

Multiarm Star Poly(ϵ -caprolactone) with Hyperbranched Polyamidoamine as Core Capable of Selective Accommodating Cationic or Anionic Guests^{*}

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Abstract Hyperbranched polyamidoamines (HPAs) were directly employed as macroinitiators to initiate the Sn(Oct)₂ catalyzed ring-opening polymerization of ϵ -caprolactone (CL), resulting in multiarm star copolymers with poly(ϵ -caprolactone) (PCL) as shells and HPA as core (HPA-*b*-PCL). From ¹H-NMR characterization it was deduced that both the primary amines and the secondary amide groups of HPAs could initiate the CL polymerization, and the initiation efficiency increased when more CL monomers were fed. The average arm-numbers of the obtained stars were in the range of 115–353. Differential scanning calorimetry measurements demonstrated that the melting and crystallization temperatures, fusion and crystallization enthalpy and the degree of crystallinity of the star polymers increased as the PCL arm length increased. HPA-*b*-PCL stars could be used as nanocarriers to efficiently accommodate anionic dyes at acidic condition, while load cationic dyes at basic condition. Compared with the dye-loading behavior of multiarm star PCL with the neutral hyperbranched polyglycerol as core, it was deduced that HPA-*b*-PCL nanocarriers accommodated anionic dyes using the HPA core, while loaded cationic dyes using both the HPA core and the PCL shell. Dynamic light scattering analyses also supported such deduction. Furthermore, HPA-*b*-PCL nanocarriers could selectively load the anionic Eosin Y or the cationic methylene blue from their mixture at pH = 6 or 9, respectively, realizing their separation.

Keywords: Nanocarrier; Hyperbranched; Polyamidoamine; Poly(ϵ -caprolactone); Star polymers.

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INTRODUCTION

Multiarm star polymers have attracted considerable attention due to their unusual bulk and solution properties^[1–3]. Two major strategies have been employed for their preparation: (1) the core-first approach: living polymerization with a multifunctional molecule as initiator; (2) the arm-first approach: quenching of living polymers with a multifunctional coupling agent or linking reactions of living polymers with a small amount of bifunctional vinyl compounds. Among these strategies, the polymerization with a multifunctional initiator and the quenching of living polymers with a multifunctional coupling agent would lead to star polymers with predetermined numbers of arms if all the possible initiating or coupling sites took part in the reaction. In contrast, the linking reactions of living polymers with a small amount of bifunctional vinyl compounds usually

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afford star polymers with a random distribution of arms per macromolecule.

Dendrimers and hyperbranched polymers are attractive compounds as macroinitiators for the preparation of multiarm star polymers by the core-first strategy. On the basis of dendritic polymers, many kinds of functional amphiphilic multiarm star polymers have been prepared^[4–32]. In such amphiphilic polymers, either the dendritic core^[4–10] or the linear arm^[11–26] or both^[27–32] are functional for the accommodation of guest molecules. Among these amphiphilic multiarm star polymers, the majority of them as nanocarriers could accommodate only one kind of guest, such as anionic one, cationic one or hydrophobic one^[4–26]. Recently, certain amphiphilic multiarm star polymers as nanocarriers were reported to have the ability of accommodate two kinds of guests including the hydrophilic one and the hydrophobic one^[27, 32]. Up to the present date researches on nanocarriers have mainly focused on their guest-loading behavior, whereas their selective accommodation for different guests was seldom reported^[33–35]. Wan *et al.* have ever utilized amphiphilic hyperbranched polymers as nanocarriers to selectively encapsulate anionic dye from the mixture of cationic dye and anionic dye^[33]. To our best knowledge, nanocarriers, especially multiarm star nanocarriers that could selectively accommodate cationic guests or anionic guests from their mixtures through adjusting the guest-loading condition are scarce^[36].

Poly(ϵ -caprolactone) (PCL), a kind of biocompatible and biodegradable aliphatic polyester, has received a significant amount of interest in both academic and industrial researches for a long time^[37, 38]. Until now, a limited number of hyperbranched polymers have been employed as core for the synthesis of multiarm star PCL, such as hyperbranched polyether^[39, 40], hyperbranched polyester^[41] and hyperbranched polyethylenimine (HPEI)^[5–7]. In this work hyperbranched polyamidoamine (HPA) was employed as macroinitiator to initiate the ring-opening polymerization of ϵ -caprolactone (CL), resulting in the multiarm star copolymers with HPA as core and PCL as arms (HPA-*b*-PCL). These HPA-*b*-PCL stars could be used as nanocarriers to accommodate anionic dyes using HPA core, while load cationic dyes using both HPA core and PCL shell. Furthermore, HPA-*b*-PCL nanocarriers could selectively load the anionic Eosin Y (EY) or the cationic methylene blue (MB) from EY/MB mixture at pH = 6 or 9, respectively, realizing their separation.

