Xanthate-Mediated Polymerization of Styrene on Hyperbranched Polyethylenimine: Synthesis, Characterization, and Guest-Encapsulating Property

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ABSTRACT: Hyperbranched polyethylenimine (HPEI) is a highly polar, multifunctional polymer bearing active amines throughout its globular structure. In this article, the amino protons, which were incompatible with living radical polymerization techniques, were alkylated with propylene oxide, leading to tertiary amines and hydroxyls, and part of the hydroxyl groups were further transformed into xanthate groups. The HPEI-xanthate could mediate the polymerization of styrene, leading to a star-like, multiarm amphiphilic polymer. It was found that the polymerization was a hybrid of living and conventional radical processes. The resulting amphiphilic, core-shell-structured polymer existed as a unimolecular micelle (UIM) in apolar solvent and could irreversibly encapsulate water-soluble anionic dyes. At high pH, the encapsulated dyes could be partly released. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3702–3709, 2009

Key words: hyperbranched polyethylenimine; nanocapsule; xanthate; core-shell structure

INTRODUCTION

Unimolecular (inverted) micelle (UIM)[1] has evoked much interest in the field of supramolecular chemistry.[2–4] Encapsulation by UIM can favor the solubilization, protection, and sequestering of guest objects. The noncovalent incorporation can be driven by topological trapping,[5] H-bonding interaction,[6] hydrophobic interaction,[7] electrostatic interaction,[8] metal–ligand interactions,[9–11] π–π stack,[12] or the combination of them. Voit and coworkers[13] showed that a core-shell-structured amphiphile composed of a shell of dodecyl and a core of hyperbranched polyester could form blends with polyethylene and polypropylene, and the polar core could accommodate water-soluble dye while the apolar shell could interact with the polymer matrix, which led to homogeneous distribution of the dye and easy colorization of the polymer matrix. Similarly, in principle, an amphiphilic macromolecular nanocapsule with a shell of polystyrene should conveniently form blends with polystyrene, and with a polar core, the nanocapsule can encapsulate a variety of water-soluble, low, or nontoxic dyes, providing alternative means for the colorization of polystyrene.

Dendrimer or dendrimer-based UIMs[14,15] could encapsulate various guests but were tedious in synthesis, whereas UIM derived from hyperbranched polymer was more cost-effective. Hyperbranched polymer[16] is among the preferred parent compounds for the construction of UIM, and UIM derived from hyperbranched polymer has been widely used in supramolecular encapsulation of a variety of guests[6,17–20] because of their topological feature.[21] Hyperbranched polyethylenimine (HPEI) is a commercially available, hydrophilic, multifunctional polymer, with active amino protons distributed in core through shell of the globular structure and constitute a platform of a variety of chemical modifications. Core-shell amphiphiles based on HPEI were synthesized via amidation, Michael addition, quaternization or alkylation of the amino groups, and the resulting globular amphiphiles could be used as nanocapsule in host–guest chemistry.[22–28] However, to date, most of the derivatives were obtained by modification with small molecules, the drawback of such amphiphilic derivative of HPEI included their tendency to aggregate[8,23] and limited miscibility

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with polymer matrix. Usually, aggregation greatly suppresses the guest-encapsulating capacity of the host UIM and is unfavorable for the homogeneous distribution of the UIM in a polymer matrix. It was found that for some core-shell amphiphiles, increasing the shell density could suppress the tendency of aggregation, but in some cases, increase the shell density was insufficient to suppress the aggregation. Increasing the shell thickness could be an alternative way to suppress aggregation, especially when the shell was a macromolecule, where only a few reports appeared.[26,29] As far as we know, (living) radical polymerization on HPEI has not appeared.

With the advent of living radical polymerization techniques such as nitroxide-mediated polymerization (NMP),[30,31] atom transfer radical polymerization (ATRP),[32,33] polymerization controlled by reversible addition-fragmentation chain transfer (RAFT),[34] or macromolecular design via the interchange of xanthates (MADIX),[35] systematical design of the shell of a UIM becomes feasible or possible. However for HPEI, modification via living radical polymerization has never been reported, because amino proton is incompatible with living radical polymerization techniques. Zheng and Pan[36] reported RAFT polymerization on polypropylenimine (PPI) dendrimer, but the terminal amino groups had to be 100% modified to ensure a living character. In this article, we showed that by alkylation of the active amino protons with the simultaneous production of hydroxyl groups, and by further transformation of partial hydroxyl groups into RAFT/MADIX chain transfer agent, polystyrene could be introduced onto HPEI as the shell while the core retain polarity. In this way, amphiphile with polar core and apolar polystyrene shell could be obtained, such a structure was favorable for the incorporation of polar guests and interaction with polystyrene matrix. Additionally, the core was pH-responsive and thus pH triggered releasing of the guests was possible.

EXPERIMENTAL

Materials

HPEI [Aldrich, $M_n = 1 \times 10^4$, $M_w/M_n = 2.5$, degree of branch (DB) = 60%, the molar ratio of NH_2 : NH : N = 33 : 40 : 27[24]] and styrene (St) were distilled under reduced pressure to remove the inhibitors. α,α-Azobisisobutyronitrile (AIBN) (purity >99%) was purified by crystallization from methanol. CS_2, benzyl bromide, methyl orange (MO), Congo red (CR), rose Bengal (RB), and propylene oxide were all purchased from Sinopharm Chemical Reagent, with the highest purity available and used directly unless stated otherwise.

