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Star-Shaped Poly(2-methyl-2-oxazoline) Using by Reactive Bromoethyl Group Modified Calix[4]resorcinarene as a Macrocyclic Initiator

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Summary

Star-shaped poly(2-methyl-2-oxazoline) (POZO) was prepared by ring-opening polymerization of 2-methyl-2-oxazoline from a novel calix[4]resorcinarene with reactive bromoethyl groups (8Br-CX4) as an initiator. The core-first method, which uses an active multifunctional core to initiate growth of polymer chains, was applied for synthesis of star-shaped POZO based on 8Br-CX4. The obtained star-shaped POZOs were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and DSC. From ^{1}H NMR, DLS and fluorescence measurements, the star-shaped POZOs formed nanometer scale micelles in aqueous media composed of hydrophobic calix[4]resorcinarene moieties and hydrophilic POZO groups.

Introduction

Calixarenes, macrocyclic compounds composed of benzene unit, have received a great deal of interest due to unique structure, molecular recognition and building blocks to construct nanometric supramolecules [1-6]. Simple preparation of calixarenes and lower and upper rim functionalization of calixarenes have resulted in a tremendous expansion in the range of derivatives [7-8].

Star polymers show interesting polymer structures, where a large number of arm chains radiate from the central core [9]. Star polymers have been applied for toughening of plastics and coatings with good processibility due to low solution and melt viscosity compared to those of linear polymers. To prepare a variety of well defined star-shape architectures, living polymerization is one of the useful approaches.

Herein, we report on synthesis of star-shaped polymer based on new high reactive multifunctional macrocyclic initiator, bromoethyl group modified calix[4]resorcinarene (8Br-CX4). By using 8Br-CX4, star-shaped poly(2-methyl-2-oxazoline) (POZO), which was a good candidate for living cationic polymerization and showed unique properties such as amphiphilic property and superior compatibility

with organic polymers [10], was synthesized. To the best of our knowledge, there are few examples of star-shaped polymer based on calixresorcinarenes, while *p-tert*-butylcalixarenes carrying polymer chains have been reported [11-13]. The obtained star-shaped POZO exhibited unique solution behavior in aqueous solution.

Experimental

General Procedure

The ^{1}H NMR spectra were recorded at 270 MHz and ^{13}C NMR spectra were recorded at 67.5 MHz with a JEOL-JNM EX270 spectrometer. Dynamic light scattering (DLS) measurement was carried out on a Beckman Coulter N5 Submicron Particle Size Analyzer at 20°C. The FT-IR spectra were obtained using a JASCO FT-IR460 plus infrared spectrometer. Differential scanning calorimetry (DSC) thermograms were obtained with a Shimadzu DSC-50, at a heating rate of 10°C min^{-1} under nitrogen atmosphere. Fluorescence excitation spectra were recorded on a Perkin-Elmer LS55 luminescence spectrometer. Gel permeation chromatography (GPC) analysis was carried out on Shodex GPC LF804 by using THF as an eluent at 25°C at the flow rate of 1 mL min^{-1} after calibration with the standard polystyrene samples. The positive-ion matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) mass measurements were performed on a Shimazu/KRATOS AXIMA-CFR spectrometer with dithranol as a matrix.

Materials

Calix[4]resorcinarene (CX4) was prepared according to the previous paper [14]. 2-Methyl-2-oxazoline was dried and distilled from KOH and stored under nitrogen. Anhydrous chloroform was used for polymerization of 2-methyl-2-oxazoline. The other solvents and reagents were used as supplied.

