

Synthesis and Characterization of Hyperbranched Cationic Polyelectrolytes via Aqueous Self-Condensing Atom Transfer Radical Polymerization

Jun Gao,^{1,2} Guangqun Zhai,^{1,2} Yan Song,¹ Bibiao Jiang¹

¹Section of Soft Matter and Macromolecular Science, Key Laboratory of Polymeric Materials of Changzhou City, Department of Materials Science and Engineering, Jiangsu Polytechnic University, Changzhou 213164, China

²Key Laboratory of Molecular Engineering of Polymers, Ministry of Education, Fudan University, Shanghai 200433, China

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ABSTRACT: The hyperbranched cationic polyelectrolytes (PDMEAB) were directly prepared via the CuBr/ligand-catalyzed (ligand = 2,2'-bipyridine or pentamethyldiethylenetriamine) aqueous self-condensing atom transfer radical polymerization (SCATRP) of a novel inimer, *N,N*-dimethyl-*N*-(2-methacryloyloxy)ethyl-*N*-(2-bromoisobutyryloxy)ethyl ammonium bromide (DMEAB). Elemental analysis and nuclear magnetic resonance (NMR) spectroscopy confirmed the structure of DMEAB. The hyperbranched architecture and number-average degree of polymerization (DP_n) of the PDMEAB was studied by ¹H- and ¹³C-NMR. The kinetic results suggested that the DP_n of the hyperbranched PDMEAB grew gradually in the ini-

tial stage and exponentially in the later stage. The differential scanning calorimetry (DSC) showed that the glass transition temperature of the hyperbranched PDMEAB was much lower than that of the linear analogue. The solution rheometry showed that the aqueous PDMEAB solutions approximately underwent a Newtonian behavior and their shear viscosity maintained almost constant upon the addition of NaCl because of the spherical conformations of the hyperbranched cationic polyelectrolytes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2522–2534, 2009

Key words: hyperbranched cationic polyelectrolyte; inimer; self-condensing atom transfer radical polymerization

INTRODUCTION

Polyelectrolytes represent a class of polymers, which could dissociate into polyions with counterions surrounded in aqueous media.¹ The most investigated polyelectrolytes embrace poly[(2-methacryloyloxy)ethyl trimethyl ammonium chloride],² sodium polyacrylate,^{3,4} sodium polystyrenesulfonate⁵ and so on. Polyelectrolytes were widely used as superabsorbents, flocculants, and viscosifiers.⁶ Although intensively studied, polyelectrolytes still remained as one of the least understood state of condensed matter.^{6–8} For example, the molecular weight (MW) and molecular weight distribution (MWD) of polyelectrolytes cannot be steadily determined by gel-permeation chromatography because the polyelectrolyte chains assume a more complex conformation, depending

