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Synthesis of cyclic poly(methyl methacrylate) by the intramolecular cyclization of α-amino, ω-carboxyl heterodifunctional poly(methyl methacrylate)

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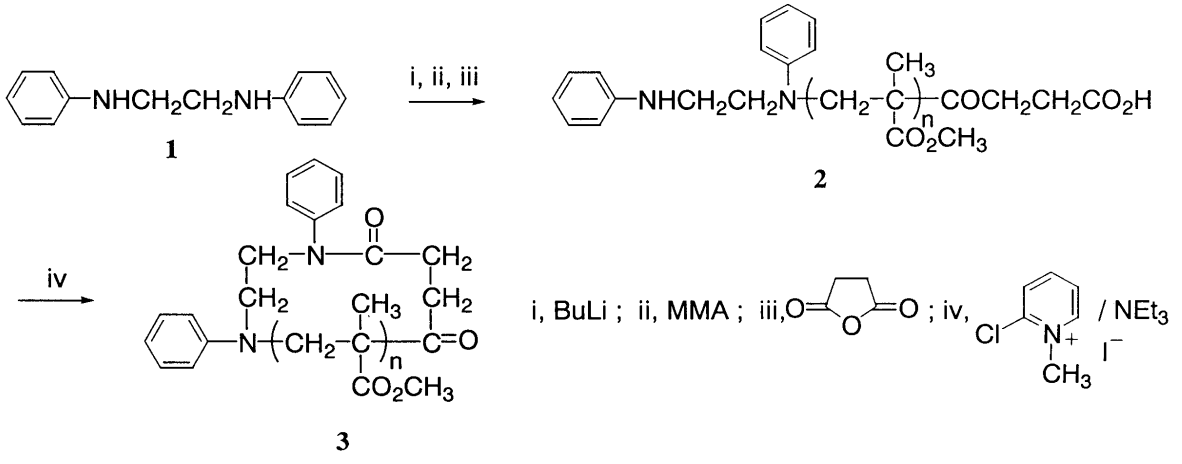
Summary

α-Amino, ω-carboxyl heterodifunctional poly(methyl methacrylate) was prepared by a living anionic polymerization of methyl methacrylate using *N,N'*-diphenylethylenediamine monolithium amide and succinic anhydride as an initiator and terminator, respectively. Its intramolecular cyclization was carried out to obtain a well-defined cyclic poly(methyl methacrylate).

Introduction

Cyclic polymers are of current interest for their special properties in solution and solid state [1,2]. Unimolecular cyclization of heterodifunctional polymer is one of useful method for obtaining a cyclic polymer. Deffieux et al. obtained cyclic polystyrenes and poly(vinyl ether)s using α-diethylacetal, ω-styrenyl heterodifunctional linear polymers after activation of their ends [3,4]. Mizawa et al. prepared α-maleimide, ω-dienyl heterodifunctional poly(methyl methacrylate) and carried out its cyclization by the intramolecular Diels-Alder reaction [5]. Recently, we prepared a cyclic polystyrene by an intramolecular cyclization of α-carboxyl, ω-amino heterodifunctional polystyrene as a linear precursor [6,7]. The advantage of this method is the easy isolation of a cyclic polymer by column chromatography since chain-extended products have terminal amine and carboxyl functionalities which strongly interact with gel.

In this paper we report a synthesis of α-amino, ω-carboxyl heterodifunctional poly(methyl methacrylate) and its intramolecular cyclization (Scheme 1).



Scheme 1. Preparation of cyclic poly(methyl methacrylate).

Experimental

Instruments. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX270 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.