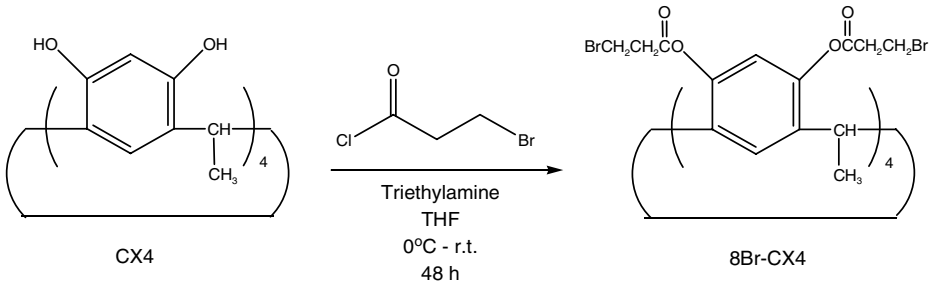
Determination of Critical Micelle Concentration (cmc) by Fluorescence Measurements

The samples for fluorescence measurements were prepared according to a reference method [15-16]. Various concentrations of star-shaped POZO were dissolved in aqueous pyrene solutions. (Concentration of the pyrene in the samples was 1.2×10^{-6} M.)

Synthesis of Calix[4]resorcinarene Octa(3-bromopropionate) (8Br-CX4)

Calix[4]resorcinarene (CX4, 1.08 g, 2.00 mmol) was dissolved in THF (15 mL). To the mixture, triethylamine (6.72 mL, 48 mmol) was added. The reaction mixture was kept at 0°C and 3-bromopropionyl chloride (8.23 g, 48 mmol) in THF (10 mL) was added dropwise over a period of 30 minutes. Then, the reaction mixture was stirred at room temperature for 24 h. After the removal of the salt by filtration, the solution was evaporated under reduced pressure. The crude product was dissolved in diethyl ether and the organic portion was washed with aqueous K_2CO_3 solution, water and then dried over Na_2SO_4. After removal of the solvent, the brown crude was obtained. The crude product was subjected to column chromatography on silica gel ($CHCl_3$: acetone = 9 : 1) to afford 8Br-CX4 as brown solid (yield 1.24 g, 38 %). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20-5.80 (m, 2H, Ar-*H*), 4.24 (br, 1H, C*H*CH_3), 3.56 (t, 2H, CH_2Br), 2.99

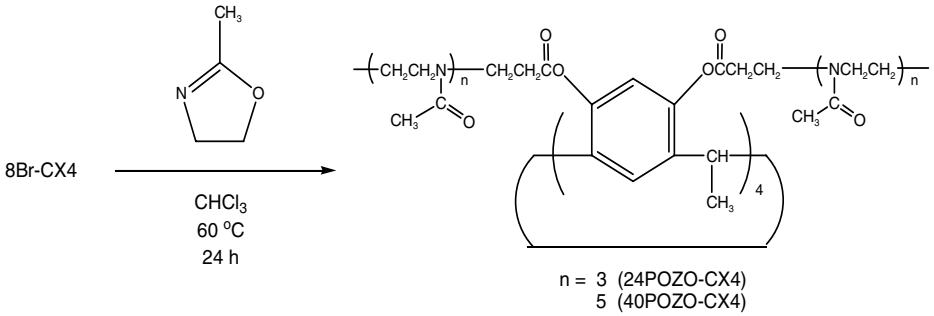
(t, 2H, CH_2CH$_2$Br), 1.48 (CHCH_3). ^{13}C NMR (67.5MHz, $CDCl_3$) δ 176.7, 171.5, 163.8 (C of C=O), 152.7, 145.9, 132.9, 127.3, 115.6, 111.9 (C of phenyl), 37.4 (*C*H$_2$C=O), 32.1 (C of methine), 25.0 (*C*H$_2$Br), 19.7 (C of methyl). Positive ion MALDI-TOF mass m/z = 1685 (M+3Na$^+$). GPC analysis (THF, polystyrene standards) : M_n = 870, M_n/M_w = 1.01. Anal. Calc. for $C_{56}H_{56}O_{16}Br_8$: C 41.40, H 3.48; found C 40.29, H 4.05. FT-IR (KBr) 1720 cm^{-1} (C=O: ester). mp 55-57°C.