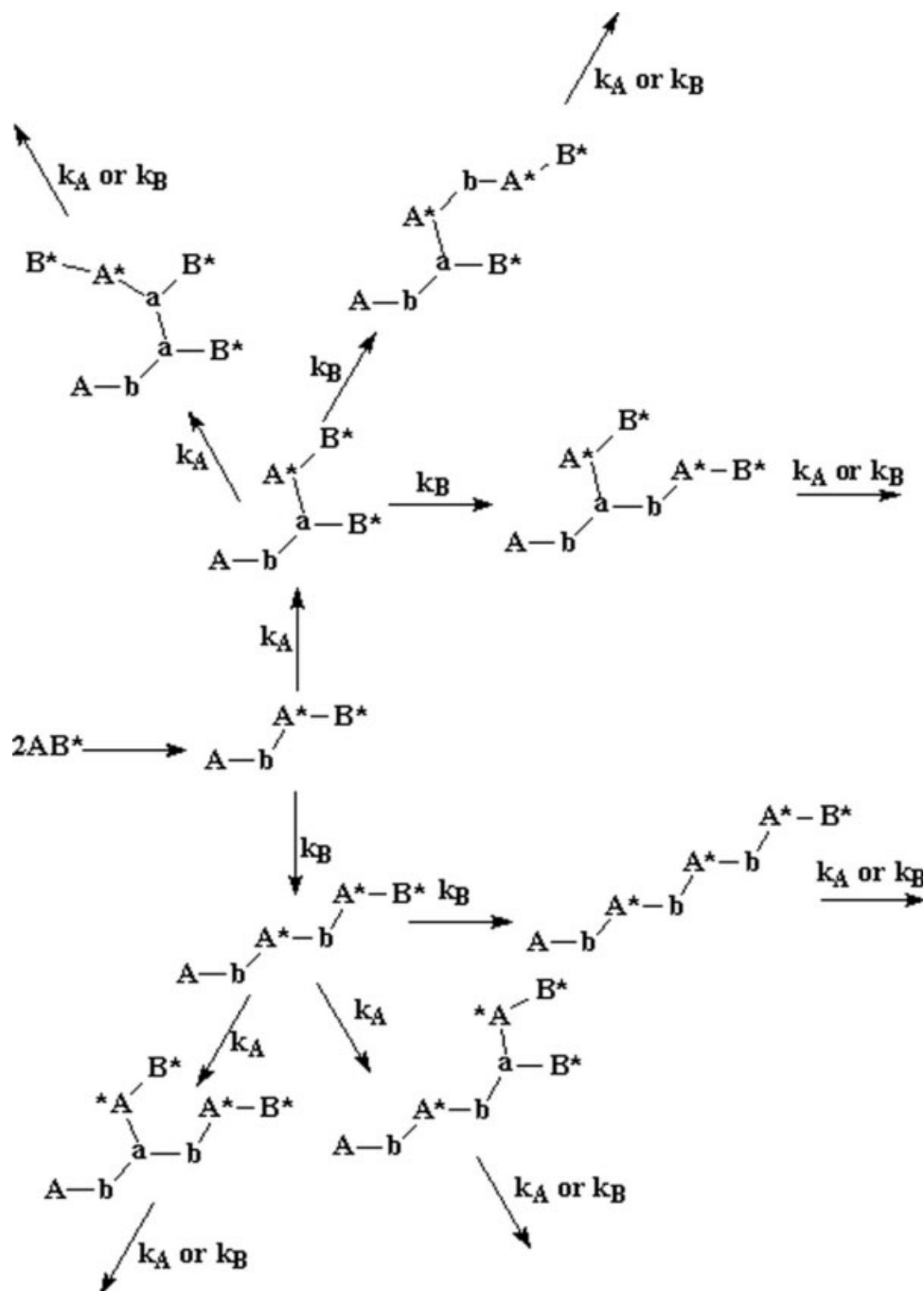
on the concentration, pH, and charge density, when dissolved in aqueous solutions.⁶

As early as 1952, Flory pointed out that the polycondensation of AB_x -type monomers would result in soluble “highly branched” polymers.⁹ Hyperbranched polymers received more attention since Webster and Kim reported that the autopolycondensation of (3,5-dibromophenyl)boronic acid or 1,3,5-tribromobenzene gave rise to soluble hyperbranched polyphenylenes.^{10,11} However, such a method was only applicable for a very limited number of precisely designed monomers, few of which were commercially available. In 1995, Fréchet proposed a novel strategy, i.e., the self-condensing vinyl polymerization (SCVP), to create hyperbranched polymers from specially tailor-made inimers (AB^*), where *A* and B^* typically represent a $C=C$ double bond and an initiator functionality, respectively.¹² The process of SCVP to produce hyperbranched macromolecules was illustrated in Scheme 1. In addition to the AB_x autopolycondensation, SCVP rendered it possible to prepare hyperbranched polymers from vinylic monomers. Furthermore, the SCVP mechanism has extended to include carbocationic, carbanionic, oxyanionic, group transfer, nitroxide-mediated, atom transfer radical, and reversible

Correspondence to: G. Q. Zhai (zhai_gq@em.jpu.edu.cn).