EXPERIMENTAL

Materials

Tin(II) 2-ethylhexanoate [Sn(Oct)₂, 97%] was purchased from Alfa Aesar and used directly. ϵ -Caprolactone (CL, 99%, Acros) was distilled from CaH₂ under reduced pressure. Triethyl amine (A.R., TEA) was dried over CaH₂ and distilled before use. Methyl acrylate (A.R.) was purchased from Tianjin University Kewei Chemical Company and used directly. Tris(2-aminoethyl)amine (A₃ monomer) was purchased from Aldrich and was distilled under reduced pressure before use. Methyl orange (MO, $M_w = 327.3 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Congo red (CR, $M_w = 696.7 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Tianjin Damao Reagent Factory. EY ($M_w = 691.85 \text{ g}\cdot\text{mol}^{-1}$) and acetic anhydride (95%) were purchased from Acros and used as received. MB ($M_w = 373.90 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Tianjin Bodi Chemical Industry. Ethidium bromide (EB, $M_w = 394.32 \text{ g}\cdot\text{mol}^{-1}$) was purchased from Alfa Aesar. De-ionized water was double-distilled before use. Tris(2-di(methyl acrylate)aminoethyl)amine (B₆ monomer) was synthesized according to the method of Dvornic^[42]. Lower molecular weight hyperbranched polyamidoamine (HPA-L) and higher molecular weight HPA (HPA-H) were synthesized according to the literatures^[42–44].

Polymerization

In a typical experiment for P-H3: 0.10 g of HPA-H and 1.43 g (12.5 mmol) of CL were put into a reaction flask, and then 45 mg of Sn(Oct)₂ (1 mol% corresponding to CL) was added. The polymerization was carried out under N₂ atmosphere at 130 °C for 24 h. After cooling down, the mixture was dissolved in chloroform, and precipitated in cold diethyl ether. The precipitation purification process was repeated twice to result in pure polymer. ¹H-NMR (chloroform-*d*): δ = 4.03 (t, $-\text{COOCH}_2-$), 3.62 (t, $-\text{CH}_2\text{CH}_2\text{OH}$), 2.38–3.40 (br, HPA), 2.28 (t, $-\text{CH}_2\text{COOCH}_2-$), 1.61 (m, $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-$, $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$), 1.35 (m, $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}-$, $-\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$).

Methodology for Dye Extraction under Different pH Conditions

The pH of dye in double distilled deionized water is 6.5. HCl and NaOH aq. were used to adjust the pH of the aqueous solution of dye to the desired pH. Then 4 mL of the aqueous solution of dye with certain pH was mixed with 4 mL of the CHCl₃ solution of multiarm star polymer for 10 min. HCl or NaOH aq. was used again to adjust the acidity of the water phase into the starting value. The solution was shaken for 10 min again and kept in dark chamber at room temperature overnight prior to measure. The concentrations of dye in water were fixed, but the concentrations of multiarm star polymer in CHCl₃ were adjusted until only part of the dye in water was transferred into the CHCl₃ phase. The UV-Vis spectrum of the water phase was recorded and the remaining dye in water was calculated according to Lambert-Beer law. Subsequently, the numbers of dye transferred into CHCl₃ phase could be therefore obtained.

Selective Accommodation for Cationic and Anionic Dyes

Certain amount of EY and MB were dissolved in phosphate buffer with pH = 6.0 or 9.0. The concentrations of EY and MB were set to be $5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and $1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, respectively. The aqueous solution of EY/MB mixture was shaken with the same volume of polymer in CHCl₃ whose concentration varied from 0.1 to 0.5 mg·mL⁻¹. After phase separation, the concentration of residual dyes in water was measured by UV-Vis spectroscopy.

Characterization

¹H-NMR spectra were recorded at 25 °C on a Bruker ARX400 spectrometer, operated at 400 MHz. ¹⁵N-NMR spectra were acquired at 25 °C on a Bruker 50.68 MHz spectrometer by using 5–7 kHz spectral width, 4 μs (45°) pulse width, a recycle delay of 4 s, and 938 scans. The data were processed with an exponentially decaying window function with a line broadening factor of 2 Hz. The molecular weight and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a Viscotek GPC270 system. As for the acetylated HPA samples, sodium nitrite solution (0.1 mol·L⁻¹) was used as eluent at a flow rate of 0.8 mL·min⁻¹ with the temperature maintained at 35 °C, and the results were calibrated against poly(ethylene oxide) standard. As for the star polymers, freshly distilled *N,N*-dimethyl formamide was used as an eluent at 35 °C. The flow rate was set to be 0.8 mL·min⁻¹. UV-Vis spectra were obtained from a Purkinje General (China) T6 UV-Vis Spectrophotometer. Differential scanning calorimetry (DSC) measurements were carried out on a Perkin Elmer DSC8000 under nitrogen atmosphere. Each sample was heated twice from –20 °C to 120 °C with a heating rate of 10 K·min⁻¹. Dynamic light scattering (DLS) measurements were performed using a Malvern Nano ZS instrument at 25 °C with 633 nm He-Ne laser light, and light collection at 90°. Chloroform was used as the solvent. The particle size was calculated with COTTIN method.

