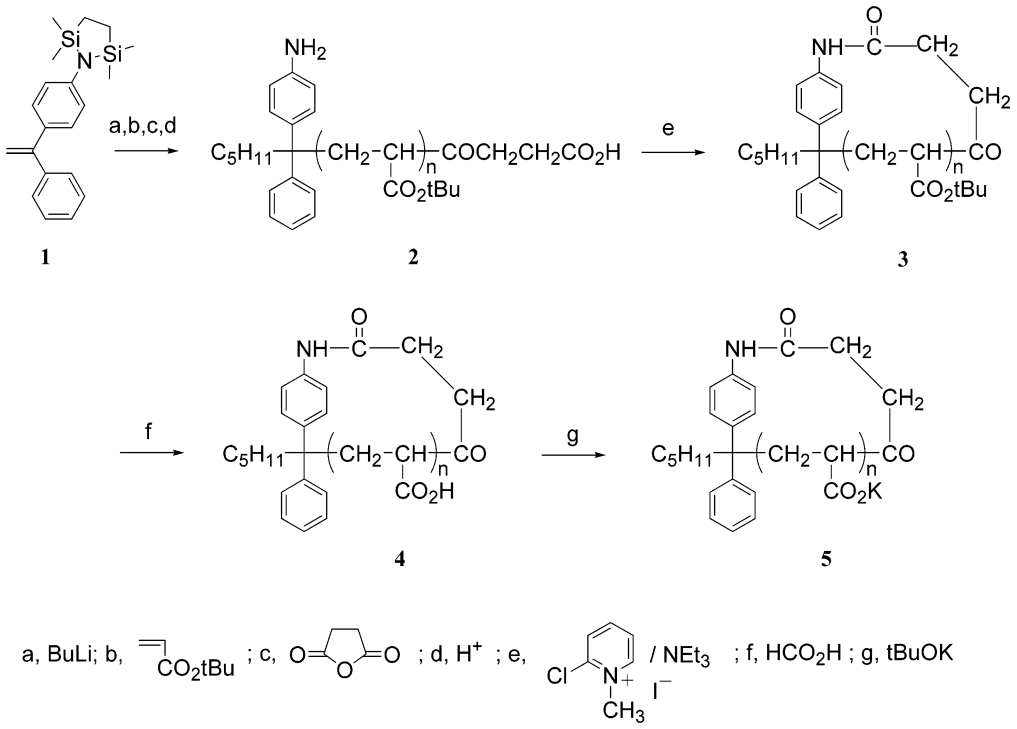
Scheme 1



1 **2** **3** **4** **5**

Cyclic Potassium Polyacrylate (5). In a typical example, a mixture of cyclic poly(acrylic acid) (**4**) (M_n = 1820) (0.15 g, 0.08 mmol) and potassium *tert*-butoxide (0.20 g, 1.8 mmol) was dissolved in a small amount of water at room temperature. The mixture was placed under reduced pressure to remove the volatile materials. The residue was washed with absolute ethanol to give 0.20 g (95%) of cyclic potassium polyacrylate (**5**) as a tan solid. IR (KBr disk, cm^{-1}): 1576 ($\nu_{C=O}$).

Results and Discussion

The cyclic poly(acrylic acid) (**4**) and cyclic potassium polyacrylate (**5**) were prepared according to Scheme 1. The key compound for **4** and **5** is α-amino, ω-carboxyl heterodifunctional poly(*tert*-butyl acrylate) (**2**) bearing amine and carboxyl functionalities at the chain ends. Our idea for heterodifunctional polymer **2** is to use LiCl-modified organolithium-initiated living polymerization[19] of *tert*-butyl acrylate with functional initiator and terminator. Since carboxyl end functionalization of acrylate monomer is already known,[20,21] our desire was to introduce an amine functionality at the α-terminal of poly(*tert*-butyl acrylate). Quirk and Lynch reported anionic polymerization of styrene using 1-[4-[*N*,*N*-bis-(trimethylsilyl)amino]phenyl-1-phenylethylene as a functional terminator to obtain amine-functionalized polystyrene.[18] Therefore, we modified this system to introduce an amine functionality using a novel functional initiator, 1-phenyl-1-[4-(2,2,5,5-tetramethyl[1,2,5]azadisilolidinyl)-phenyl]hexyllithium, which is formed in the reaction of 1-phenyl-1-[4-(2,2,5,5-tetramethyl[1,2,5]azadisilolidinyl)-phenyl]ethylene (**1**) with butyllithium. Compound **1** is a crystalline solid and easily purified by sublimation.