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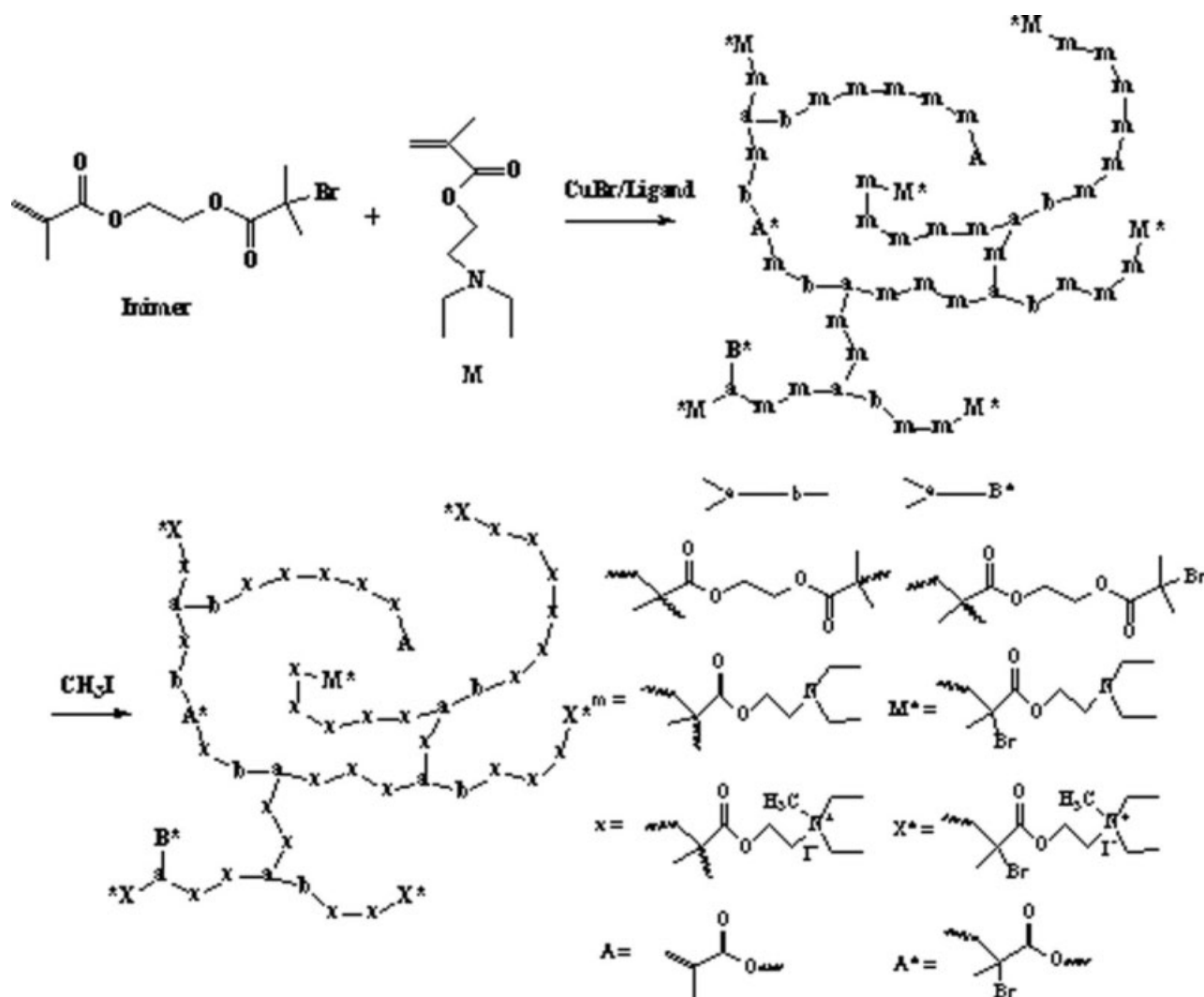


Scheme 1 General route to hyperbranched polymers via SCVP of AB* inimers.

addition-fragmentation chain transfer polymerization.^{13–15} The preparation and structure-property relationship of hyperbranched polystyrenes (PSs) and poly(meth)acrylates of different MW, MWD, and degree of branching (DB) have been studied in details.^{13–17} The results confirmed that the branched polymers assumed a more compact conformation, a lower melt viscosity and a less degree of chain entanglement because of the spherical topology.^{13–17}

Several groups have reported on highly branched or hyperbranched polyelectrolytes. Laschewsky pre-

pared a series of cationic polyelectrolytes (polysoaps) via the polycondensation of several AB₂-type monomers, which in common contained one C–Br group and two tertiary amine moieties.¹⁸ However, these monomers were prepared through a laborious multi-step process and the number-average degree of polymerization (DP_n) of the cationic polyelectrolytes obtained were generally <50.¹⁸ In comparison with the linear analogues, those hyperbranched cationic polyelectrolytes exhibited a reduced viscosifying effect.¹⁸ BASF and Hyperpolymers commercialized



Scheme 2 Synthetic route to highly branched cationic polyelectrolytes (by Müller AHE).

the hyperbranched polyethyleneimine (PEI) via the self-condensing proton-transfer polymerization of ethylene imine. Such PEIs as well as their quaternized derivatives have been well studied in various applications.^{19–23}

Recently, Müller has proposed a well-established approach to produce highly branched anionic and cationic polyelectrolytes via a two-step procedure: self-condensing atom transfer radical copolymerization (SCATRCPC) of a (meth)acrylate inimer with isobutyl acrylate and 2-(diethylamino)ethyl methacrylate (DEAEMA), followed by alcoholysis or quaternization to produce highly branched anionic and cationic polyelectrolytes, respectively, as shown in Scheme 2.^{24,25} Because it used electrostatically neutral inimers and ionizable comonomers to generate branching sites and charged units, respectively, a high dosage of inimers would improve the DB and adversely reduce the charge density. On the contrary, using more comonomers could enhance the charge density but decrease the DB accordingly.