RESULTS AND DISCUSSION

Syntheses and Characterization of Multiarm Star Copolymers

HPAs were synthesized from the condensation polymerization of A₃ monomer, tris(2-aminoethyl)amine, and B₆ monomer, tris(2-di(methyl acrylate)aminoethyl)amine, according to the literatures^[42–44]. In the synthesis, excess A₃ monomer was used to avoid gelation and crosslinking. The ratios of A₃: B₆ were set to be 10:1 in HPA-L and 8:1 in HPA-H. Table 1 shows the structural information of the two HPAs (HPA-L and HPA-H) synthesized in this work. HPAs contain three kinds of nitrogens that come from the primary amine, tertiary amine and amide groups, respectively. From ¹⁵N-NMR spectra (Fig. S1 in the Supporting Information) the ratios of primary amine, tertiary amine and amide groups in HPAs can be learned (Table 1) because these three kinds of nitrogens are separated from each other very well. Because the amine end groups could interact with the GPC columns, the obtained HPAs were acetylated before the GPC measurements. The molecular weights of HPAs were calculated from GPC and ¹⁵N-NMR. The results shows that HPA-L has a number-average molecular weight (*M_n*) of 12.6 kDa and a polydispersity (PDI) of 1.56, while HPA-H has a *M_n* of 31.6 kDa and a PDI of 1.74. On the basis of the data of *M_n* and ratio of primary amine, tertiary amine and amide groups, the average numbers of primary amine, tertiary amine, amide, A₃ and B₆ units in HPAs are deduced (Table 1).

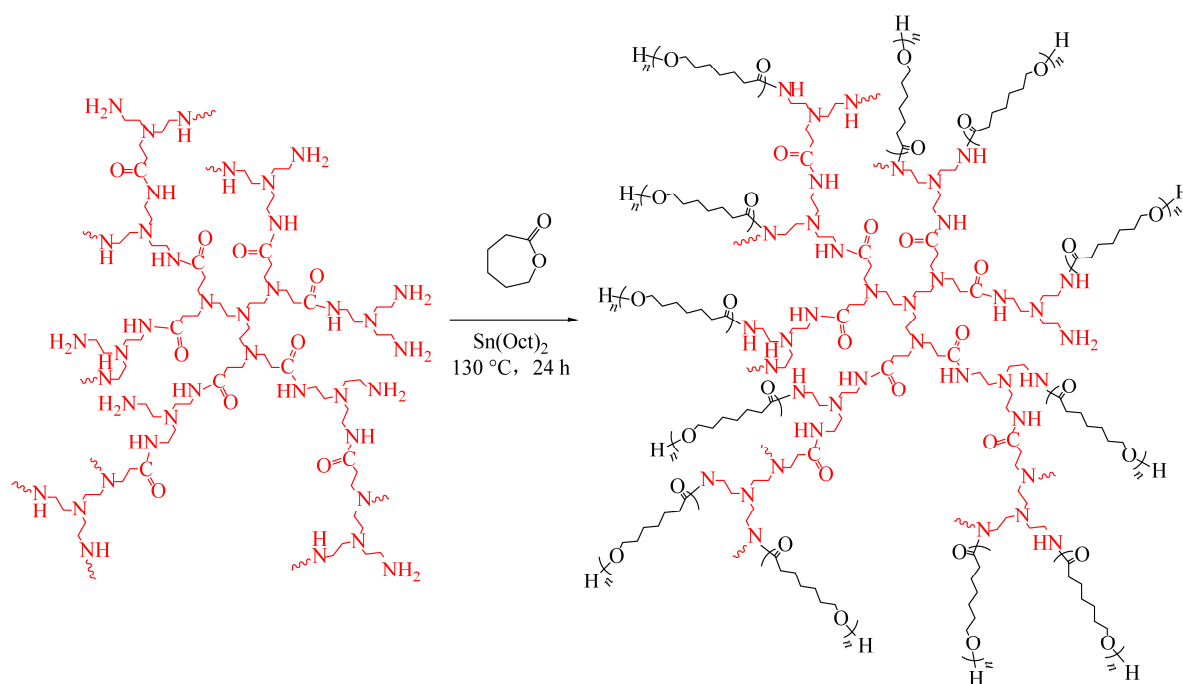
Table 1. Structural information of hyperbranched polyamidoamines

HPA	M_n^a (10^3)	PDI ^a	$\text{NH}_2\text{:N:NHCO}^b$	Numbers of functional groups and monomeric units				
				NH_2	N	NHCO	A_3 unit	B_6 unit
HPA-L	12.6	1.56	0.97:1.29:1	71	96	72	48	12
HPA-H	31.6	1.74	1.15:1.07:1	198	239	173	124	29

^a Measured by GPC; ^b $\text{NH}_2\text{:N:NHCO}$ denotes the molar ratio of primary amine, tertiary amine and amide groups in HPAs.

The $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening polymerizations of CL using HPAs as the macroinitiator were carried out at 130 °C for 24 h, as shown in Scheme 1. Subsequently, the reaction mixtures were characterized by $^1\text{H-NMR}$, and the signals were assigned as depicted in Fig. 1(A). In comparison with the $^1\text{H-NMR}$ spectrum of the CL monomer (Fig. 1B), beyond the signals originating from the obtained star polymer, the signals from the CL monomer completely disappeared (Fig. 1A); this indicated that the polymerization conversion reached nearly 100% under the polymerization conditions. The purified polymers were also characterized by $^1\text{H-NMR}$, featuring the same integration area as well as multiplicities and positions of the signals similar to those of the $^1\text{H-NMR}$ spectra found for unpurified polymers. From the integration ratio (I) of methylene groups adjacent to ester functional groups (a1 and a2 in Fig. 1A) to those adjacent to hydroxyl terminal groups (b in Fig. 1A), the degree of polymerization per PCL arm [$\text{DP}_{n(\text{arm})}$] was calculated according to Eq. (1), and the results are listed in Table 2.

