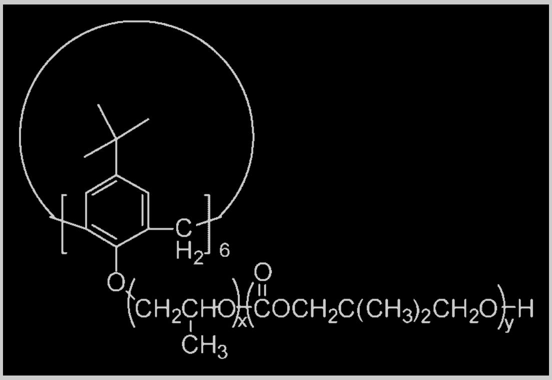
Summary: The syntheses and characterizations of well-defined star-shaped amphiphilic polymers containing a hydrophobic *p-tert*-butyl-calix[6]arene core and six hydrophilic PPO or PPO-*b*-PDTC arms are described. The average number of PO units in each arm could be adjusted by choosing a suitable amount of raw material.



Schematic structure of the amphiphilic star-shaped block copolymer containing a hydrophobic *p-tert*-butyl-calix[6]-arene core and six PPO-*b*-PDTC arms.

Synthesis and Characterization of Amphiphilic Star-Shaped Polymers With Calix[6]arene Cores

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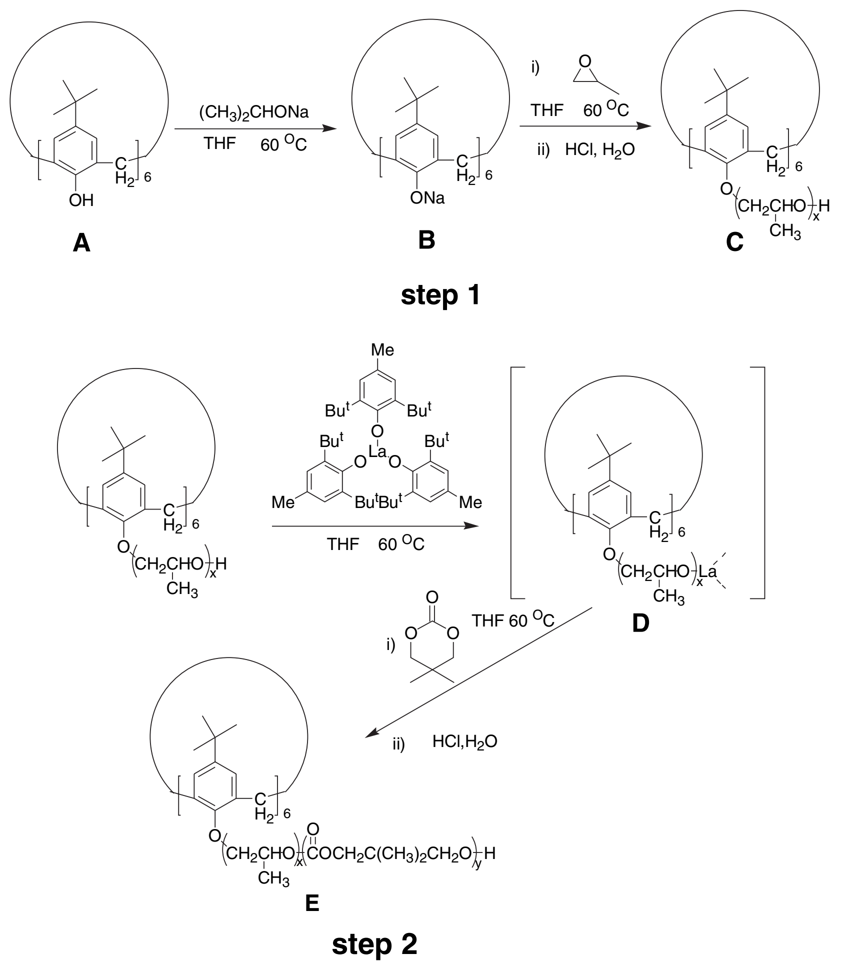
Introduction