Measurements

The ^{1}H-NMR spectra were recorded on a Varian Gemini 2000 spectrometer (400 MHz), with the solvent proton signal or TMS for reference. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were determined by gel permeation chromatography (GPC) using Waters 150-C, calibrated with standard poly(styrene), eluent: tetrahydrofuran, flow rate: 1 mL/min, sample concentration: 10 mg/mL, injection volume 200 μL. Yields were measured gravimetrically. UV−vis spectra were recorded on a 760 CRT UV−vis spectrometer. Dynamic laser light scattering (DLS) spectrometer (Malvern Autosizer 4700) with a laser source of wavelength at 532 nm as light source and a CONTIN Analysis Mode was used.

Synthesis

N-Alkylation of HPEI with propylene oxide (2)

Propylene oxide (21 g, 0.36 mol) was added to a solution of HPEI (**1**, 10.5 g, 0.244 molar equiv of CH_2CH_2NH) in 45 mL of ethanol, the mixture was kept under stirring at room temperature for 2 days. The volatiles were removed under reduced pressure to yield an extremely viscous, colorless liquid (**2**) 24.6 g (100% yield based on HPEI). Dialysis (Spectro/Por, WMCO: 500) against chloroform for 24 h did not reduce the mass, indicating no small molecular contaminants in the product.

HPEI-xanthate (3)[37]

KOH (5.36 g, 95 mmol) was added to a solution of **2** (4.04 g, 40 mmol of OH) in DMSO (20 mL) under vigorous stirring at room temperature, followed by addition of CS_2 (30.4 g, 400 mmol) slowly dropwise and the system turned into red. After the addition, within 1 hour, the system was allowed stirred for another 12 h. Benzyl bromide (16.37 g, 95 mmol) was added and the mixture was kept under stirring for 48 h at room temperature. Chloroform (3 × 70 mL) was used to extract the reaction mixture, the combined chloroform layer was washed with water. The chloroform layer was separated, dried over $MgSO_4$. After removal of the inorganic salt and part of the chloroform, the residue was dropped into ether, the precipitate was collected, purified by repeat dissolution in chloroform, precipitation in diethyl ether, and was finally dried in vacuum oven. 7.36 g yellow powder (**3**) was obtained.

Polymerization of St (4)

A typical experiment at molar ratio of $[St]_0$: $[xanthate]_0$: $[AIBN]_0$ = 150 : 1 : 0.2 was carried out as

follows: a mixture of St (8.74 g, 84 mmol), **3** (0.2 g, 0.56 mmol of xanthate groups), and AIBN (18 mg, 0.112 mmol) in DMF (1.0 mL) was degassed by bubbling with N_2 for 15 min, and then the solution was charged evenly in six glass tubes under nitrogen atmosphere and the tubes were sealed by flame. The tubes were immersed in thermostatic oil bath at 60°C without stirring. After the desired time, the mixture was cooled and diluted with chloroform, followed by dropping into a large amount of ethanol (95%) and collected by centrifugation. Purification was carried out by repeating dissolution in chloroform and precipitation from ethanol, and finally dried under vacuum at 60°C for 12 h.

The theoretic molecular weight of each arm could be calculated by the following equation:

$$M_n(\text{cald}) = (\text{moles of styrene})/(\text{moles of xanthate}) \times 104 \times \text{conversion} + 125,$$

where 104 was the molar mass of St and 125 was molar mass of the end group derived from xanthate.

Cleavage of the polystyrene (PS) arm from 4

Typically, to a solution of Polymer **4** (0.02 g) in THF (3 mL), $NaBH_4$ (0.01 g) in ethanol (0.5 mL) was added, followed by stirring under sealed for 12 h. The THF was removed by evaporation, the residue was mixed with water, and the pH was adjusted to 3 with aqueous HCl. The mixture was extracted with chloroform and the organic layer was separated. The chloroform was concentrated on a rotary evaporator and dropped into 95% ethanol under stirring. The precipitate was collected, washed with ethanol, and dried in vacuum oven at 60°C.

Dye encapsulation and releasing

To learn how many MOs could be loaded in one Polymer **4**, solution samples of **4** in chloroform were prepared and exposed to different amounts of aqueous MOs, and the MOs transferred to the oil layer were detected. Typically, aqueous MO samples at a diversity of concentrations (4 mL each sample, 1×10^{-6} – 1×10^{-4} mol/L) were mixed with **4** at a specified concentration (4 mL, 1 g/L) in chloroform with vigorous shaking. Each mixture was allowed to stand aside until the biphasic mixture became clear (1–5 days) and the chloroform layer was separated for UV−vis measurement. The UV−vis absorbance was plotted against the concentration of MO, where a turning point (saturation point) would generally be found.

For the guest-releasing test, the aforementioned chloroform solution of Polymer **4**, which was saturated with MO, was exposed to alkali water (pH = 12). After vigorous shaking, followed by phase balancing, the aqueous layer was separated for UV−vis measurement.

To learn if the dye-encapsulating ability of Polymer **4** was dependent on its concentration, solution samples of Polymer **4** were prepared with concentration varied between 10^{-9} and $10^{-6}M$, and each sample was exposed to highly excessive MOs in water. The MOs transported to the oil layer were measured by UV−vis spectrometer, and the absorbance was plotted against the concentration of **4**, where a linear relationship was an indication of UIM. In case the absorbance was higher than 1 (or lower than 0.1), the chloroform solution was diluted (concentrated) until the absorbance fell within 0.1–1, and the measured absorbance value was amplified (reduced) to equivalent concentration.