Scheme 1

Synthesis of Star-Shaped POZO Using 8Br-CX4 as an Initiator

A typical procedure is as follows (Scheme 2). To a solution of 2-methyl-2-oxazoline (2.04 g, 24.0 mmol) in chloroform (10 mL), 8Br-CX4 (0.408 g, 1.00 mmol) was added at 0°C under nitrogen. The reaction mixture was heated at 60°C for 24 h. The resulting solution was reprecipitated with diethyl ether repeatedly. The solid precipitate was filtered off. After drying under vacuum, star-shaped POZO was quantitatively obtained as a slight yellow solid.



Scheme 2

^{1}H NMR (270 MHz, $CDCl_3$) δ 9.60-5.80 (m, 2H, Ar-*H*), 4.24 (br, 1H, C*H*CH$_3$), 3.48 (br, N-CH_2CH_2-) 3.56 (t, 2H, CH_2Br), 2.99 (t, 2H, CH_2CH$_2$Br), 1.48 (CHCH_3). ^{13}C NMR (67.5MHz, $CDCl_3$) δ 173.5, 171.2 (N-*C*=O), 165.4, 164.5 (O-*C*=O), 132.0, 127.5 (C of phenyl), 61.8, 59.2 (C of end group of POZO), 47.5, 46.8, 45.0, 43.5 (C of ethylene group of POZO), 38.1 (-*C*H$_2$-C=O-), 29.5 (*C*H-CH$_3$), 23.0 (CH-*C*H$_3$), 21.2 (O=C-*C*H$_3$), 17.3 (C of methyl group of POZO). FT-IR (KBr) 1740 cm^{-1} (C=O, ester group), 1640 cm^{-1} (C=O, amide group).

Results and Discussion

Novel reactive macrocyclic compound, bromoethyl group modified calix[4]resorcinarene (8Br-CX4) was synthesized (Scheme 1). Chemical structure of 8Br-CX4 was characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, elemental analysis and MALDI-TOF mass. The ^{1}H NMR spectrum of 8Br-CX4 is shown in Figure 1a. The protons of phenyl (peak a), methine (peak b), ethylene (peaks c and d) and methyl group (peak e) derived from CX4 and bromoethyl group were observed. Splitting of the signals was due to the structure and conformation of 8Br-CX4 [14, 17-18].

New star-shaped POZOs using 8Br-CX4 as an initiator were prepared by varying feed ratio of 2-methyl-2-oxazoline to 8Br-CX4. The star-shaped polymers were denoted as 24POZO-CX4 and 40POZO-CX4, which have 24 and 40 molar ratios of 2-methyl-2-oxazoline to 8Br-CX4, respectively. The star-shaped POZOs polymerized from 8Br-CX4 were characterized by ^{1}H NMR, ^{13}C NMR and FT-IR measurements. The typical ^{1}H NMR spectrum of the star-shaped POZO is shown in Figure 1b. The protons of phenyl, methine, ethylene and methyl groups from CX4 were observed at 9.6-5.8, 4.2, 2.9 and 1.4 ppm, respectively. In addition, the ethylene and methyl protons of POZO moieties were recognized at 3.8-3.2 and 2.2-1.8 ppm, respectively. In ^{13}C NMR spectra, the signal of bromomethyl groups of 8Br-CX4 at 25.0 ppm disappeared and new peak at 43.5 ppm appeared after polymerization, indicating that polymerization should occur at eight arms of 8Br-CX4. From the integration ratio of the methine proton of CX4 moiety to the methyl protons of POZO moieties, degree of polymerization (DP) of oxazoline unit was calculated. The results of the polymerization are summarized in Table 1. DP increased according to increasing feed