Thus, it seems logically impossible to achieve both a high DB and a high charge density simultaneously via the above Müller's method. Besides, the direct SCATRCPC of those inimers with ionic monomers such as (2-methacryloyloxy)ethyl trimethyl ammonium chloride and sodium styrenesulfonate was also difficult because those inimers were virtually water-insoluble.^{13,15}

To overcome the aforementioned difficulties, we proposed an innovative and efficient strategy, i.e., the direct self-condensing atom transfer radical polymerization (SCATRP) of positively charged inimers for the preparation of highly cationic polyelectrolytes. Herein, we designed a novel inimer, *N,N*-dimethyl-*N*-(2-methacryloyloxy)ethyl-*N*-(2-bromoisobutyryloxy)ethyl ammonium bromide (DMEAB), which consisted of the (2-bromoisobutyryloxy)ethyl moiety for the chain initiation, (2-methacryloyloxy)ethyl moiety for the chain addition and ammonium bromide to impart the water solubility. In this article, we reported the preparation of the

hyperbranched PDMEAB via the CuBr/ligand-catalyzed (ligand = 2,2'-bipyridine or pentamethyldiethylenetriamine) aqueous SCATRP. Besides, the physical properties of the hyperbranched PDMEAB, in comparison with the linear counterparts, were also studied. Such a strategy could also be applied to other monomers such as vinylpyridine and *N,N*-dimethylaminoethyl acrylate in preparing hyperbranched cationic polyelectrolytes.

EXPERIMENTAL SECTIONS

Materials

N,N-dimethylaminoethyl methacrylate (DMAEMA) was purchased from Xinyu Fine Chemical Co., Wuxi, China; 2-bromoethanol was purchased from Shanghai Bangcheng Chemical Co., Shanghai. Acrylic acid (AAc), CuBr, 2,2'-bipyridine (bPy), ammonium peroxy sulfate (APS) were from Shanghai Chemical Reagent Co, Shanghai. CuBr were purified by stirring in acetic acid, washing with ethanol, and then dried in vacuum at 70°C. Thionyl chloride, petamethyldiethyltriamine (PMDETA), and other reagents were used as received.

Synthesis of *N,N*-Dimethyl-*N*-(2-methacryloyloxy)ethyl-*N*-(2-bromoisobutyryloxy)ethyl ammonium bromide

α -bromoisobutyric acid (16.70 g, 100 mmol) and thionyl chloride (13.09 g, 110 mmol) were added into a flask and sealed to react at 70°C for 24 h to prepare α -bromoisobutyric acid chloride, which was added dropwise into a flask containing 2-bromoethanol (11.88 g, 95 mmol). After a 24-h-reaction at 70°C, the intermediate, 2-bromoethyl bromoisobutyrate (BEBiB), was washed using water several times. Saturated aqueous NaHCO₃ solution was added to adjust the pH to about seven. Because it has a specific gravity larger than that of water and is almost water insoluble, the slightly brown liquid, BEBiB, could be easily separated from the aqueous mixture (yield: ~ 90%). For the quaternization, crude DMAEMA (17.27 g, 110 mmol), BEBiB (28.40 g, 100 mmol), and THF (100 mL) were added into a 250-mL flask to react at room temperature for about 36 h under the mild stirring until a large amount of white and fine powders precipitated from the solutions. The powders, DMEAB, were filtered and dried in vacuum at room temperature for 24 h (yield: ~ 80–85%).

Aqueous SCATRP of DMEAB (hyperbranched PDMEAB)

A representative SCATRP of DMEAB was specified as follows: DMEAB (4.31 g, 10 mmol), CuBr (14.4 mg, 0.1 mmol), PMDETA (34.6 mg, 0.2 mmol), and

solvent (8 mL, H₂O/ethanol or H₂O/THF, 1 : 1 v/v) were added into a 50-mL round-bottom flask equipped with a magnetic stir bar. The flask was cycled between vacuum and nitrogen five times to remove the oxygen, and then the mixture was sealed and allowed to react at 90°C under mild stirring. The aliquots were collected from the mixture at different time intervals, and precipitated in excessive acetone. After recovery from acetone, the polymer was washed using 3 × 3 mL acetone, and then dried at 80°C for 8 h, leading to brown powders (yield: ~ 50–70%), which were highly hygroscopic. The experimental details were summarized in Table I.