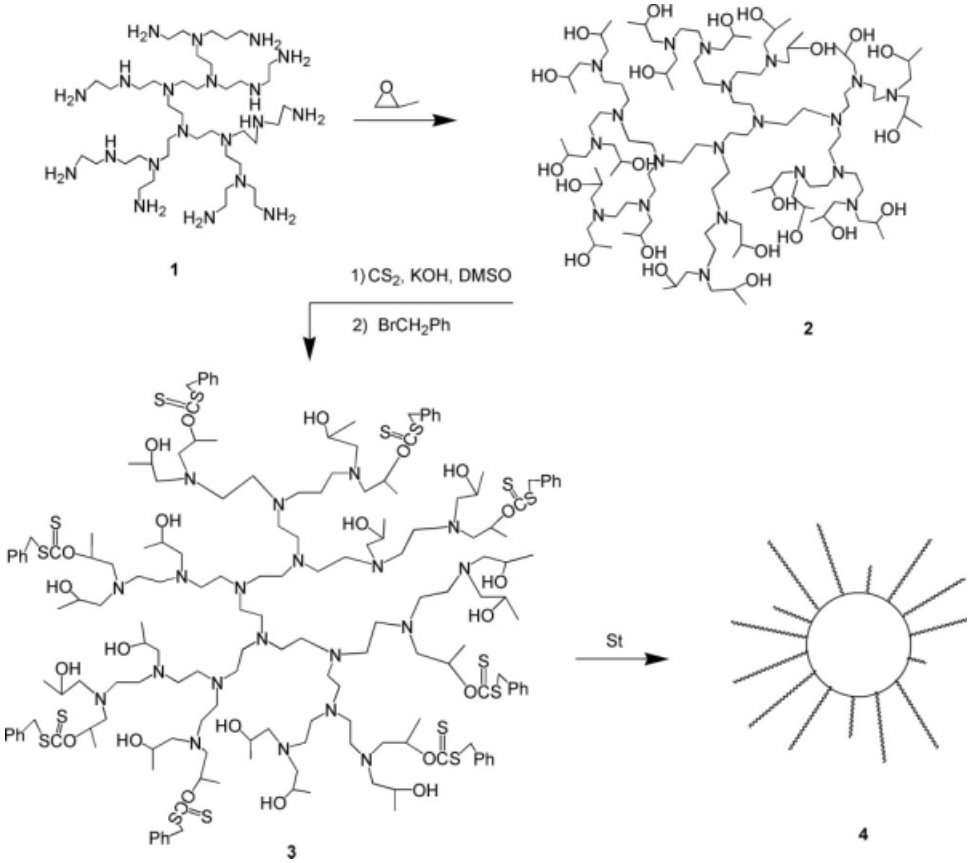
RESULTS AND DISCUSSION

Synthesis of HPEI-xanthate

To render the HPEI compatible with living radical polymerization, the amino protons of HPEI had to be 100% consumed. Although the terminal amino protons of a PPI dendrimer were successfully transformed into RAFT chain transfer agent,[36] similar transformation of all the amino protons of HPEI into RAFT chain transfer agent was unattained. It was known that an epoxy compound could efficiently transform primary or secondary amine into tertiary amine under mild condition, with the simultaneous production of hydroxyl groups, so a synthetic route was designed here, as shown in Scheme 1. The propylene oxide was selected for the complete transformation of the amino protons into alkyl.

Experimentally, a solution of HPEI was exposed to excess of propylene oxide in absolute ethanol under stirring for certain time at room temperature, removal of the excess of propylene oxide and ethanol yielded a colorless, extremely viscous liquid in a quantitative yield. ^{1}H-NMR analysis (Fig. 1) showed that the amino protons had been transformed, from $=NH$ to $=NCH_2CH(OH)CH_3$ or from $-NH_2$ to $-N[CH_2CH(OH)CH_3]_2$.

The signal at 4.46 ppm was due to OH groups (this signal disappeared from the ^{1}H-NMR spectra in the presence of D_2O), a doublet peak at 1.0 ppm was due to the methyl ($-CH_3$), and the singlet peak at 3.62 ppm was due to the methine proton adjacent to OH. The intensity of the three peaks was exactly 1 : 3 : 1, indicating any of them resulted from the ring opening of propylene oxide. Because of the existence of dense population of OH groups (242 OHs per polymer, cf. Scheme 1), the modified polymer **2** was soluble only in polar solvents and H-bonding complementary solvents such as dimethylformamide



Scheme 1 Outline of the synthesis of core-shell amphiphile.

(DMF), dimethyl sulfoxide (DMSO), water, pyridine, methanol, and ethanol.

Partial OH groups of Compound **2** were further derived into xanthate in DMSO with CS_2 and benzyl bromide in the presence of KOH.[37] Here, complete transformation of the OH groups to xanthates was not desired mainly for two reasons: (1) the residual OH groups favored the polarity of the core, and (2) high congestion of xanthate groups on a globe scaffold was unfavorable for the control of the polymerization.[38] After partial OH groups transformed into xanthate of $OC(=S)SCH_2Ph$, which were nonpolar groups, the solubility of Compound **3** in apolar solvents was somewhat enhanced. The polymer was purified by repeated dissolution in chloroform/precipitation in ether, the purified polymer was subjected to ^{1}H-NMR measurement. Figure 2 shows that after the modification, a feature peak due to the phenyl group appeared at 7.0–8.0 ppm.