The ^{1}H NMR of the heterodifunctional poly(*tert*-butyl acrylate) (**2**) exhibited peaks around 7.2−6.5 ppm due to the phenyl protons of α-1-(4-aminophenyl)-1-phenylhexyl group, as shown in Figure 1. The methylene protons due to ω-2-carboxypropionyl group were observed at 2.4−2.6 ppm. The intramolecular cyclization of **2** was carried out in dichloromethane under high dilution conditions using 2-chloro-1-methylpyridinium iodide as a condensation agent by a similar procedure reported previously.[4] The cyclic poly(*tert*-butyl acrylate) (**3**) was purified by silica gel column chromatography. Unreacted starting material and the linear chain-extended byproducts carry terminal amine and carboxyl functionalities that strongly interact with silica gel. The evidence for the cyclic structure was confirmed by MALDI−TOF MS, as shown in Figure 2. Each peak in the spectrum represents a cyclic poly(*tert*-butyl acrylate) (**3**) which was cationized by the attachment of sodium cation. The spacing between the peaks is 128.2 Da, corresponding to the molar mass of *tert*-butyl acrylate. The observed peak masses are in good agreement with the calculated values for the proposed structure **3**. The peak marked with an asterisk was smaller by 56 Da

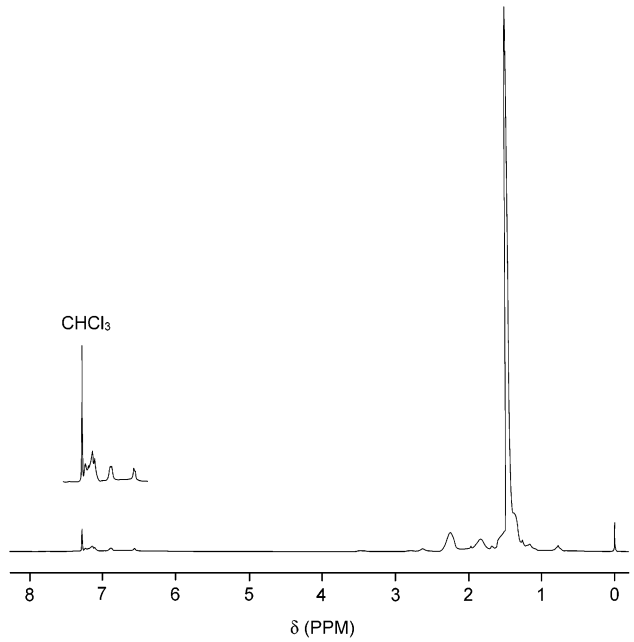


Figure 1. ^{1}H NMR spectrum of α-amino, ω-carboxyl heterodifunctional poly(*tert*-butyl acrylate) (**2**) of M_n = 2980.

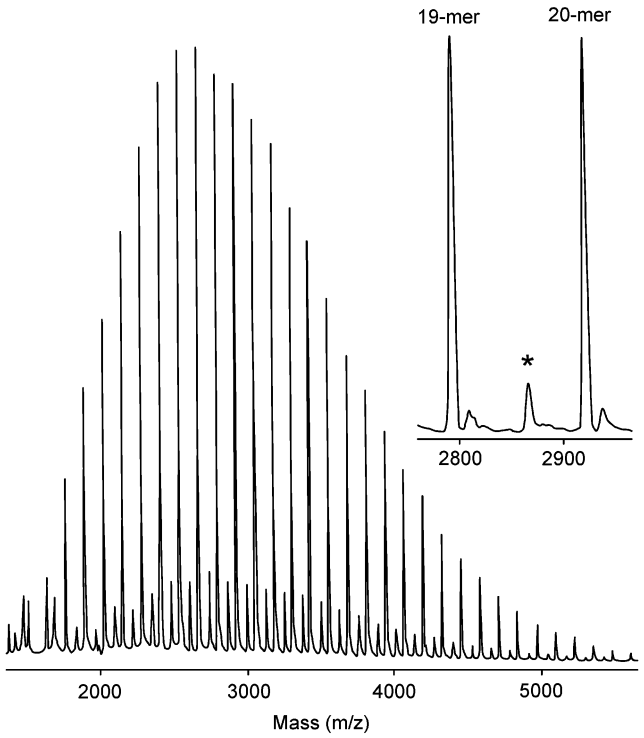


Figure 2. MALDI−TOF MS spectrum of cyclic poly(*tert*-butyl acrylate) (**3**) of $M_n = 2970$.