Conventional radical polymerization of DMEAB and AAc (linear PDMEAB and linear NaPAAC)

For the preparation of the linear PDMEAB, DMEAB (10 g, 23.2 mmol), APS (0.01 g, 0.044 mmol), and deionized water (20 mL) were added into a 100-mL round-bottom flask equipped with a magnetic bar. The flask was sealed to reaction under the mild stirring at 60°C for 24 h. The PDMEAB was precipitated in acetone, washed with acetone three times to remove the unreacted monomer, and then dried at 100°C. For the preparation of the linear NaPAAC, acrylic acid (10.0 g) was 65% neutralized by aqueous NaOH solution in a flask, which was thermostated by an ice-water bath at 0°C to prevent AAc from the thermal autopolymerization. APS (0.05 g) and a magnetic bar were added. The flask was sealed to react at 70°C for 12 h. The NaPAAC was precipitated from ethanol and washed using ethanol three times, then dried at 100°C about 12 h.

Structural characterization

Nuclear magnetic resonance (¹H- and ¹³C-NMR) spectroscopy was carried out on a Bruker 300 NMR spectrometer and a Bruker DMX 500M NMR spectrometer, respectively, using CDCl₃ or D₂O as the solvent. The elemental analysis of DMEAB was performed on a Vario ELIII Elemental Analyzer at Department of Chemistry, Fudan University, Shanghai, China. Glass transition temperature (*T*_g) of the polymers was analyzed on a Perkin-Elmer Pyris-1 differential scanning calorimeter within the range of 50–200°C at a heating rate of 10°C/min and the N₂ flow rate was fixed at 10 mL/min. The differential refractive indices (dn/dc values) of the aqueous PDMEAB solutions were measured on a Wyatt Optilab[®] REX differential refractometer ($\lambda = 690$ nm) and NaNO₃ was added to adjust the ionic strength of the aqueous solutions. The rheometry of the aqueous PDMEAB or NaPAAC solutions was carried out on an Anton Paar Physica MCR 301 rheometer under the coaxial cylinder mode, with the

TABLE I
NMR Results of the Hyperbranched PDMEAB

Entry number	[DMEAB]/[CuBr]/[Ligand]	Ligand	Temp (°C)	Time (h)	Solvent	DP _n	EB
1	100/1/2	PMDETA	70	12	H ₂ O/Ethanol	9	0.63
2	100/1/2	PMDETA	90	12	H ₂ O/Ethanol	35	0.43
3	100/1/2	PMDETA	90	12	H ₂ O/DMF	2	0.67
4	100/1/2	PMDETA	90	12	H ₂ O/THF	25	0.43
5	100/0.5/1	PMDETA	90	16	H ₂ O/Ethanol	86	0.56
6	100/1/2	PMDETA	90	16	H ₂ O/Ethanol	125	0.41
7	100/1/2	bPy	90	12	H ₂ O/Ethanol	33	0.39

shear rate from 0.1 to 3000 s⁻¹ at 25°C. The concentration of all the solutions was fixed at 3 g/L.