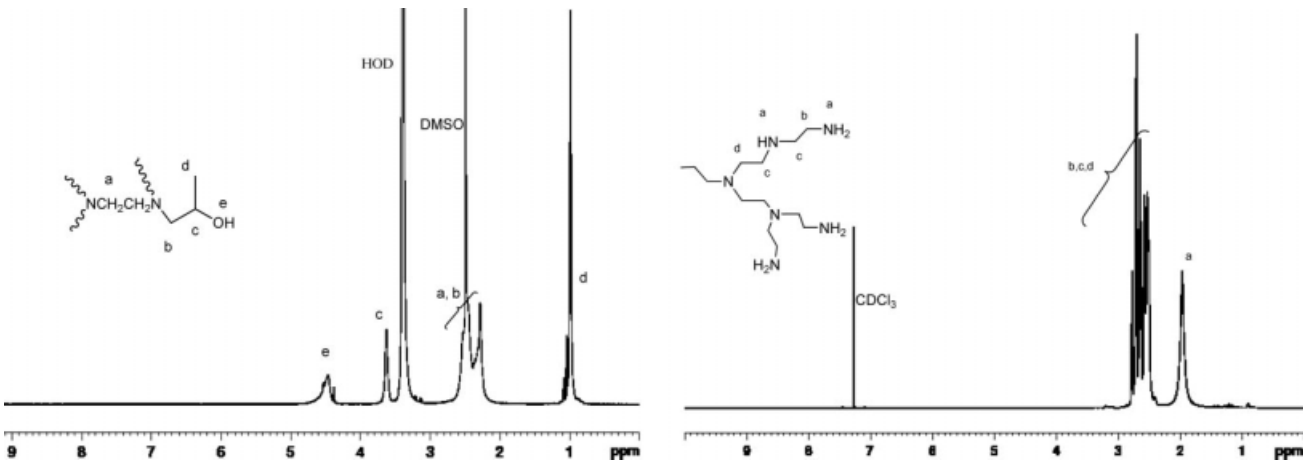


Figure 1 ^{1}H-NMR of HPEI (right, $CDCl_3$) and alkylated HPEI **2** (left, DMSO-d_6).

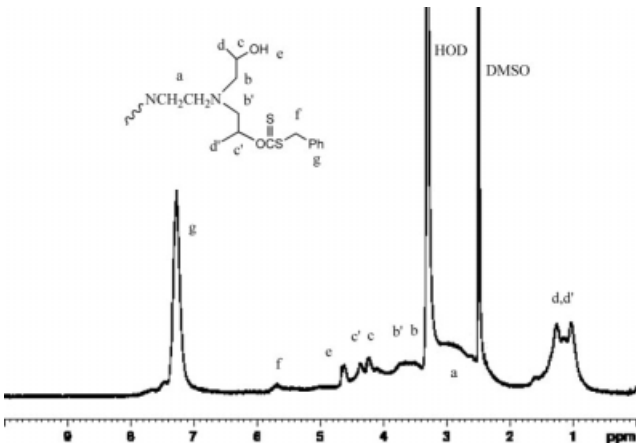


Figure 2 ^{1}H-NMR of xanthate-functionalized compound **3** (DMSO-d_6).

To detect the exact ratio of OH groups being modified, integration comparison of this peak with the methyl group (around 1.0 ppm) was carried out, it could be derived that 54% of the OH groups were transformed into xanthate groups (141 xanthate groups per polymer).

FTIR spectrum also supported the expected structure of Compound **3** (Fig. 3). The peak at 3428 cm^{-1} was due to the OH group (it could not be due to water because there was hardly any absorption at 1650 cm^{-1}, which was characteristic of water), the absorption at 3023, 1600, 1497, 1450 cm^{-1} were due to phenyl group. The peaks at 760 and 700 cm^{-1} were characteristic of monosubstituted phenyl.

Controlled polymerization of styrene

It was known that the xanthate group like Compound **3** was RAFT/MADIX mediator for the living radical polymerization of unconjugated vinyl monomers, single xanthate with similar structure had been successfully used for the living radical polymerization of vinyl acetate[35,37] and *N*-vinyl amides,[39,40] but was less efficient to control the polymerization of conjugated monomers such as styrene and acrylic monomers. Compound **3** was designed for the controlled polymerization of vinyl acetate, but it showed a limited solubility in the latter. Addition of DMF led to a homogeneous solution, but no trace of polymerization was found for the solution within 3 days heating at 60°C in the presence of AIBN, similar inhibition was observed previously.[37] Compound **3** showed a better solubility in styrene, but a small amount of DMF was still needed to ensure complete dissolution. Polymerization of styrene was found feasible, leading to Polymer **4**. Figure 4 shows that the polymerization proceeded rather quickly, 87% of yield was obtained for 24-h reaction (see the "Experimental" section for polymerization conditions), higher yield seemed to become difficult under current conditions. The plot of $\ln[M]_0/[M]$ versus time deviated from linear relationship, indicating that the polymerization was not strictly living.