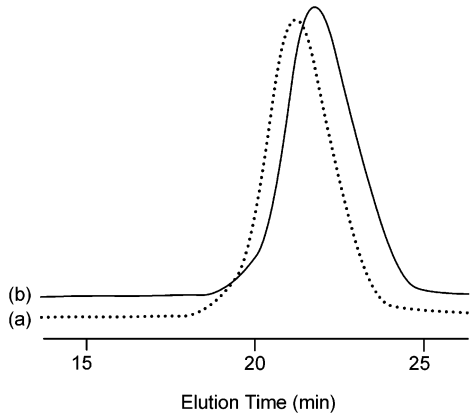


Figure 3. GPC curves of (a) linear poly(*tert*-butyl acrylate) (**2**) and (b) cyclic poly(*tert*-butyl acrylate) (**3**) (DP = 21).

than **3**. The value of 56 corresponds to the molar mass of isobutylene (C_4H_8), indicating the decomposition of the *tert*-butyl group during the laser irradiation. Actually, the peak intensity of this peak increased with the increase of the laser power. Figure 3 shows GPC curves of cyclic poly(*tert*-butyl acrylate) (**3**) and its parent linear polymer **2** with degree of polymerization (DP) of 21. The molecular weight of **3** determined by GPC was found to be 3580 as polystyrene standards, which was much lower compared to its parent polymer **2** ($M_n = 3990$ as polystyrene standards). The change of the elution volume can be explained by the lower hydrodynamic volume of the cyclic structure than that of the linear one.[2]

The hydrolysis reaction of cyclic poly(*tert*-butyl acrylate) (**3**) was successfully carried out in formic acid at 60 °C. Conversion of **3** into cyclic polyacid **4** was ascertained by ^{1}H NMR. The methyl protons due to the *tert*-butyl group at 1.4 ppm disappeared completely. The polyacid **4** is soluble in dioxane, methanol, and dilute alkaline water.

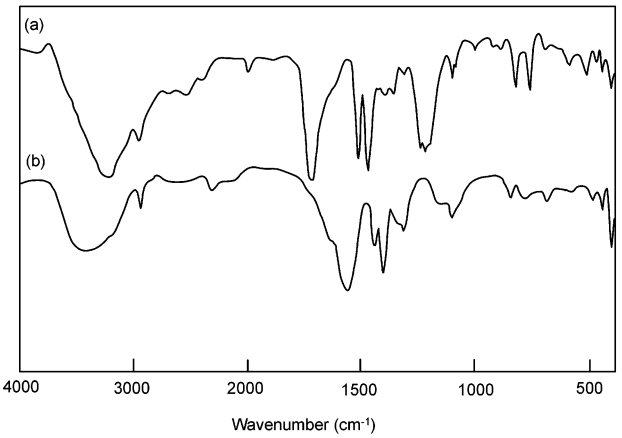


Figure 4. IR spectra of (a) cyclic poly(acrylic acid) (**4**) and (b) cyclic potassium polyacrylate (**5**) (DP = 21).

Finally, cyclic poly(acrylic acid) (**4**) was converted to cyclic potassium polyacrylate (**5**) by the treatment with potassium *tert*-butoxide. The IR spectra of free polyacid **4** and its potassium salt **5** are shown in Figure 4. The carbonyl peak at 1710 cm^{-1} shifted to 1576 cm^{-1}, indicating a complete conversion of free carboxylic acid to potassium carboxylate. The polyelectrolyte **5** is not soluble in ethanol but completely soluble in water.

In summary, we have synthesized a well-defined cyclic poly(acrylic acid) and cyclic potassium polyacrylate which represent interesting model polyelectrolytes. Further investigations on viscometry of these water-soluble cyclic polyelectrolytes are underway in our laboratory.

References and Notes

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