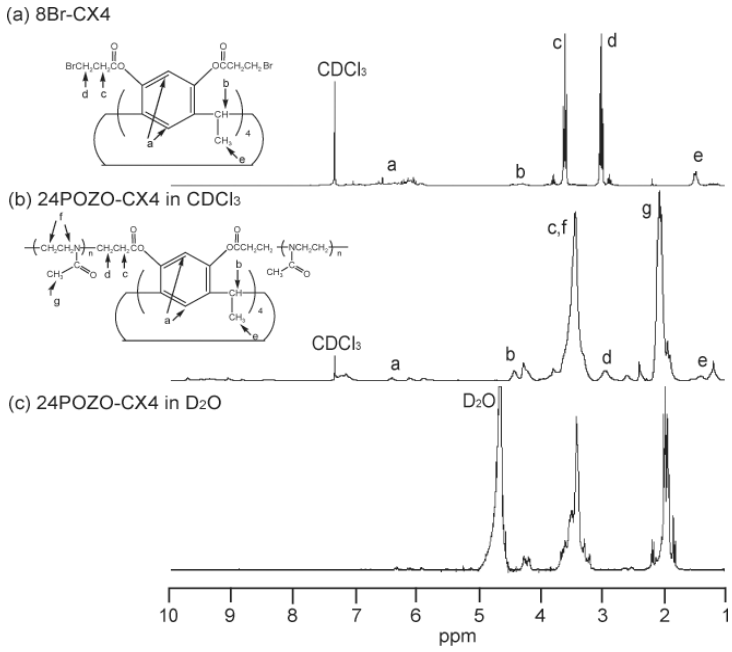


Figure 1. ^{1}H NMR spectra of (a) 8Br-CX4 in $CDCl_3$, (b) 24POZO-CX4 in $CDCl_3$ and (c) 24POZO-CX4 in D_2O.

Table 1. Synthesis of star-shaped POZOs initiated by 8Br-CX4

sample name	8BR-CX4 / monomer	number of monomer to 8BR-CX4 (degree of polymerization)[a]
24POZO-CX4	1/24	37.2
40POZO-CX4	1/40	72

[a]Measured by ^{1}H NMR.

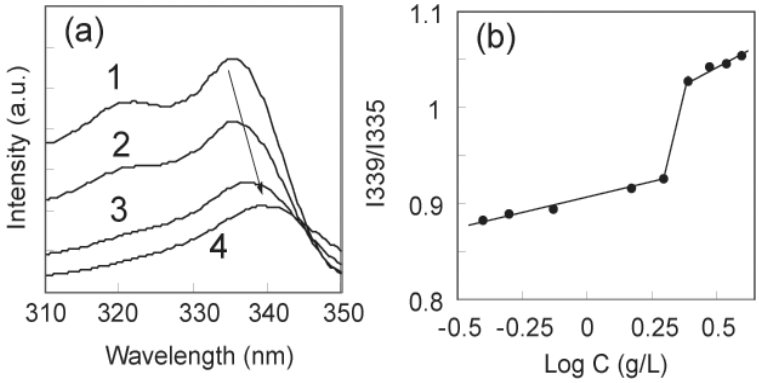


Figure 2. (a) Excitation spectra of pyrene (emitted at 393 nm) as a function of concentration of 24POZO-CX4. Concentrations of 24POZO-CX4 are (1) 0.05, (2) 0.75, (3) 2.5 and (4) 12 g/L. (b) Intensity ratio (I_{339}/I_{335}) of pyrene (from the excitation spectra) vs. log C for 24POZO-CX4 at 25°C.

ratio of 2-methyl-2-oxazoline to 8Br-CX4. The star-shaped POZOs were soluble in $CHCl_3$, DMF, DMSO, methanol and water, while 8Br-CX4 was insoluble in methanol and water, indicating that the star-shaped POZOs exhibited amphiphilic property.