Direct GPC measurement of any of the as-prepared star-like polymer in THF showed monomodal traces. Figure 5 shows the GPC trace of one sample of the as-prepared star-polymer. The molecular weight was much lower than the calculated one because of column affinity, which was due to the amino groups in the core of the star-polymer. The star-polymer was prepared via the Z-approach [the multifunctional macromolecular core as Z group of the chain transfer agent of ZC(=S)SR].[41–44] The merit of Z-approach was that star–star coupling could be avoided, whereas the drawback was that linear chain–chain coupling was enhanced due to steric congestion, especially at high conversion or high density of the chain transfer agent. That is, a

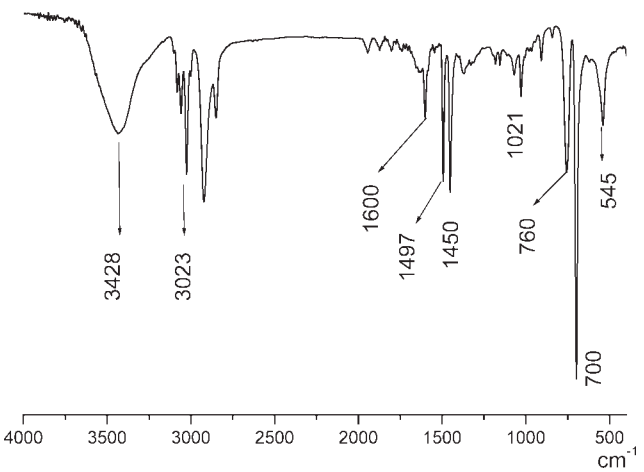


Figure 3 FTIR spectrum of Compound **3** (cf. Scheme 1).

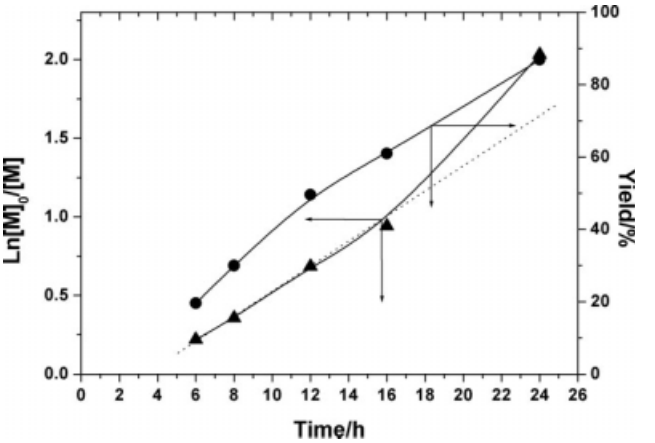


Figure 4 Dependence of polymer yield and $\ln[M]_0/[M]$ on reaction time. Polymerization condition: $[St]_0$: [xanthate]$_0$: $[AIBN]_0$ = 150 : 1 : 0.2, 60°C.

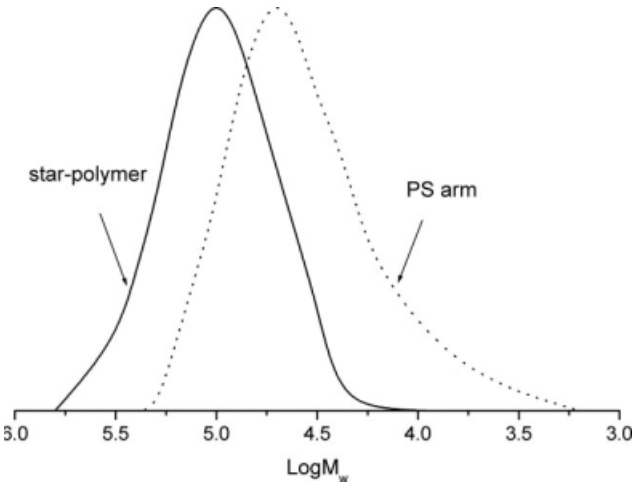


Figure 5 GPC traces of Compound **4** before (star-polymer) and after (PS arm) the cleavage of the PS arm (the polymer was obtained with 87% of monomer conversion, see Fig. 4).

peak due to the linear chain–chain irreversible coupling did not appear most probably because of its minor contribution and overlapping with the main polymer trace. On the other hand, the PS arm could be cleaved from the star-like polymer because the xanthate group was base-labile. Employing $NaBH_4$ could break the arms. To separate the PS arm, the mixture was adjusted to acidic, the naked core was protonized and became hydrophilic and moved to the water phase, thus the PS arm could be separated by extraction with chloroform. GPC analysis showed that the molecular weight distribution of PS arm was wide, typically within 1.95–2.60, and the measured molecular weight was much higher than the calculated value (Fig. 6), but the molecular weight increased with the conversion of monomer, indicating that the polymerization was controlled. It is known that the xanthate is not an ideal mediator for

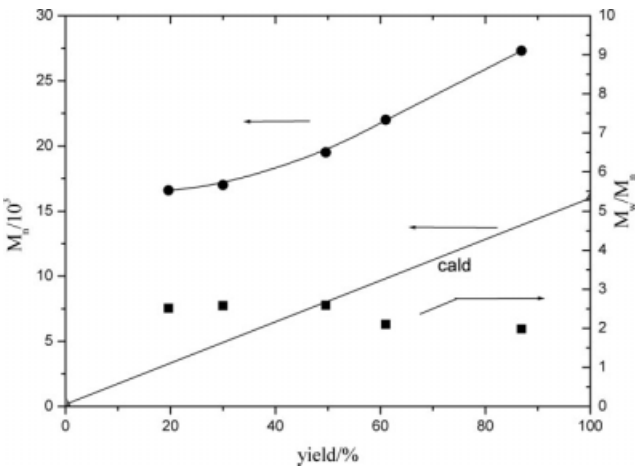


Figure 6 Dependence of M_n and M_w/M_n on polymer yield (for polymerization condition see Fig. 4).