Star-shaped polymers have smaller hydrodynamic radii and lower solution and melt viscosities than the corresponding linear polymers with the same molecular weight and composition.[1] Amphiphilic star-shaped block copolymers have recently attracted much attention because they can assemble into nanosized unimolecular micelles containing hydrophobic cores surrounded by hydrophilic shells, which are of great interest for medical uses such as micelle-assisted drug delivery.[2] The two main strategies commonly employed for preparation of star-shaped block copolymers are the so-called "arm-first" method and the "core-first" method. Calix[*n*]arenes are cyclic polymers obtained from the condensation of formaldehyde with *p*-alkylphenols.[3] The number *n* in calix[*n*]arene denotes the number of phenol units in the calixarene molecule. The hydroxyl group of each phenol unit in calixarene is active; it is therefore possible to prepare star-shaped polymers by using calixarenes as macro-initiators. Taton et al. reported eight-arm poly(ethylene oxide) (PEO) stars prepared by the core-first method from a octahydroxylated calix[8]arene precursor.[4] In this paper, the first-time synthesis of an amphiphilic star-shaped polymer consisting of six hydrophilic poly(propylene oxide) (PPO) arms and a hydrophobic core by means of an anionic ring-opening polymerization of propylene oxide (PO) onto a calix[6] arene core is described. In addition, an amphiphilic star-shaped six-arm copolymer PPO-*block*-PDTC was synthesized through the ring-opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) initiated by the star-shaped polymer described above as a macro-initiator and lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) as the catalyst. The novel amphiphilic star-shaped polymers prepared might have potential applications as self-assembling entities, biodegradable materials and for drug delivery. The study of their biodegradability and applications is in progress.



Scheme 1. Syntheses of the polymer **C** and the copolymer **E**.

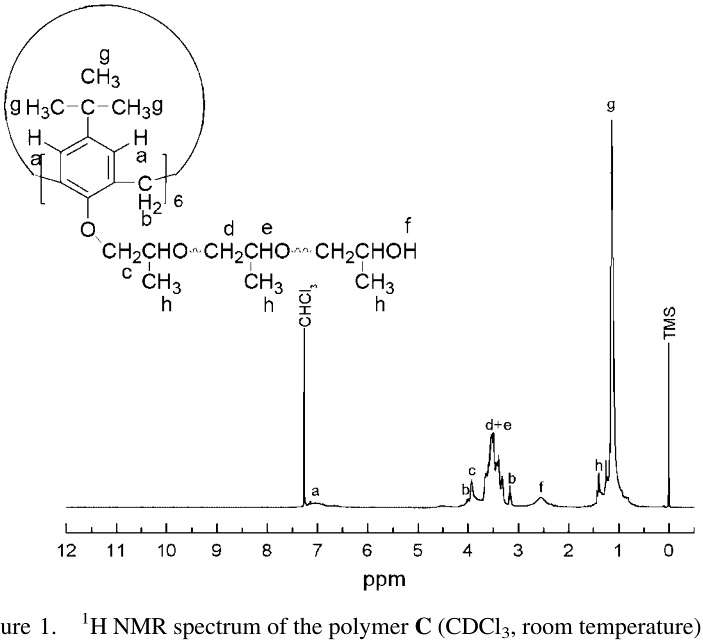


Figure 1. ^1H NMR spectrum of the polymer **C** ($CDCl_3$, room temperature).

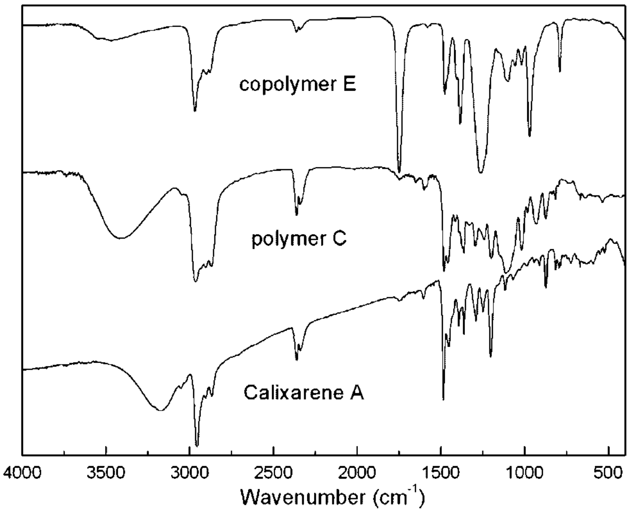


Figure 2. IR spectra of the calixarene **A**, the polymer **C** and the copolymer **E** (solid).