RESULTS AND DISCUSSION

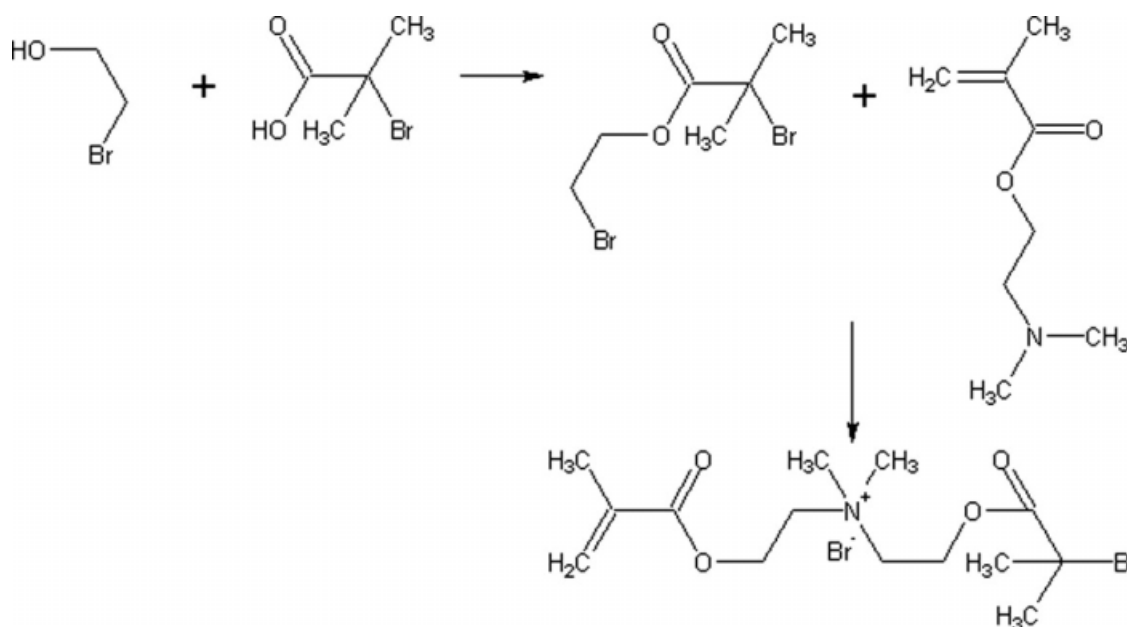
Molecular design and synthesis of DMEAB

Several groups have designed and exploited a large variety of inimers to obtain hyperbranched (co)polymers via SCVP, including (meth)acrylates,¹³⁻¹⁵ styrenics,^{13-15,26} and maleimide.²⁷ As far as we were aware, none of them was water soluble or electrostatically charged. We conceived that a charged moiety, such as ammonium, pyridinium, and imidazolium could impart the water solubility to the inimers, and furthermore, the SCVP of such positively charged inimers could directly result in the hyperbranched cationic polyelectrolytes. Because widely involved in both ATRP and cationic polyelectrolytes, vinylpyridine,^{28,29} DMAEMA,^{3,30} or *N,N*-dimethylaminoethyl acrylate³¹⁻³³ might function as the precursor to the positively charged inimer via the quaternization with BEBiB (or other

analogues). However, vinylpyridine was not selected because of its acute toxicity. On the other hand, to achieve hyperbranched architecture, B* ought to be structurally similar to A to some extent (see Scheme 1), e.g., bromoisobutyrate versus methacrylate, 2-bromopropionate versus acrylate and halophenyl versus styrene or vinylpyridine, giving rise to almost equal reactivity.^{14,17} On the basis of the structure of BEBiB, DMAEMA was chosen in our study.

Herein, we designed and synthesized the first positively charged inimer, DMEAB, which consisted of the (2-bromoisobutyryloxy)ethyl moiety for the chain initiation, (2-methacryloyloxy)ethyl moiety for the chain propagation and ammonium bromide to impart the water solubility, respectively. The synthetic route to DMEAB was illustrated in Scheme 3. Because of the steric hindrance, the reaction between tertiary C—Br and tertiary amine moieties was negligible, whereas the primary C—Br bond quaternized DMAEMA to give rise to the DMEAB.

The chemical composition and structure of DMEAB were analyzed by elemental analysis and



Scheme 3 Synthetic route to DMEAB.