$$\text{DP}_{n(\text{arm})} = I_{(\text{a1} + \text{a2})/I_{(\text{b})}} + 1 \quad (1)$$

**Scheme 1** Preparation of multiarm star copolymer with HPA as core and PCL as arms**Table 2.** Syntheses of HPA-*b*-PCL multiarm star copolymers

Sample	Initiator	Feed ratio of CL to $\text{NH}_2 + \text{NHCO}$	$\text{DP}_{n(\text{arm})}$	Initiating efficiency (%)	Arm number	$M_{n(\text{NMR})}$ (10^3)	$M_{n(\text{GPC})}$ (10^3)	PDI
P-L1	HPA-L	6.8	8.5	80	115	1.24	1.87	2.1
P-L2	HPA-L	13.5	13.6	99	142	2.33	3.12	2.3
P-L3	HPA-L	19.8	19.7	100	147	3.42	4.69	2.4
P-H1	HPA-H	6.5	8.4	77	285	3.05	1.95	2.0
P-H2	HPA-H	12.9	14.4	90	333	5.78	3.75	2.4
P-H3	HPA-H	19.5	20.5	95	353	8.56	5.15	2.2

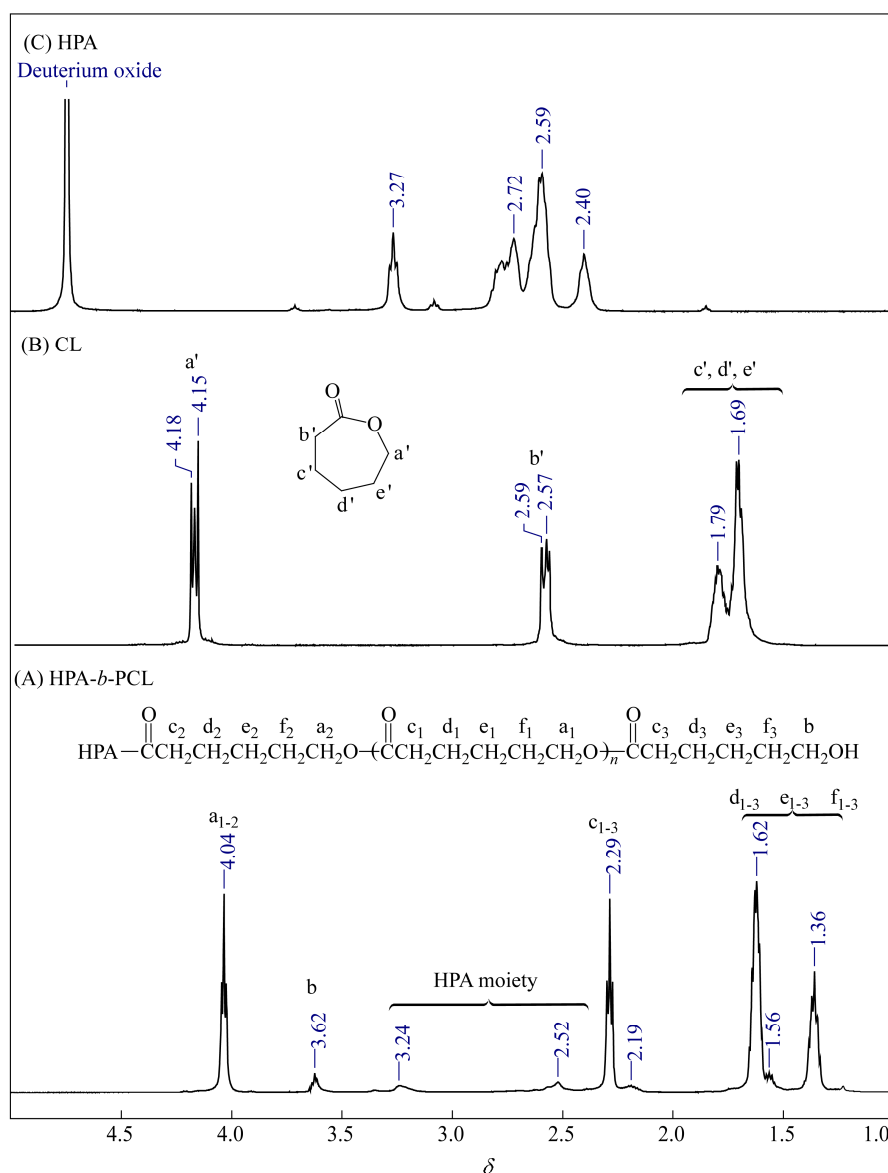


Fig. 1 Typical ^1H -NMR spectra of (A) multiarm star HPA-*b*-PCL in CDCl_3 , (B) CL monomer in CDCl_3 and (C) HPA in D_2O