the RAFT polymerization of styrene for its low chain transfer ability, which usually leads to wide molecular weight distribution. On the other hand, most probably not all xanthate groups took part in the growth simultaneously due to the dense xanthate groups on the HPEI surface. To prove this hypothesis, *O*-ethyl-*S*-benzyl-xanthate[39] was synthesized and employed as RAFT/MADIX mediator for the polymerization of styrene. It was found that the polymerization was similarly not well controlled (data not shown): the molecular weight was higher than the calculated one and the molecular weight distribution was typically within 2.5–1.8, but with the conversion of monomer, the molecular weight evolved close to the calculated one. Different from the *O*-ethyl-*S*-benzyl-xanthate, Compound **3** led to polymer with molecular weight far from the calculated one even at high conversion of monomer. One possible reason was that not all the xanthate groups took part in the polymerization because of the shell congestion.[38]

Encapsulation and release of water-soluble dyes

Amphiphilic macromolecular nanocapsule derived from HPEI could encapsulate a number of anionic dyes and could undergo stimuli-triggered guest release, but the guest-encapsulating ability was greatly suppressed at high concentration because of

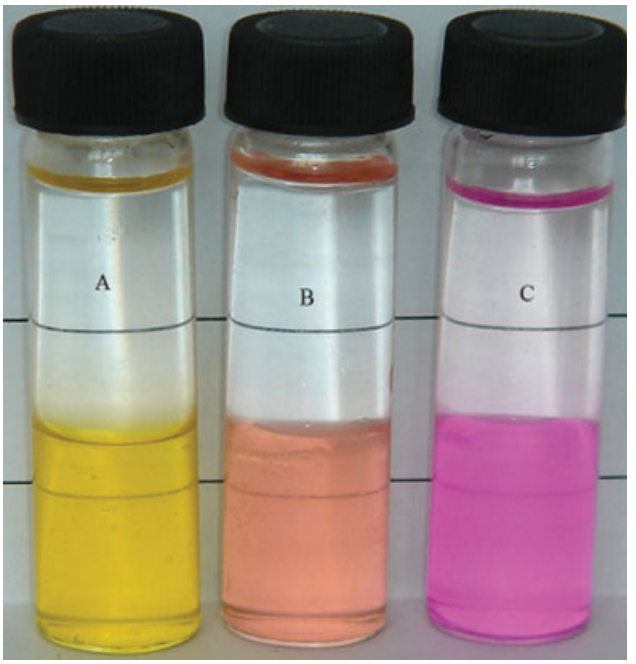


Figure 7 Upon the addition of Compound **4** [M_n (cald) = 4.46×10^5)] to the biphasic system of water/chloroform, the chloroform-insoluble dyes of MO (A), CR (B), and RB (C) completely moved from the water phase to the chloroform phase. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

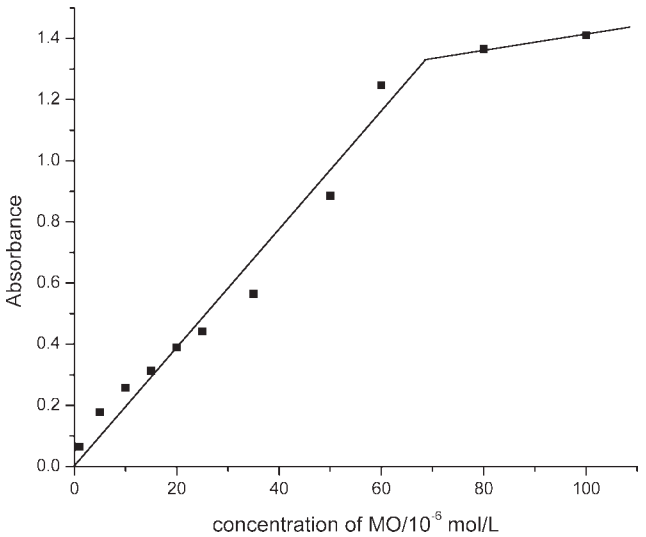


Figure 8 MOs transferred to the oil by a chloroform solution of Polymer **4** [M_n (cald) = 4.46 × 10^5] at 1 g/L in dependence of the concentration of MO. The data were obtained from UV/vis measurement.

the aggregation of the nanocapsule.[8,23] In this article, tertiary amines and the hydroxyls populated in the core of Compound **4** rendered the core polar, which was favorable for the accommodation of hydrophilic guests, and because the amino groups could be reversibly protonized, pH stimuli-triggered release was possible in principle. Figure 7 showed that anionic, water-soluble MO, CR, and RB could be encapsulated by Compound **4** via liquid–liquid extraction.

Figure 8 shows the encapsulating behavior under neutral or near neutral condition by Compound **4** [M_n(cald) = 4.46 × 10^5] was a two-stage process, in the first stage, irreversible encapsulation occurred, whereas in the second stage, reversible encapsulation occurred. The turning point was regarded as the saturation point, where a saturated encapsulating ability was derived to be 0.022 g MO/1 g polymer or 30 MOs/**4**. The relatively high encapsulating capacity should partly be attributed to the topology, in contrast, it had been shown that a linear polymer hardly encapsulated dyes.[21,25] Although the encapsulation was irreversible before saturation, releasing of dyes was found at high pH. At pH 12, 60% of the MO could be released into water, for RB, it was 31%, whereas for CR, no release was observed. However, upon shaking with aqueous HCl, the CR-saturated chloroform layer became blue (CR becomes blue under acidic condition), indicating that the CR in the core was still accessible to the hydrogen ions. The test of another Compound **4** [M_n(cald) = 5.6 × 10^5] showed an encapsulating capacity of 32 MOs per polymer, which was the same as the previous sample within the measurement error. This result suggested that the shell layer did not accommodate MOs, all the MOs were entrapped in the core.