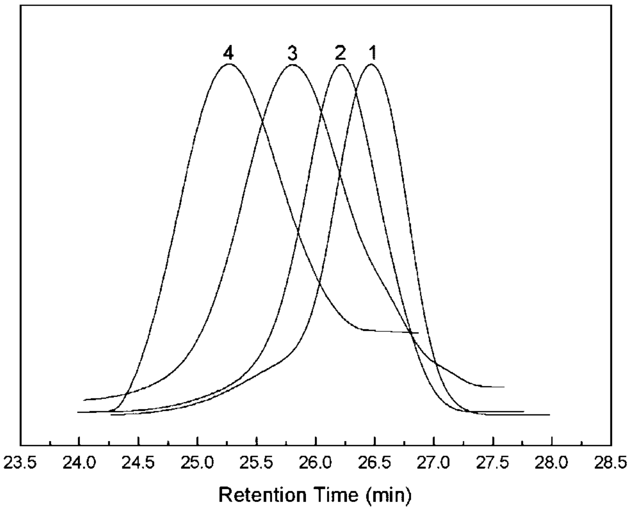


Figure 3. SEC patterns of the polymers $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_4}$ (THF, 1.0 mL · min^{-1}).

Experimental Part

p-tert-Butyl-calix[6]arene was prepared according to a procedure reported previously.[5] DTC was synthesized by the exchange reaction of 2,2-dimethyl-1,3-propanediol with diethyl carbonate, recrystallized and dried over P_2O_5 before use.[6] Lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) was synthesized as described previously.[7] Sodium isopropylate was prepared by direct reaction of sodium with isopropyl alcohol. Other chemicals were purified by standard methods.

The polymer consiting of six-arm PPO and a *p-tert*-butyl-calix[6]arene core (**C**) was synthesized by the reaction of sodium *p-tert*-butyl-calix[6]arene (**B**) with PO as shown in Scheme 1 (step 1). As an example, 0.036 g (1.6 mmol) sodium were added into a two-neck round bottle containing a mixture of 40 mL THF and 2.0 mL isopropyl alcohol. When the sodium was completely dissolved, 0.25 g (0.26 mmol) *p-tert*-butyl-calix[6]arene (**A**) were introduced and heated at 60 °C for 1 h, then 1.0 mL (0.83 g, 14 mmol) PO were added into the transparent solution, stirred at 60 °C for 24 h. The reaction was terminated using hydrochloric acid. After removing sodium chloride by filtration and THF by distillation, the polymer was dissolved in dichloromethane and washed with ice water several times to eliminate the PPO formed by chain transfer reaction. 0.790 g polymer **C** were obtained after removing dichloromethane by distillation.

The copolymer **E** containing six PPO-*block*-PDTC arms was synthesized by the block copolymerization of DTC with polymer **C** in the presence of lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) as shown in Scheme 1 (step 2). The reaction was carried out in a 20-mL ampoule using a Schlenk technique. Polymer **C** (0.078 g, 0.022 mmol) was introduced into the ampoule together with THF under argon atmosphere. A solution of lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) (0.038 mol · L^{-1}) in THF (1.0 mL) was injected into the ampoule with a syringe. The ampoule was heated at 60 °C for 0.5 h, and then 2.0 mL solution of DTC in THF (0.38 mol · L^{-1}) was added and heated to 60 °C for

Table 1. Results of PO polymerization initiated by sodium calixarene.