It has been verified that primary amine is an effective initiator for the $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening polymerization of CL^[6, 7]. Moreover, the amide units in PAMAM dendrimer have been claimed to be capable of initiating the $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening polymerization of lactide^[45]. Therefore, the possible initiating sites in HPA are primary amine and amide groups. In the HPA-initiated ring-opening polymerization of CL, the feed ratios of CL monomers to the primary amine and amide groups of HPA were set in the range of 6–20, as shown in Table 2. Once the polymerization conversion nearly reached 100%, the average $\text{DP}_{n(\text{arm})}$ values of the obtained polymers could be interpreted from the corresponding ^1H -NMR spectra. Comparing the feed ratio of monomer to initiating sites with $\text{DP}_{n(\text{arm})}$, the initiating efficiencies of HPAs in all the polymerization batches are calculated and listed in Table 2. It is clear that the initiating efficiencies of both HPA-L and HPA-H in different polymerization batches are more than 70%. Since the molar content of primary amine in the possible initiating sites is less than 60% (see Table 1), it can be further deduced that both primary and amide groups of HPAs

initiate the $\text{Sn}(\text{Oct})_2$ -catalyzed ring-opening polymerization of CL. From Table 2 it can be further seen that increasing the feed ratio of monomer to initiating sites favors the enhancement of initiating efficiency. Moreover, the lower molecular-weight HPA shows a little higher initiating efficiency than the higher molecular-weight HPA. This can be explained as follows: The lower molecular weight dendritic polymer is normally more flexible and has a more open structure, whereas the higher molecular weight dendritic polymer shows the inverse characters. Therefore, the inner amide initiating sites of the lower molecular-weight HPA are more reactive toward the initiating reaction than those of the higher molecular weight HPA because of the less steric hindrance effect. On the basis of the initiating efficiencies of HPAs in different polymerization batches, the average arm-numbers of the obtained multiarm star HPA-*b*-PCL copolymers can be calculated (Table 2). With HPA-L as the macroinitiator, the average arm-numbers of HPA-*b*-PCL copolymers are in the range of 115–147, while the average arm-numbers of HPA-*b*-PCL copolymers with HPA-H as the core are in the range of 285–353.

The obtained multiarm star copolymers were characterized by GPC coupled with a refractive index (RI) detector and a light scattering (LS) detector. In all the GPC diagrams only mono-modal signal can be observed, indicating that no PCL homopolymers exist in the obtained star polymers. The LS signals of HPA-*b*-PCL copolymers are very weak; therefore the absolute molecular weights of these star copolymers cannot be obtained from GPC. For effective comparison, the relative molecular weights of these star copolymers are interpreted from the RI diagrams using linear PMMA as the reference (Table 2). It is clear that the M_n values determined by GPC [$M_{n(\text{GPC})}$] are considerably smaller than the absolute M_n calculated from ^1H -NMR spectra [$M_{n(\text{NMR})}$]. This is a normal phenomenon since the M_n values determined by traditional GPC technique are deduced from the hydrodynamic volumes of polymers. Multiarm star has a very compact structure and its hydrodynamic volume is much smaller than that of the corresponding linear polymer with the same molecular weight. The PDIs of the multiarm star polymers are relatively broad, and this indicates that the polymerizations are not enough controlled. One possible reason for the relatively broad dispersity may be the different initiation rates of the primary amine and amide groups.

The obtained multiarm star polymers are block copolymers of HPA with PCL. HPA is an amorphous polymer, whereas PCL is a semi-crystalline polymer. From Table 3 it is clear that the weight percentage of PCL segments in the copolymers is very high, no less than 90%, thus the bulk thermal properties of the obtained HPA-*b*-PCL copolymers will be determined mainly by PCL segments. Herein DSC is employed to investigate the thermal properties of the multiarm star copolymers in the temperature range of -20 to 120 $^{\circ}\text{C}$. Figure 2 shows the typical DSC curves of the HPA-*b*-PCL stars under the first heating run, the first cooling run and the second heating run. The melting temperature T_m and the fusion enthalpy ΔH_m are taken from the second heating

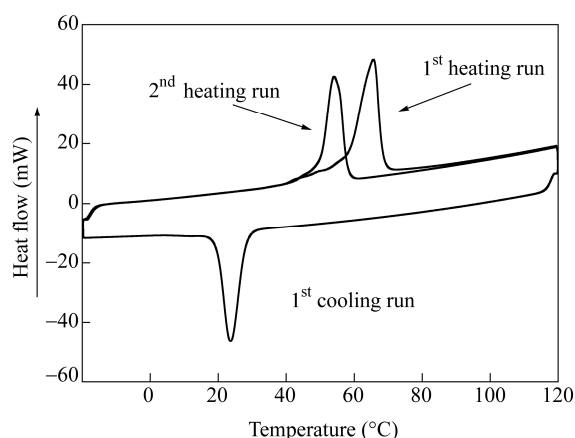


Fig. 2 Typical DSC curves of HPA-*b*-PCL (sample P-L3)

run, while the crystallization temperature T_c and the crystallization enthalpy ΔH_c are taken from the first cooling run. The degree of crystallinity (X_c) of PCL segments is calculated according to Eq. (2).

$$X_c(\%) = \Delta H_c / \Delta H_{100} \times 100 \quad (2)$$

X_c represents the degree of crystallinity of PCL, ΔH_{100} is the heat of crystallization for a 100% crystalline PCL, $\Delta H_{100} = 136.4 \text{ J/g}$ ^[46]. All the thermal data of the star polymers are compiled in Table 3. It is clear that with the same HPA core the T_m , T_c , ΔH_m , ΔH_c and X_c values of the star polymers increase as the PCL arm length increases.