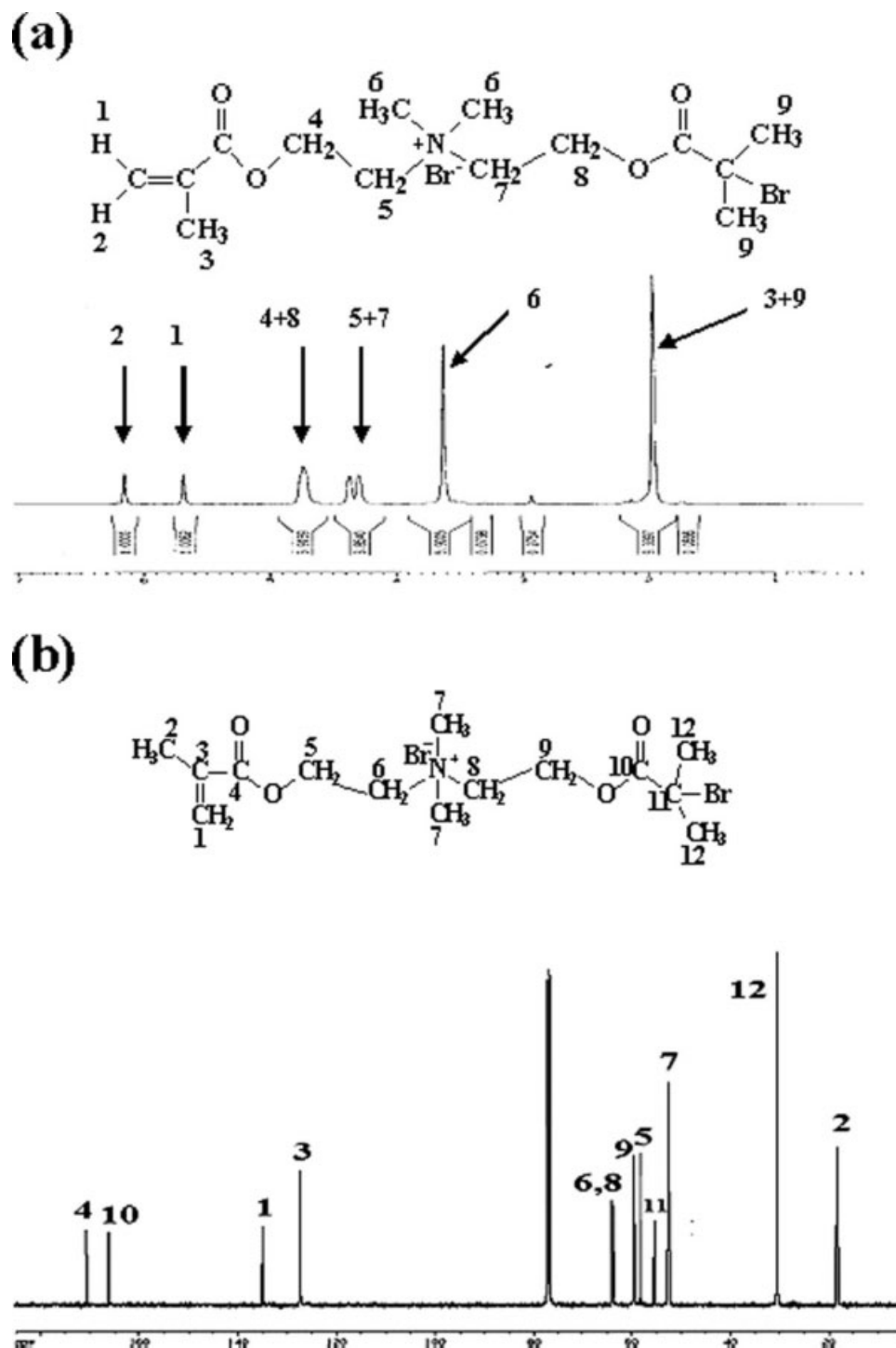
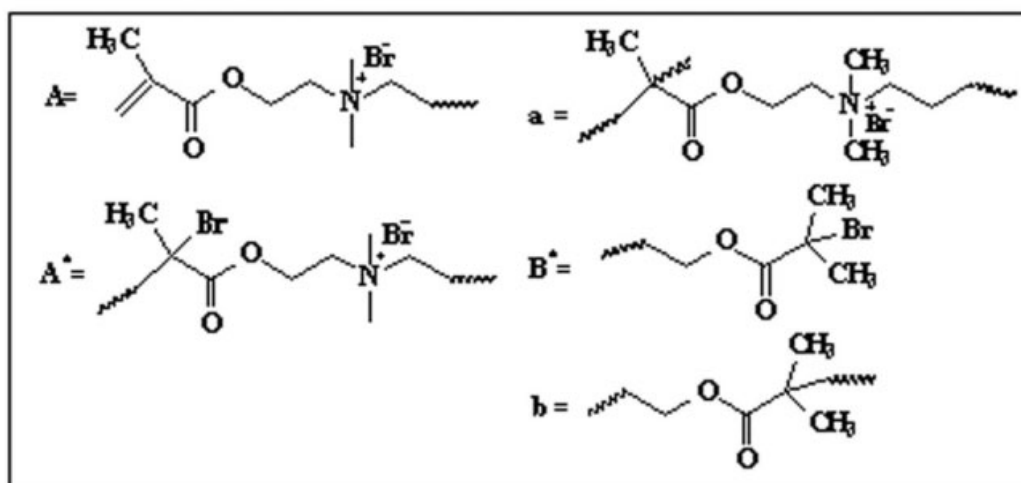
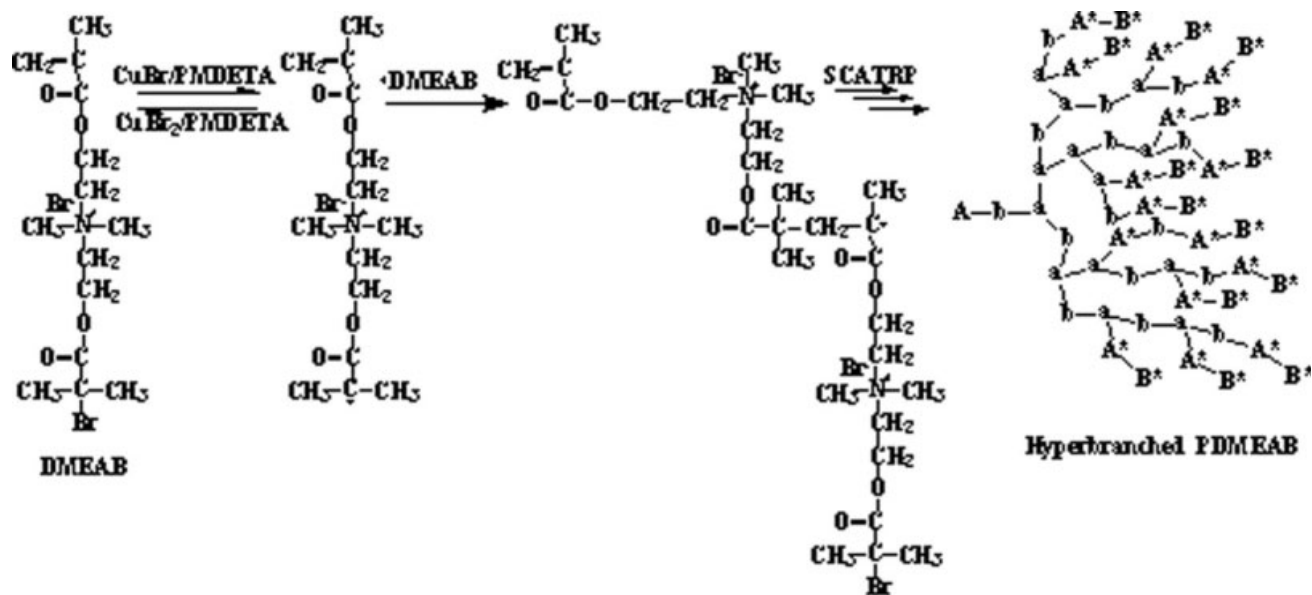