α-Amino, ω-Carboxyl Heterodifunctional Poly(MMA) (2). To the solution of LiCl (0.84 g, 20 mmol), *N*,*N*′-diphenylethylenediamine (**1**) (0.42 g, 2.0 mmol), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (0.23 g, 2.0 mmol) in 100 mL of THF was added n-butyllithium (1.59 M in hexane, 2.0 mmol) and the mixture was stirred at room temperature for 10 min, resulting in a deep green color. After the reaction mixture was cooled to -78 °C, methyl methacrylate (MMA) (2.2 g, 22 mmol) in 20 mL of THF was added dropwise. The color of the reaction mixture changed to light yellow during the addition of the monomer. After stirring 20 min, succinic anhydride (0.25 g, 25 mmol) in 10 mL of THF was added to the living poly(MMA) solution, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was poured into aqueous hydrochloric acid and extracted with dichloromethane. 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 dichloromethane as the eluent. After the first band was collected, the eluent was changed to ethyl acetate. The second band was collected and freeze-dried to give 1.6 g (73%) of **2** as an off-white solid: ^{1}H NMR ($CDCl_3$, δ) 7.2-6.6 (m, phenyls), 3.7-3.4 (m, CH_3O), 2.5-1.7 (m, CH_2), 1.3-0.7 (m, CH_3).

Cyclic Poly(MMA) (3). Into a solution of triethylamine (24 mg, 0.24 mmol) and 1-methyl-2-chloropyridinium iodide (31 mg, 0.12 mmol) in 600 mL of dichloromethane was added precursor **2** (M_n = 2460) (0.25 g, 0.1 mmol) dissolved in 150 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 was collected, the eluent was changed to ethyl acetate. The second band was collected and freeze-dried to give 0.18 g (75%) of **3** as a white solid: ^{1}H NMR ($CDCl_3$, δ) 7.4-6.6 (m, phenyls), 3.7-3.3 (m, CH_3O), 2.3-1.8 (m, CH_2), 1.3-0.7 (m, CH_3).

Results and Discussion

Heterodifunctional Poly(MMA) (2). Our idea for heterodifunctional poly(MMA) bearing amine and carboxyl functionalities at the chain ends is to use LiCl-modified organolithium-initiated living polymerization [8] with a functional initiator and terminator. Since carboxyl end functionalization of acrylate monomer is already known [9], we were interested in an amine-functionalized initiator to introduce the α-amine functionality. Okamoto et al. reported anionic polymerization of diphenyl-2-pyridylmethyl methacrylate

using *N,N'*-diphenylethylenediamine monolithium amide as an initiator to obtain an one-handed helical polymer with narrow molecular weight distribution, suggesting a living-like polymerization [10]. Therefore, we modified this initiation system to achieve a controlled polymerization of MMA. The anionic polymerization of MMA initiated with *N,N'*-diphenylethylenediamine monolithium amide was investigated under various conditions. The GPC analysis of the reaction mixtures revealed that poly(MMA) with narrow molecular weight distribution was produced when the polymerization was carried out in the presence of LiCl and TMEDA in THF at -78 °C.

The poly(MMA) carbanion was terminated with succinic anhydride to introduce ω-carboxyl functionality according to the literature [9,11]. The polymer was purified by column chromatography. The structure of the obtained polymer was analyzed by ^{1}H NMR, ^{13}C NMR, GPC, and MALDI-TOF MS. The ^{1}H NMR spectrum exhibited peaks around 7.1, 6.8 and 6.6 ppm due to the phenyl protons of α-phenyl-(2-phenylaminoethyl) group as shown in Figure 1. The ^{13}C NMR spectrum exhibited a peak at 205 ppm due to the ketone carbonyl carbons of ω-2-carboxypropionyl group. The GPC curve exhibited an unimodal peak with M_n of 1700 as a polystyrene standard (Figure 2a). MALDI-TOF MS is a powerful technique which can characterize end-group functionalities of relatively low molecular mass polymers with a narrow molecular weight distribution. Figure 3 shows the MALDI-TOF MS of **2**. There are two series of equidistant mass peaks. The smaller mass corresponds to $[M_n + Na]^+$. The other mass corresponds to $[M_n - H + 2Na]^+$. The existence of two series of mass peaks supports that the polymer has carboxyl functionality [12]. The observed peak masses are full agreement with the calculated masses for the proposed structure **2**. In spite of the fact that the yield of **2** was not quantitative, it was possible to isolate pure α-amino, ω-carboxyl heterodifunctional poly(MMA). The M_n and M_w/M_n of **2** obtained by MALDI-TOF MS was 2460 and 1.05, respectively.