Table 3. Thermal properties of HPA-*b*-PCL multiarm star copolymers measured by DSC

Polymers	PCL content (wt%)	T_m^a (°C)	ΔH_m^b (J/g)	T_c^c (°C)	ΔH_c^d (J/g)	X_c^e (%)
P-L1	90	46.2/49.1 ^f	60.0	13.5	57.5	42
P-L2	95	50.6	66.1	20.2	63.4	46
P-L3	96	54.6	71.1	23.6	66.5	49
P-H1	90	46.6/49.7 ^f	60.1	16.6	58.8	43
P-H2	95	52.0	64.1	21.5	62.0	45
P-H3	96	54.1	66.7	22.8	64.1	47

^a T_m is the melting point taken as the melting peak temperature in the second heating run; ^b ΔH_m represents the fusion enthalpy in the second heating run; ^c T_c is the crystallization point taken as the peak temperature in the first cooling run; ^d ΔH_m represents the crystallization enthalpy in the first cooling run; ^e X_c represents the degree of crystallinity of PCL. $X_c(\%) = \Delta H_c / \Delta H_{100} \times 100$, ΔH_{100} is the heat of crystallization for a 100% crystalline PCL, $\Delta H_{100} = 136.4 \text{ J/g}$; ^f Double melting peaks.

Multiarm Star Polymers as Nanocarriers for Loading Hydrophilic Guests

HPA-*b*-PCL has a distinct core-shell structure. The hydrophobic PCL shell renders HPA-*b*-PCL insoluble in water, but soluble in organic solvents, such as chloroform, dichloromethane. Compared with PCL, the HPA core is more hydrophilic. Therefore, whether HPA-*b*-PCL could be used as nanocarrier for accommodating hydrophilic guests was measured. The used typical water-soluble guests included the anionic MO, CR and EY, and the cationic MB and EB (Fig. S2 in the Supporting Information). The normal liquid-liquid loading protocol was adopted (Fig. S3 in the Supporting Information): the same volume solutions of dye in buffer with certain pH and the polymers in CHCl_3 were taken, mixed and shaken. The evidence that dyes were loaded by polymers was that after phase separation, the colorless organic phase became colored and the concentration of dyes in the water phase decreased, which could be confirmed from the decrease in UV-Vis absorbance of the dyes in the water phase. As the concentration of the multiarm star polymer in CHCl_3 increased, the water phase became light colored and finally colorless, and this indicated that all dyes were transferred into the organic phase. From Fig. 3 it can be seen that when suitable pH is chosen, HPA-*b*-PCL can not only efficiently accommodate anionic guests, but also cationic guests. For instance, HPA-*b*-PCL can efficiently load anionic dyes at acidic condition,

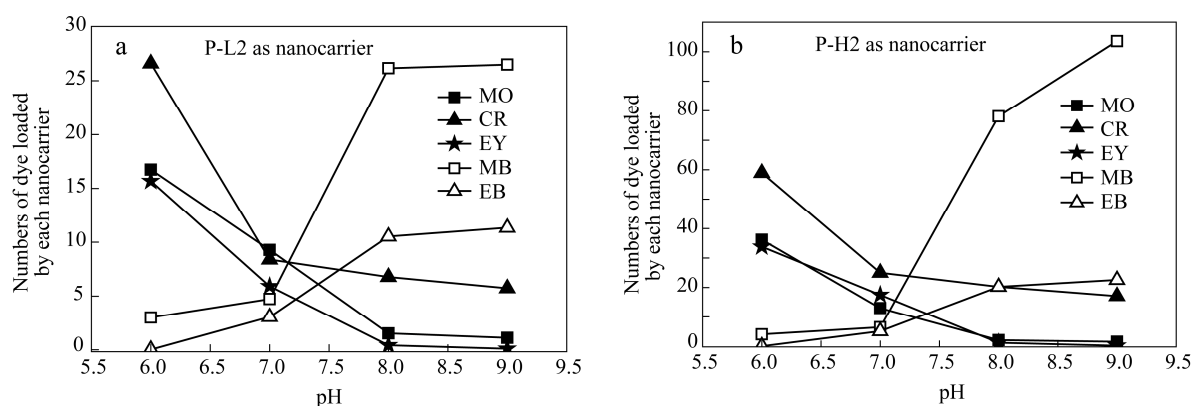


Fig. 3 Influence of pH on the dye loading capacity of (a) HPA-*b*-PCL with a lower molecular weight HPA core (P-L2) and (b) HPA-*b*-PCL with a higher molecular weight HPA core (P-H2)

whereas the efficient accommodation for cationic dyes should be performed at a basic environment. The comparison between Fig. 3(a) and Fig. 3(b) demonstrates that enlarging the polar HPA core size is an effective way to enhance the dye loading capacities of the star nanocarriers when the length of the hydrophobic PCL shell is similar.