To learn whether Compound **4** existed in the form of cluster or in the form of UIM, the encapsulating ability was tested upon changing the concentration of Compound **4**. It was known that if a host existed as UIM, its encapsulating ability would be independent of its concentration in the solution,[45–47] whereas if the host existed in cluster or aggregate, the encapsulating ability was dependent on the concentration.[8,23] In the latter case, the encapsulating ability generally would be enhanced with dilution because of higher swelling of the host and better accessibility to the guest. The encapsulating ability of Compound **4** [M_n(cald) = 5.6 × 10^5] at various concentrations is shown in Figure 9.

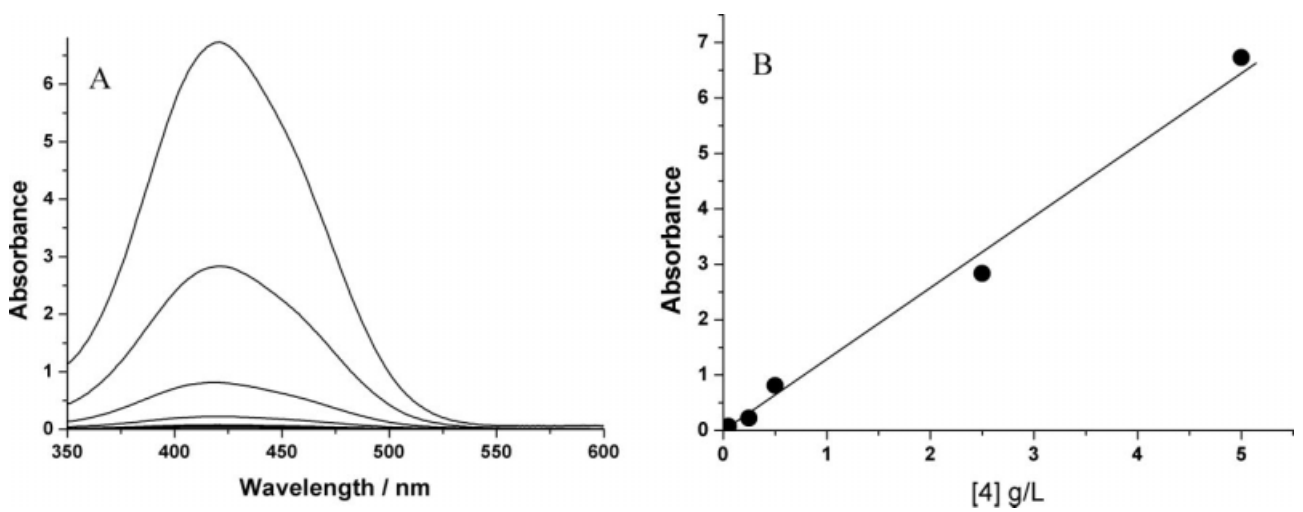


Figure 9 UV/vis spectra of MOs transferred to the oil by Polymer **4** [M_n (cald) = 5.6 × 10^5] in dependence of the concentration of **4** in chloroform (A) and the plot of absorbance of MOs transferred to the oil versus the concentration of **4** (B).

In which, a linear relationship was found with the concentration varied between 0.005 and 5 g/L (or 8.9×10^{-9} – $8.9 \times 10^{-6}M$), indicating that the host polymer was a unimolecular container. Moreover, dynamic light scattering experiment did not detect any large particles in the chloroform solution of **4**, also supporting the polymer existed as molecular container.

CONCLUSIONS

The primary and secondary amine of HPEI could be completely transformed into tertiary amine, along with the production of the hydroxyl groups. Part of the hydroxyl groups could be further transformed into xanthate groups, and the xanthate-functionalized HPEI could be used to prepare star polymer via the Z-approach route. Vinyl acetate was inhibited by the xanthate, styrene could be polymerized but the polymerization was a hybrid of living and conventional radical process. The resulting macromolecular nanocapsule in solution existed in form of UIM and could encapsulate water-soluble anionic dyes, and upon the stimulus of pH, the dyes could be partly released.