Since the star-shaped POZOs have hydrophobic CX4 segments and hydrophilic POZO chains, they form a novel micelle structure in aqueous media. Figure 1c shows ^{1}H NMR spectrum of 24POZO-CX4 in D_2O. In D_2O, the signals of CX4 (9.6-5.8 ppm (peak a), 2.9 ppm (peak d) and 1.4 ppm (peak e)) were broadened and disappeared (Figure 1c), while the whole peaks from both CX4 and POZO moieties were clearly observed in $CDCl_3$ (Figure 1b). The observation indicates the formation of nanometer scale assembly of the star-shaped POZO in aqueous solution. In aqueous media, molecular motion of the hydrophobic CX4 moieties is limited by hydrophilic POZO moieties. To examine micelle size distribution, dynamic light scattering (DLS) measurement was carried out. The average size of the micelles from 24POZO-CX4 in aqueous media was ca. 300 nm.

The critical micelle concentration (cmc) of the star-shaped POZO in an aqueous solution was determined by using pyrene as a fluorescence prove. Figure 2a shows excitation spectra of pyrene at various concentrations of 24POZO-CX4. Above the critical concentration, the shift of pyrene absorption peak from 335 to 339 nm was found. It indicates that pyrene molecules located into the hydrophobic CX4 core of micelles. The intensity ratios (I_{339}/I_{335}), which were used to determine the cmc value of micelles, are shown in Figure 2b. The cmc was determined from the intersection of the straight lines in Figure 2b. The cmc value of 24POZO-CX4 was ca. 2 g/L.

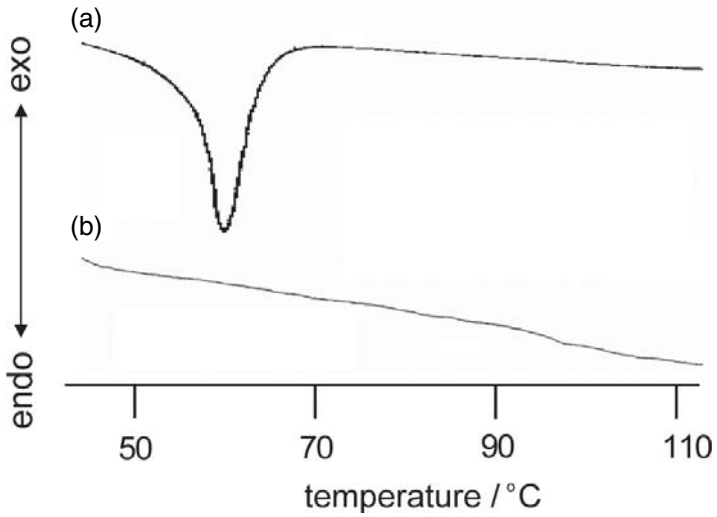


Figure 3. DSC thermograms of (a) 8Br-CX4 and (b) 40POZO-CX4.

Thermal property of the star-shaped POZO was investigated by DSC. Thermograms of (a) 8Br-CX4 and (b) 40POZO-CX4 are shown in Figure 3. The melting point of 8Br-CX4 was clearly observed at 55-57°C (Figure 3a). On the other hand, in 40POZO-CX4, the endothermic peak from 8Br-CX4 completely disappeared (Figure 3b). These observations indicate that crystallinity of 8Br-CX4 decreased due to the introduction of amorphous POZO chains at upper rim of 8Br-CX4.

Conclusions

Novel macrocyclic compound of 8Br-CX4 was successfully synthesized. The reactivity of the bromoethyl groups of 8Br-CX4 are so high that various functional groups should be introduced by using 8Br-CX4 as a reactive calix[4]resorcinarene. Based on 8Br-CX4, star-shaped POZOs were prepared. They showed an interesting micelle structure on nanometer scale in aqueous solution. It is well known that calix[4]resorcinarene derivatives capture metal cations and guest molecules. The amide groups of POZO also form complex with metal cations. Therefore, the star-shaped POZO is expected to exhibit interesting recognition abilities toward metal cations and guest molecules. The work is now under investigation.

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