Polymer **C**	PO/Calixarene	Conv.	X_{cal} a)	$\bar{M}_{n,cal}$ b)	X_{nmr} c)	$\bar{M}_{n,nmr}$ d)	$\bar{M}_{n,sec}$ e)	MWD e)
	mol/mol	%		kg · mol^{-1}		kg · mol^{-1}	kg · mol^{-1}	
1	20	49.2	1.6	1.5	1.3	1.4	1.4	1.14
2	55	64.9	5.9	3.0	7.2	3.5	1.7	1.12
3	100	62.3	10.4	4.6	9.4	4.2	2.1	1.20
4	150	77.2	19.3	7.7	24.3	9.4	3.0	1.16

a) Average number of PO units in each arm calculated from the molar ratio of PO/calixarene and conversion.
b) Calculated from $972 + 58 \times X_{cal} \times 6$.
c) Calculated according to Equation (1).
d) Calculated from $972 + 58 \times X_{nmr} \times 6$.
e) Molecular weight distribution measured by SEC in THF calibrated with commercial polystyrene standards.

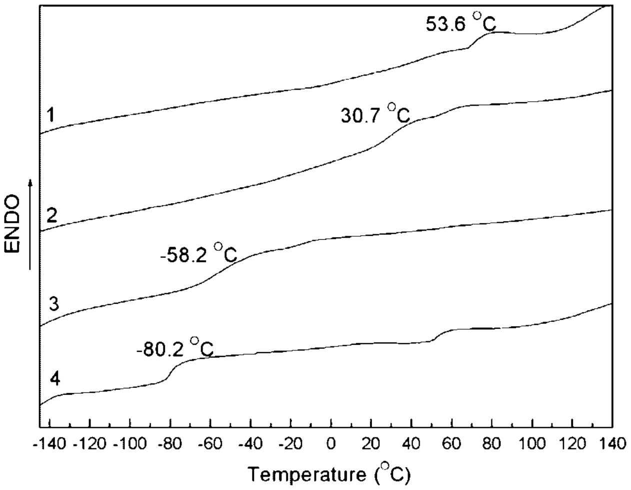


Figure 4. DSC curves of the polymers C_1, C_2, C_3 and C_4 (10.0 °C · min^{-1}).

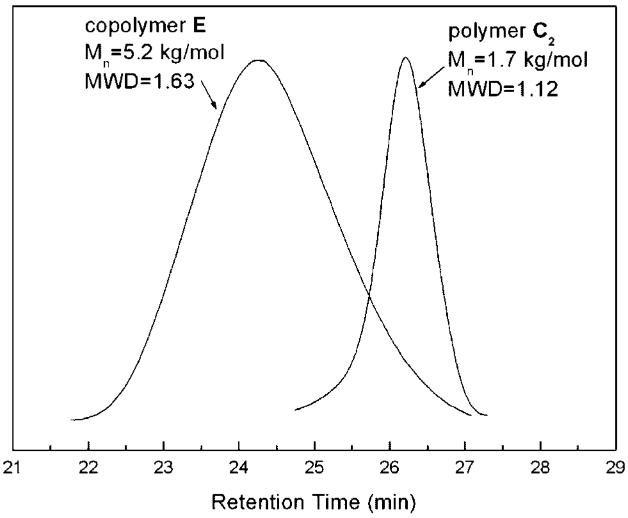


Figure 6. SEC patterns of the copolymer **E** and the polymer C_2 (THF, 1.0 mL · min^{-1}).

another 4 h. The ring-opening polymerization of DTC was accomplished using the active species **D**. The copolymerization was terminated with hydrochloric acid. Copolymer **E** was precipitated in hexane, filtrated and dried in vacuum to a constant weight, yielding 50.0 % conversion of DTC.

^{1}H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard. A Bruker Vector 22 Fourier-transform infrared (FTIR) spectrometer was used to record IR spectra. Size-exclusion chromatographic (SEC) measurements were performed on a Waters 150-C apparatus with columns Styragel HT 3, HT 4, HT 5 and Waters 2410 RI detector in THF (1.0 mL · min^{-1}) at 25 °C. DSC measurements were performed on a TA Q100 apparatus. The samples were cooled to −150 °C and twice heated to +150 °C at a heating rate of 10 °C · min^{-1}.