Both cationic and anionic dyes can be loaded by HPA-*b*-PCL nanocarriers, however, it is unclear where these dyes are located in the HPA-*b*-PCL nanocarriers. For verification of the location of the anionic and cationic guests, multiarm star copolymers with PCL as arm and the neutral hyperbranched polyglycerol (PG) as core were prepared according to literature^[39] and used as reference. Unlike HPA-*b*-PCL stars, PG-*b*-PCL stars could not load the anionic dyes at any pH condition. Therefore, it can be deduced that the anionic guests loaded by HPA-*b*-PCL nanocarriers must be located in the HPA core. It is reasonable since at acidic environment the polyamine groups of HPA core can be partially or completely quaternized, leading to strong ionic interaction with the anionic dyes. After being contacted with basic solution, the quaternized ammonium ions are transformed back into the neutral state, and the strong ionic interaction between HPA-*b*-PCL and anionic dyes disappears. Therefore, at basic conditions HPA-*b*-PCL nanocarriers cannot effectively accommodate anionic dyes. As for cationic dyes, it was found that PG-*b*-PCL stars could load them at basic conditions, but not at acidic conditions, and more cationic dyes were loaded when the PCL arm was longer. This implies that the PCL shell can supply the perching place for cationic guests at basic conditions. At basic conditions one of the main interactions between PCL shell and cationic guests might come from the polar interaction between the electron-donating ester carbonyl groups of PCL shell and the electron-deficient cationic groups of dyes^[47]. Since the HPA core contains many electron-donating amide carbonyl and amine groups at basic conditions, it can be deduced that the HPA core is also the perching place for cationic dyes. After being contacted with acidic solution, the lone-pair electrons of carbonyls and amine groups are partially or completely protonated, which results in the weakening of their electron-donating properties. Therefore, at acidic condition HPA-*b*-PCL nanocarriers cannot effectively accommodate cationic dyes.

The effect of PCL arm length on the dye loading capacities of the HPA-*b*-PCL nanocarriers was further studied. From Fig. 4 it can be seen that when the polar core size is fixed, the influence of PCL arm length on the anionic and cationic dye loading capacity is different. As for cationic dyes, the increase of PCL arm length is accompanied with an improvement of the guest loading capacities. Whereas for anionic dyes, the guest loading capacity increases when the $DP_{(arm)}$ increases from around 8.5 to 14, but it decreases when the $DP_{(arm)}$ increases to around 20. The obvious different influences of arm length on the accommodation of cationic and anionic dyes are explained tentatively as follows. At least two factors should be considered for the influence of PCL length variation on the anionic guest loading behavior of HPA-*b*-PCL stars. One is the variation of core-shell polarity difference, and the other is the steric hindrance effect of PCL arms. Normally increasing the core-shell polarity

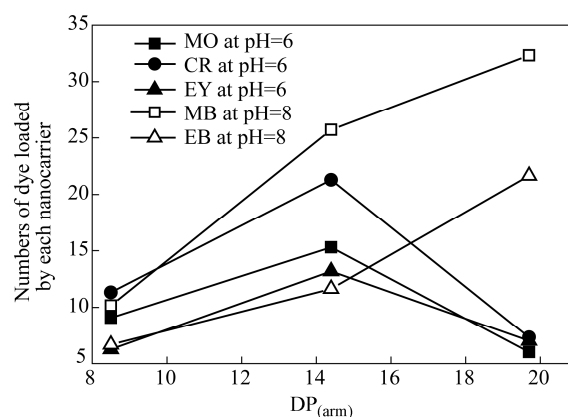


Fig. 4 Influence of PCL arm length on the dye loading capacity of HPA-*b*-PCL nanocarriers (HPA-L as the core)

difference of nanocarrier favors the increase of its guest encapsulation^[48, 49]. When the HPA core of HPA-*b*-PCL stars is fixed, the increase of PCL arm length decreases the shell polarity, *i.e.*, the core-shell polarity difference becomes larger at higher values of $DP_{n(\text{arm})}$. Therefore, increasing the arm length favors the increase of guest-loading capacity. Whereas increasing the PCL arm length also raises the difficulty of the guest molecules to access the HPA core, thus is harmful for the guest load. Such two opposite factors decide that maximal loading capacity for anionic dyes is reached at certain suitable PCL arm length. As for cationic dyes, PCL arms can supply perching places for them. Therefore, increasing the PCL arm length favors to load more cationic dyes.

