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
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

\(\varepsilon\)-caprolactone (99%; Acros) was distilled under reduced pressure prior to use. Methyl chloroacetate, potassium carbonate, potassium iodide (analytical reagent) and lithium aluminum hydride (LiAlH\(_4\); 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. \(^1\)H-NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in CDCl\(_3\) 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), K\(_2\)CO\(_3\) (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 CHCl\(_3\)/MeOH (0.80 g, 85% yield). MS for C\(_{56}\)H\(_{72}\)O\(_{12}\): m/z = 960 (M + Na)*. \(^1\)H-NMR (CDCl\(_3\), 500 MHz): \(\delta = 1.00\) (s, 36H, CH\(_3\)), 3.69 (s, 12H, CH\(_2\)), 3.12 and 4.88 (d, 8H, ArCH\(_2\)Ar), 4.74 (s, 8H, ArOCH\(_2\)), 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 C\(_{84}\)H\(_{108}\)O\(_{18}\): m/z = 1427 (M + Na)*,