Results and Discussion

The ^{1}H NMR spectrum of polymer **C** (Figure 1) demonstrates the successful polymerization of PO. The peak at

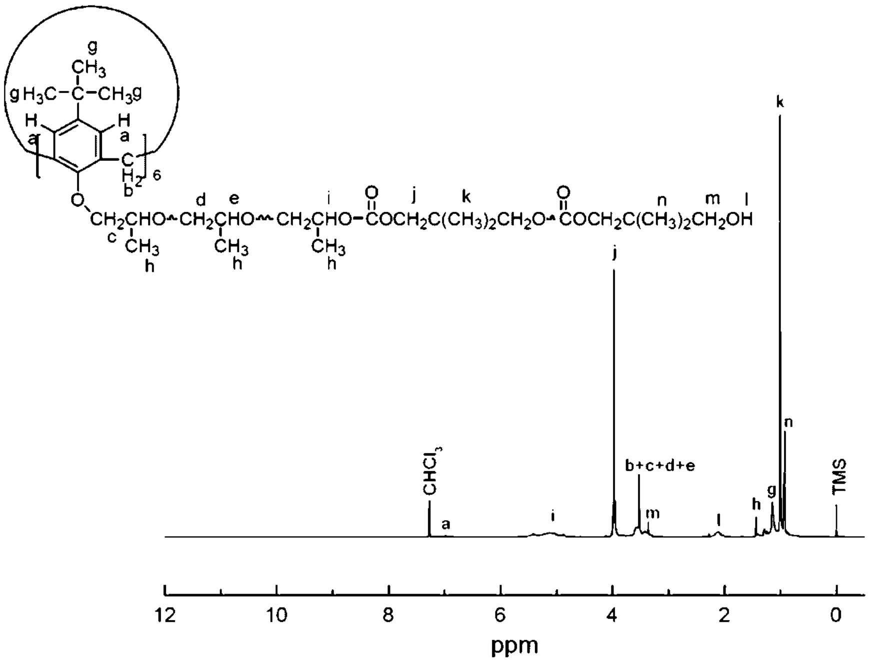


Figure 5. ^{1}H NMR spectrum of the copolymer **E** ($CDCl_3$, room temperature).

3.93 ppm (H^c) shows the direct links (ArO–$\mathbf{CH_2}$) of the PPO arm to the *p-tert*-butyl-calix[6]arene core. The ring-opening polymerization of PO was initiated with the sodium *p-tert*-butyl-calix[6]arene (**B**) via a β-ring-cleavage mechanism. Furthermore, there is no signal in the region from 9 to 11 ppm, indicating that no phenolic hydroxyl groups remained in the polymer **C**, that all functional groups of the initiator have reacted, and that the star-shaped six-arm PPO polymer with a *p-tert*-butyl-calix[6]arene core (polymer **C**) has been obtained. The average number X_{nmr} of PO units on the six arms can be calculated from the intensities of H^a, H^b, H^c, H^d and H^e (I^a, I^b, I^c, I^d and I^e),

$$X_{\mathrm{nmr}} = \frac{2}{3I^a}(I^b + I^c + I^d) = \frac{2}{3I^a}(I^{b,c,d,e} - I^a) \qquad (1)$$

The IR spectra of the calixarene **A** and the polymer **C** are displayed in Figure 2. The broad absorption at 3 177 cm^{-1}, shifted to 3 420 cm^{-1}, reveals the complete reaction of phenolic hydroxyl groups in calixarene **A** and the formation of alkylic hydroxyl groups in the PPO chain. The stretching vibration of the C–O bonds in the PPO backbone is clearly visible at 1 115 cm^{-1}. The polymerization results are summarized in Table 1. The data show that the average number X of PO units in each arm can be modified by adjusting the molar ratio of PO and calix[6]arene in the feed. SEC patterns of polymers $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_4}$ (Figure 3) all show single peaks and narrow molecular-weight distributions indicating that there is no linear PPO or unreacted calixarene in the samples. PO can be polymerized by using the calixarene initiator **B** and PPO with a different molecular weight can be prepared. Figure 4 shows the DSC curves of polymers $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3}$ and $\mathbf{C_4}$ with different PPO chain lengths. Polymers with longer PPO arms display lower values of T_g.

