Synthesis and characterization of calixarene-based poly(ε-caprolactone) stars catalyzed by yttrium complex

Abstract Two calixarene derivatives (2a, 2b) have been synthesized and used as macro-initiators to prepare star-shaped poly(ε-caprolactone)s (SPCLs) via controlled ring-opening polymerization of ε-caprolactone in the presence of yttrium tris(2,6-di-tert-butyl-4-methylphenolate) [Y(DBMP)₃]. The molecular weight of SPCLs was characterized by end group ¹H-NMR analyses and size-exclusion chromatography (SEC). The results indicate that SPCLs based on a calix[4]arene derivative (2a) are well-defined four-arm star polymers with reasonably narrow molecular weight distributions in the given molecular weight range, while SPCLs based on a calix[6]arene derivative (2b) are star polymers with not so defined structures. Differential scanning calorimetry (DSC) analyses suggest that the maximal melting point, the crystallization temperature and the degree of crystallinity of SPCLs increases with the increasing molecular weight and are lower than those of the linear poly(ε-caprolactone) (LPCL) counterpart. Furthermore, polarized optical microscopy (POM) indicates that SPCL exhibits irregular spherulites with poor morphology and slower crystallization rate, whereas LPCL shows fast crystallization rate and good spherulitic morphology.

Keywords star polymers, calixarene, poly(ε-caprolactone), rare earth catalyst, ring-opening polymerization

Calixarenes are cyclic oligomers obtained from the condensation reaction of formaldehyde with para-alkyl-phenols. The calixarenes with four, six or eight p-tert-butylphenol units can be easily prepared. They have been regarded as the third-generation host molecules after the crown ethers and cyclodextrins showing potential applications in sensors, molecule probes, liquid crystals, polymer syntheses, etc [1–5]. Nowadays, increasing attention has been paid on the syntheses of polymers containing calixarenes because of their unique physical and chemical properties. Gnanou [6] and Sawamoto [7] used functionalized calix[n]arenes as ATRP initiators for the polymerization of acrylates and styrene to prepare star polymers. Kennedy et al. reported eight-arm poly(isobutylene) stars prepared by living cationic polymerization from a calix[8]arene-based initiator [8]. Gnanou’s group [9] also prepared eight-arm poly(ethylene oxide) (PEO) stars based on calix[8]arene precursors via anionic polymerization. Very recently, our research group [10] described the synthesis of calix[6]arene-based amphiphilic polymers consisting of six PPO-block-PDTC arms by ring-opening polymerization. Poly(ε-caprolactone) (PCL) is one of the most attractive and promising biodegradable aliphatic polyesters which can be used as synthetic biomaterial or controlled drug release matrix due to its good drug permeability, biocompatibility and non-toxicity [11]. PCLs with tailor made architectures have attracted much attention in relation to functional materials. Star-shaped poly(ε-caprolactone) (SPCLs), having high molecular weight but relatively short chains, exhibit smaller hydrodynamic radius and lower viscosity compared to linear poly(ε-caprolactone) (LPCL) with similar molecular weight and are expected to display peculiar morphology, thermal property and degradation performance. Stannous octanoate [Sn(Oct)₂] is the most widely used catalyst for the preparation of SPCLs [12], but high temperature is needed for the polymerization which leads to the unavoidable transesterification. In recent years, our group has exploited a series of rare earth phenolate complexes as efficient catalysts for CL homo- and co-polymerization under mild conditions [13]. In this paper, two kinds of multifunctional calixarene precursors have been synthesized (2a, 2b, Fig. 1), and calixarene-based star-shaped poly(ε-caprolactone)s (SPCLs) have been prepared by the core-first method at 40°C using the precursors as macro-initiators in the presence of yttrium tris(2,6-di-tert-butyl-4-methylphenolate) [Y(DBMP)₃] (Fig. 2) via controlled ring-opening polymerization. All the samples were characterized by nuclear
magnetic resonance spectroscopy (NMR) and size-exclusion chromatography (SEC). Differential scanning calorimetry (DSC) was used to investigate the thermal and crystallization behaviors of SPCLs. In the meantime, the crystalline morphology of SPCLs was also investigated by polarized optical microscopy (POM).

1 Experimental

1.1 Materials and measurements
e-caprolactone (99%; Acros) was distilled under reduced pressure prior to use. Methyl chloroacetate, potassium carbonate, potassium iodide (analytical reagent) and lithium aluminum hydride (LiAlH₄; 97%; Alfa) were used as received without further purifications. p-tert-butylcalix[4]arene and p-tert-butylcalix[6]arene were synthesized according to the procedure described in the literature [1]. THF was distilled from the ketyl prepared from sodium and benzophenone. Y(DBMP)₃ was synthesized as we reported formerly [14]. Other reagents and solvents were purified by general methods.

The molecular weight and molecular weight distribution of the polymers were determined by size-exclusion chromatography (Waters 208 apparatus with a Waters 2410 refractive-index (RI) detector). The calibration was performed with commercial polystyrene standards. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1.0 mL·min⁻¹ at 30°C. ¹H-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl₃ with tetramethylsilane as the internal standard. ESI-positive MS was performed using Bruker Esquire 3000 plus spectrometer with an ESI interface. Differential scanning calorimetry (DSC) measurements were performed on a TA Q100 apparatus. All the samples were first heated from 0°C to 100°C, held for 2 min to erase the thermal history, then cooled to 0°C at a rate of 20°C·min⁻¹, and finally heated to 100°C at a rate of 10°C·min⁻¹. The intrinsic viscosities of PCLs were measured with an Ubbelohde viscometer in DMF at (30.0 ± 0.1)°C. The morphologies of PCLs were monitored with an Olympus BX51 polarized optical microscope (POM).

1.2 Synthesis of compound 1a

A mixture of p-tert-butylcalix[4]arene (0.65 g, 1 mmol), methyl chloroacetate (0.86 g, 8 mmol), KI (12.7 mg, 0.1 mmol), K₂CO₃ (1.38 g, 10 mmol) and anhydrous acetone (60 mL) was stirred under argon atmosphere and refluxed for 48 h. After removing acetone, 100 mL water was added, followed by adjusting the PH to 7 with hydrochloric acid, and then extracted with dichloromethane. The organic extract was dried over magnesium sulfate, filtered and concentrated to obtain a white solid. The crude product was recrystallized from CHCl₃/MeOH (0.80 g, 85% yield). MS for C₅₈H₈₂O₁₄: m/z = 960 (M + Na)⁺, ¹H-NMR (CDCl₃, 500 MHz): δ = 1.00 (s, 36H, C(CH₃)₃), 3.69 (s, 12H, CH₃), 3.12 and 4.88 (d, 8H, ArCH₂ Ar), 4.74 (s, 8H, ArOCH₂), 6.71 (s, 8H, ArH).

1.3 Synthesis of compound 1b

Following the general procedures described above, compound 1b was obtained from p-tert-butylcalix[6]arene in 80% yield. MS for C₈₄H₁₀₈O₁₈: m/z = 1427 (M + Na)⁺.