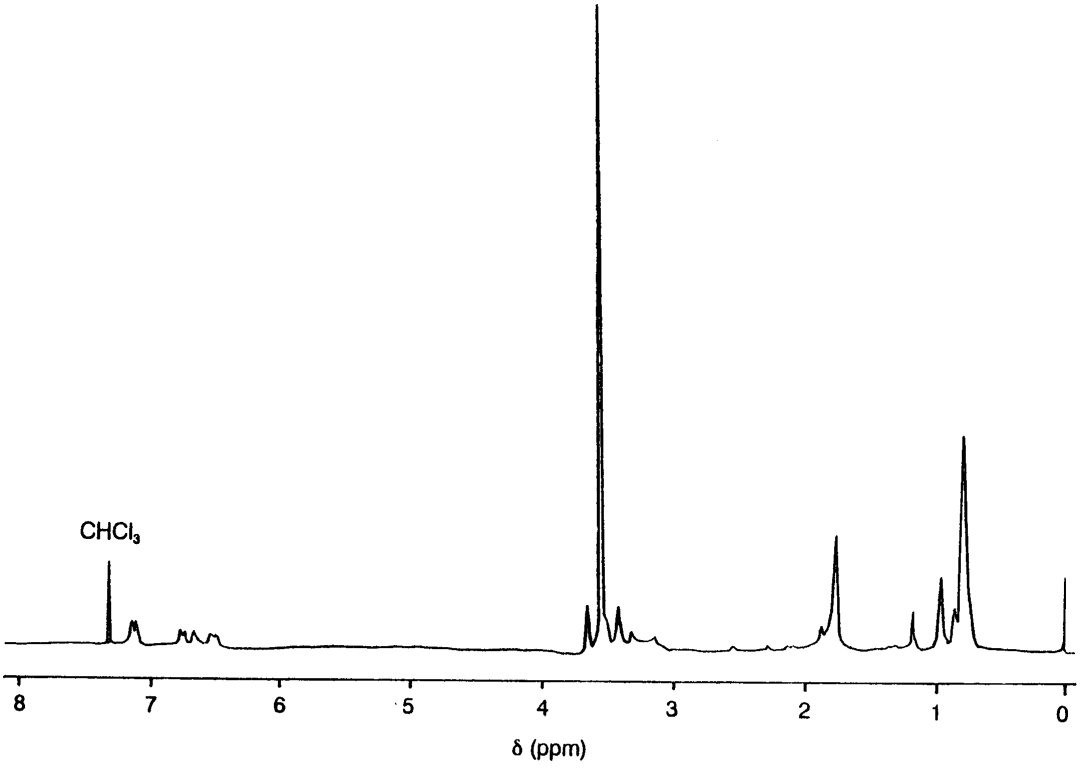


Figure 1. ^{1}H NMR of linear poly(MMA) **2** in $CDCl_3$.

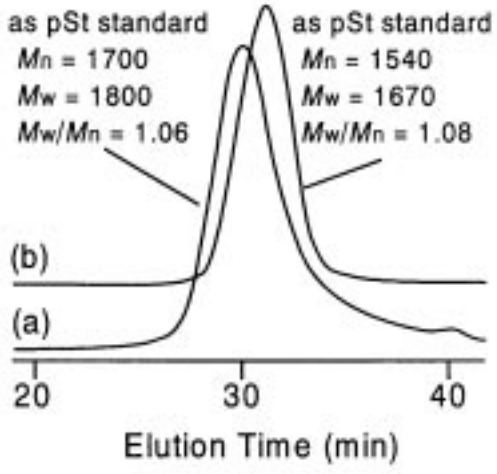


Figure 2. GPC curves of (a) linear poly(MMA) **2** and (b) cyclic poly(MMA) **3**.