References

1. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Johnson, A. L.; Behera, R. K. Angew Chem Int Ed 1991, 30, 1176.
2. Weener, J. W.; Baars, M. W. P. L.; Meijer, E. W. In Dendrimers and Other Dendritic Polymers; Frechet, J. M. J.; Tomalia, D. A., Eds.; Wiley: West Sussex, 2001; Chapter 16, pp 387–424.
3. Baars, M. W. P. L.; Meijer, E. W. Dendrimers II Top Curr Chem 2000, 210, 131.
4. Zimmerman, S. C.; Lawless, L. J. Dendrimers IV Top Curr Chem 2001, 210, 951.
5. Maciejewski, M. J Macromol Sci Chem 1982, 17, 689.
6. Sunder, A.; Kramer, M.; Hanselmann, R.; Mulhaupt, R.; Frey, H. Angew Chem Int Ed 1999, 38, 3552.
7. Newkome, G. R.; Moorefield, C. N.; Baker, G. R.; Saunders, M. J.; Grossman, S. H. Angew Chem Int Ed 1991, 30, 1178.
8. Wan, D. C.; Pu, H. T.; Cai, X. Y. Macromolecules 2008, 41, 7787.
9. Scott, R. W. J.; Wilson, O. M.; Crooks, R. M. J Phys Chem B 2005, 109, 692.
10. Wan, D. C.; Pu, H. T. Mater Lett 2007, 61, 3404.
11. Wan, D. C.; Fu, Q.; Huang, J. L. J Appl Polym Sci 2006, 102, 3679.
12. Hawker, C. J.; Wooley, K. L.; Frechet, J. M. J. J Chem Soc Perkin Trans 1 1993, 1287.
13. Schmaljohann, D.; Potschke, P.; Hassler, R.; Voit, B. I.; Froehling, P. E.; Mostert, B.; Loontjens, J. A. Macromolecules 1999, 32, 6333.
14. Jansen, J. F. G. A.; Meijer, E. W.; de Brabender van den Berg, E. M. M. J Am Chem Soc 1995, 117, 4417.
15. Jansen, J. F. G. A.; de Brabender van den Berg, E. M. M.; Meijer, E. W. Science 1995, 266, 1226.
16. Gao, C.; Yan, D. Prog Polym Sci 2004, 29, 183.
17. Kitajyo, Y.; Kinugawa, Y.; Tamaki, M.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. Macromolecules 2007, 40, 9318.
18. Kitajyo, Y.; Nawa, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Kaga, H.; Satoh, T.; Kakuchi, T. Polymer 2007, 48, 4683.
19. Kitajyo, Y.; Imai, T.; Sakai, Y.; Tamaki, M.; Tani, H.; Takahashi, K.; Narumi, A.; Kaga, H.; Kaneko, N.; Satoh, T.; Kakuchi, T. Polymer 2007, 48, 1237.
20. Satoh, T.; Tamaki, M.; Kitajyo, Y.; Maeda, T.; Ishihara, H.; Imai, T.; Kaga, H.; Kakuchi, T. J Polym Sci Part A: Polym Chem 2006, 44, 406.
21. Stiriba, S. E.; Kautz, H.; Frey, H. J Am Chem Soc 2002, 124, 9698.
22. Stumbe, J. F.; Turk, H.; Krause, S.; Komp, A.; Delineau, L.; Prokhorova, S.; Kautz, H.; Haag, R. Angew Chem Int Ed 2002, 41, 4252.
23. Kramer, M.; Kopaczynska, M.; Krause, S.; Haag, R. J Polym Sci Part A: Polym Chem 2007, 45, 2287.
24. Liu, H.; Chen, Y.; Zhu, D.; Shen, Z.; Stiriba, S. E. React Funct Polym 2007, 67, 383.
25. Chen, Y.; Shen, Z.; Pastor-Perez, L.; Frey, H.; Stiriba, S. E. Macromolecules 2005, 38, 227.
26. Liu, H.; Shen, Z.; Stiriba, S. E.; Chen, Y.; Zhang, W.; Wei, L. J Polym Sci Part A: Polym Chem 2006, 44, 4165.
27. Xu, S. J.; Luo, Y.; Haag, R. Macromol Rapid Commun 2008, 29, 171.
28. Cao, X. L.; Li, Z. Q.; Song, X. W.; Cui, X. H.; Cao, P. F.; Liu, H. J.; Cheng, F.; Chen, Y. Eur Polym J 2008, 44, 1060.
29. Wan, D. C.; Yuan, J. J.; Pu, H. T. Macromolecules 2009, 42, 1533.
30. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Macromolecules 1993, 26, 2987.
31. Hawker, C. J.; Bosman, A. W.; Harth, E. Chem Rev 2001, 101, 3661.
32. Matyjaszewski, K.; Xia, J. Chem Rev 2001, 101, 2921.
33. Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689.
34. Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, K.; Tam, P. T. L.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Macromolecules 1998, 31, 5559.
35. Destarac, M.; Bzducha, W.; Taton, D.; Gauthier-Gillaizeau, I.; Zard, S. Z. Macromol Rapid Commun 2002, 23, 1049.
36. Zheng, G.; Pan, C. Y. Macromolecules 2005, 38, 6841.
37. Bernard, J.; Favier, A.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. Polymer 2006, 47, 1073.
38. Wan, D. C.; Pu, H. T. J Appl Polym Sci 2007, 106, 3688.
39. Wan, D. C.; Satoh, K.; Kamigaito, M.; Okamoto, Y. Macromolecules 2005, 38, 10397.
40. Wan, D. C.; Zhou, Q.; Pu, H. T.; Yang, G. J. J Polym Sci Part A: Polym Chem 2008, 46, 3756.
41. Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. Macromolecules 2003, 36, 1505.
42. Dureault, A.; Taton, D.; Destarac, M.; Leising, F.; Gnanou, Y. Macromolecules 2004, 37, 5513.
43. Barner-Kowollik, C.; Davis, T. P.; Stenzel, M. H. Aust J Chem 2006, 59, 719.
44. Barner, L.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. Macromol Rapid Commun 2007, 28, 539.
45. Newkome, G. R.; Young, J. K.; Baker, G. R.; Potter, R. L.; Audoly, L.; Cooper, D.; Weis, C. D.; Morris, K.; Johnson, C. S. Macromolecules 1993, 26, 2394.
46. Hawker, C. J.; Frechet, J. M. J. J Chem Soc Perkin Trans 1 1992, 2459.
47. Hawker, C. J.; Chu, F. K. Macromolecules 1996, 29, 4370.