DLS was used to measure the state of HPA-*b*-PCL stars in chloroform before and after accommodating the dyes (Fig. S4 in the Supporting Information). Before accommodating the dye guests, the DLS profiles of HPA-*b*-PCL stars derived from HPA-L show the unimodal distribution and the average diameters of these stars in chloroform are less than 10 nm (Fig. S4A in the Supporting Information), indicating that HPA-*b*-PCL stars derived from HPA-L in chloroform are in the unimolecular state. As for the HPA-*b*-PCL stars derived from HPA-H, their DLS profiles show bimodal distribution (Fig. S4B in the Supporting Information). The average diameters of the small-sized portion and the big-sized portion are around 10 nm and 100 nm, respectively, implying that both unimolecules and aggregates exist in the chloroform solution of HPA-*b*-PCL stars derived from HPA-H. Comparing the sizes of these unimolecular HPA-*b*-PCL stars, it can be known that the size of HPA-*b*-PCL stars can be increased by increasing the size of HPA core and the length of the PCL arm. After accommodating the anionic dyes, the average size of the unimolecular HPA-*b*-PCL star does not change obviously, but aggregates are prone to be formed (Fig. S4C in the Supporting Information). As for the HPA-*b*-PCL star loaded with the cationic dyes, the average size of the unimolecular HPA-*b*-PCL star increases obviously. The different influence of cationic and anionic dyes on the size of the unimolecular HPA-*b*-PCL star might be ascribed to their different distribution in the HPA-*b*-PCL star. The anionic dyes reside in the HPA core. Since HPA core is relatively rigid, it can only be swollen a little after loading the anionic dyes. The linear PCL arm is flexible. The accommodation of cationic dyes in the PCL domain leads to the appearance of the electrostatic repelling among different PCL chains and PCL units. Thus, the flexible PCL chains are stretched and the average size increases obviously.

The above experiments demonstrate that the obtained HPA-*b*-PCL stars can efficiently load cationic or anionic dyes at different pH environment using different sections. Therefore, in this part we explored whether HPA-*b*-PCL nanocarriers could selectively accommodate one kind of dyes at certain pH, realizing the separation of cationic and anionic dyes from their mixture. The anionic EY and the cationic MB are mixed together in water and their UV-Vis absorbance peaks can be separated well from each other (see black lines in Fig. 5). Once this aqueous EY/MB mixture is contacted with pure chloroform, a little amount of EY/MB complexes can transfer

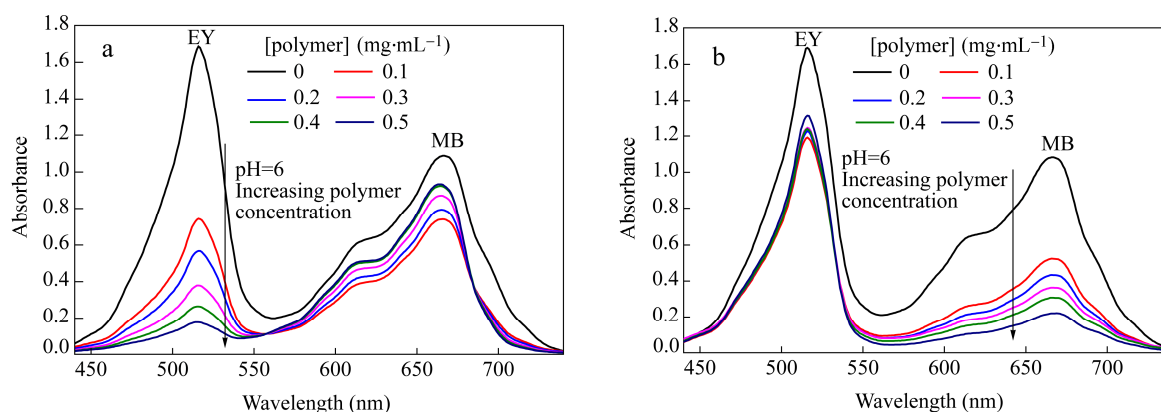


Fig. 5 UV-Vis spectra of the aqueous solution of EY/MB mixture contacted with different concentrations of HPA-*b*-PCL in chloroform at (a) pH = 6 and (b) pH = 9 (P-H2 as the sample)

into chloroform solvent. At pH = 6, with the gradual addition of HPA-*b*-PCL nanocarriers into the chloroform phase the absorbance intensity of EY in water decreases markedly, whereas the absorbance intensity of MB increases a little (Fig. 5a). This implies that with the gradual addition of HPA-*b*-PCL nanocarriers, more and more EY molecules are transferred from water into the chloroform phase. Moreover, HPA-*b*-PCL nanocarriers also capture the EY molecules from the EY/MB complexes in chloroform, leading that the freed MB molecules transfer back from chloroform phase to water phase. At pH = 9, the situation is opposite. With the gradual addition of HPA-*b*-PCL nanocarriers into the chloroform phase the absorbance intensity of MB in water decreases markedly, whereas the absorbance intensity of EY increases a little (Fig. 5b). This simple experiment verifies that the obtained HPA-*b*-PCL nanocarriers can selectively capture cationic or anionic dyes at specific pH conditions, realizing their separation from the mixture.

CONCLUSIONS

HPAs have been successfully employed as macroinitiators for the Sn(Oct)₂ catalyzed ring-opening polymerization of CL, which resulted in core-shell type multiarm star copolymers with average 115–353 PCL arms. Both the primary amines and the secondary amide groups of HPAs could initiate the CL polymerization, and the initiation efficiency increased when more CL monomers were fed. The melting and crystallization temperatures, fusion and crystallization enthalpy and the degree of crystallinity of the HPA-*b*-PCL stars increased as the PCL arm length increased. The resulting HPA-*b*-PCL stars could be used as nanocarriers to efficiently accommodate anionic dyes using its HPA core at acidic conditions, while load cationic dyes using both HPA core and PCL shell at basic conditions. Furthermore, the novel nanocarriers could selectively accommodate the anionic EY or the cationic MB from the EY/MB mixture when pH was controlled to be 6 or 9, realizing their separation.

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