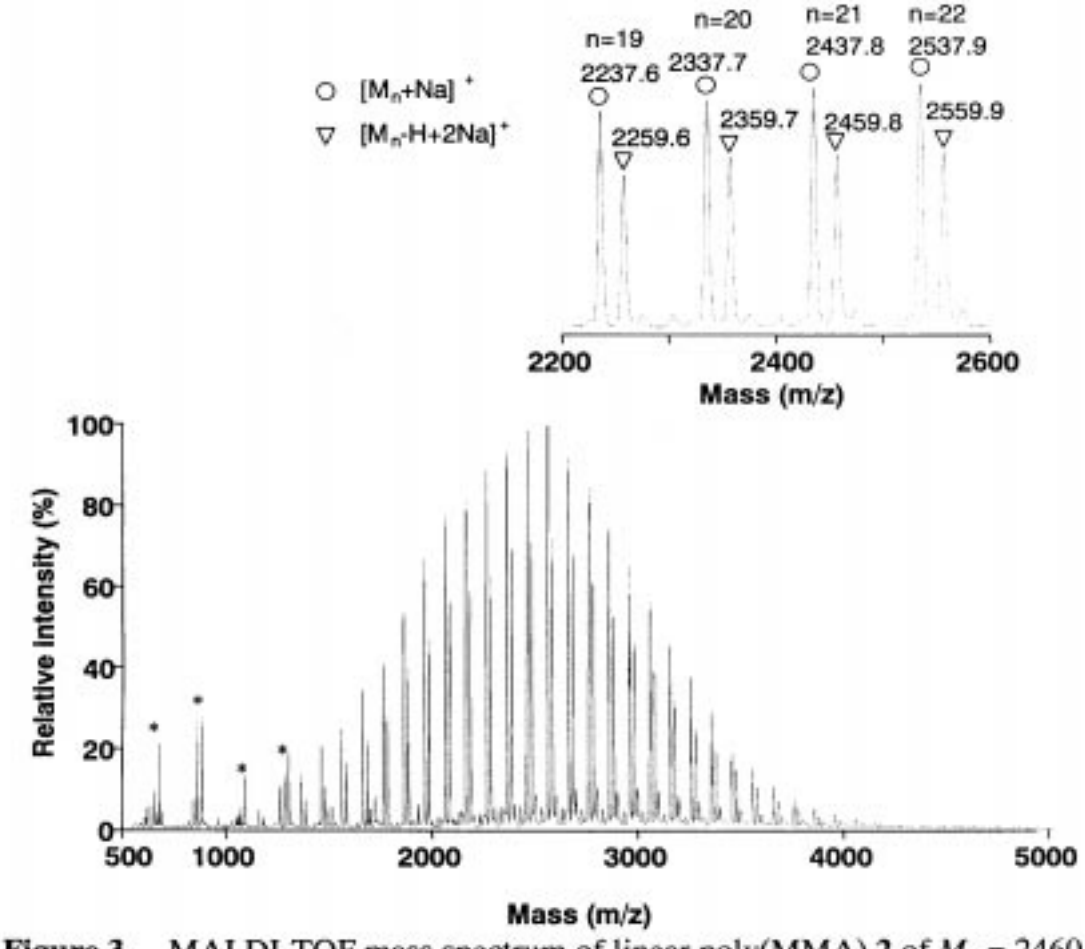


Figure 3. MALDI-TOF mass spectrum of linear poly(MMA) **2** of M_n = 2460. Peaks marked with * correspond to impurities and/or matrix peaks.

Cyclic Poly(MMA) (3). The intramolecular cyclization of **2** was carried out in dichloromethane under high dilution conditions by the similar procedure reported

previously [7]. The cyclic poly(MMA) (**3**) was purified by silica gel column chromatography. The IR spectrum of **3** exhibited an absorption peak at 1625 cm^{-1} assigned to the amide group. The GPC curve of **3** is shown in Figure 2b. The molecular weight was found to be 1540 as a polystyrene standard, which was much lower compared to its parent polymer **2** (M_n = 1700 as a polystyrene standard). The change of the elution volume can be explained by the lower hydrodynamic volume of the cyclic structure than that of the linear one [13]. Finally, the cyclic structure of **3** was confirmed by MALDI-TOF MS as shown in Figure 4. Each peak in the spectrum represents a cyclic poly(MMA) which was cationized by the attachment of sodium cation. The spacing between the peaks is 100.1 Da, corresponding to the molar mass of MMA. The observed peak masses are full agreement with the calculated masses for the proposed structure **3**. It is noteworthy that the purity of the obtained cyclic poly(MMA) **3** was quite high without contamination of the linear precursor **2**. The M_n and M_w/M_n of **3** obtained by MALDI-TOF MS was 2390 and 1.05, respectively.