The amphiphilic star-shaped block copolymer **E** was synthesized through the ring-opening polymerization of DTC using Polymer $\mathbf{C_2}$ as macro-initiator and lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) as catalyst via the active species **D** as shown in Scheme 1 (step 2). The direct links of the PPO and PDTC blocks, –COOC**H**(CH_3)–, showed up at about 5.00 ppm (H^i) and the –$\mathbf{CH_2}$O**H** groups (H^m, H^l) from the chain ends at about 3.5 and 2.0 ppm in the ^{1}H NMR spectrum of copolymer **E** (Figure 5), which demonstrates that the O–La bond in the active species **D** initiates the ring-opening polymerization of DTC via an acyl-oxygen bond cleavage.[8] The signal of –CH(CH_3)O**H** (2.5 ppm) representing the chain end of polymer $\mathbf{C_2}$ disappeared, illustrating that all functional groups of polymer $\mathbf{C_2}$ reacted. The IR spectrum of copolymer **E** (Figure 2) illustrates the PDTC segments at 1 700 cm^{-1}. The average number Y of DTC units in each arm was determined to be 3.7 from the intensities of H^k and H^n (I^k and I^n) according to

$$Y = \frac{I^k}{I^n} + 1 \qquad (2)$$

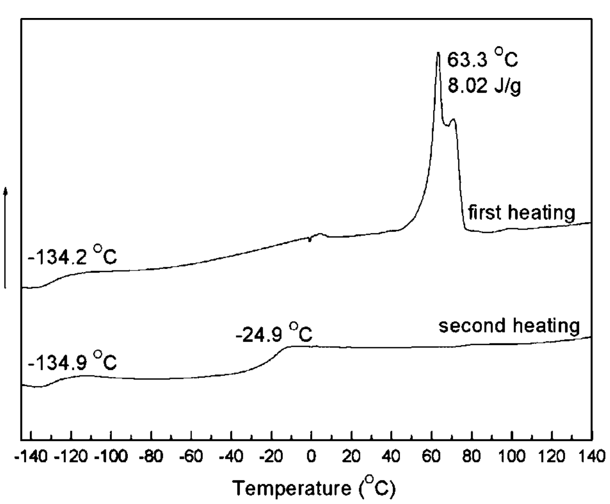


Figure 7. DSC curves of the copolymer **E** (10.0 °C · min^{-1}).

The molecular weight of copolymer **E** was calculated to be $130 \times Y \times 6 + 3\,500 = 6\,400$. The average number X of PO units and Y of DTC units in each arm as obtained from the ^{1}H NMR spectra are close to the values calculated from the amount of raw material used and the observed conversion. The SEC patterns of copolymer **E** together with its starting polymer $\mathbf{C_2}$ are shown in Figure 6. The resulting copolymer **E** and the starting polymer $\mathbf{C_2}$ both display single peaks indicating no linear PDTC was produced. DSC curves obtained after the first and the second heating of copolymer **E** are shown in Figure 7. After the first heating, T_g of -134.2 °C due to the PPO segment and a T_m of 63.3 °C due to the PDTC segment are clearly observable. After the second heating, T_m has disappeared and T_g is shifted to -24.9 °C appeared.

Conclusion

Amphiphilic star-shaped polymers containing a *p-tert*-butyl-calix[6]arene core with six PPO or PPO-*block*-PDMTC arms, respectively, have been successfully synthesized for the first time. The structures of these star-shaped polymers are confirmed by ^{1}H NMR, IR, SEC and DSC. The molecular weights of the star-shaped polymers calculated from the ^{1}H NMR spectra agree with the values predicted from the raw materials used and the observed conversion.

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