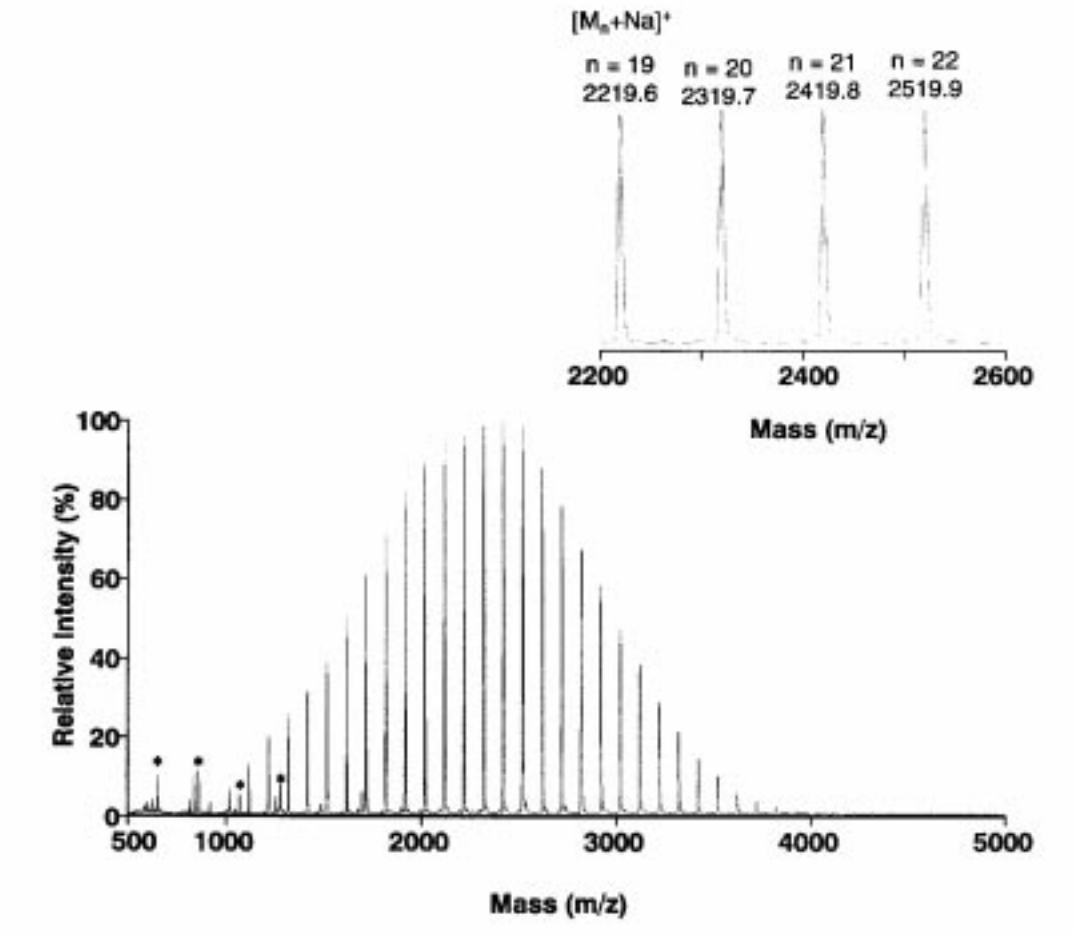


Figure 4. MALDI-TOF mass spectrum of cyclic poly(MMA) **3** of M_n = 2390. Peaks marked with * correspond to impurities and/or matrix peaks.

In summary, α-amino, ω-carboxyl heterodifunctional poly(MMA) was prepared by a living anionic polymerization of MMA using *N*,*N*'-diphenylethylenediamine monolithium amide and succinic anhydride as an initiator and terminator, respectively. Its intramolecular cyclization gave a cyclic poly(MMA) with a well-defined structure.

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