Figure 1 (a) $^1\text{H-NMR}$ and (b) $^{13}\text{C-NMR}$ spectra of DMEAB in CDCl_3 .

NMR. The elemental analysis result showed the composition of DMEAB was as follows: Calcd. C 38.98, H 5.81, N 3.25; Found C 40.82, H 5.87, N 3.22. Figure 1(a) shows the $^1\text{H-NMR}$ spectrum of DMEAB. The peak at δ 3.6 ppm was assigned to the $-\text{N}^+(\text{CH}_3)_2$ moiety, with that at δ 1.9 ppm ascribed to the protons of other methyl groups. The peaks at δ 4.3–4.4, 4.7, and 5.7–6.2 ppm were attributed to the $-\text{O}-\text{CH}_2-\text{CH}_2-$, $-\text{O}-\text{CH}_2-\text{CH}_2-$, and $\text{CH}_2=$ moi-

eties, respectively. The ratio of the corresponding peak integrals was determined to be about 5.9 : 9.3 : 3.9 : 3.9 : 2, close to the theoretical value of 6 : 9 : 4 : 4 : 2, indicating a good purity. Figure 1(b) shows the $^{13}\text{C-NMR}$ spectrum of DMEAB. The peaks at δ 127–135 ppm were associated with the $\text{CH}_2=$ species, and those at δ 170–172 ppm resulted from the $-\text{COO}-$ species. These results confirmed that DMEAB had a structure as anticipated Scheme 3.



Scheme 4 Synthetic route to hyperbranched cationic polyelectrolytes via SCATRP of DMEAB.

Aqueous SCATRP of DMEAB

After the synthesis and purification, the solubility of DMEAB in various solvents was briefly examined. Because of the hydrophobic effects of (2-bromoisobutyryloxy)ethyl and (2-methacryloyloxy)ethyl moieties, the solubility in pure water was about 0.1–0.2 g/mL at room temperature, but it was much enhanced in H₂O/ethanol, H₂O/THF, and H₂O/DMF (1 : 1, v/v). Thus, the SCATRP of DMEAB was conducted in these aqueous mixtures using CuBr/ligand (ligand = bPy or PMDETA) as the catalyst, as illustrated in Scheme 4.

Effect of solvent

The SCATRP of DMEAB was initially carried out in H₂O/DMF under the catalysis of CuBr/bPy or CuBr/PMDETA, and the reaction temperature was

varied from 50 to 90°C. However, no considerable viscosification was observed even after a 24-h-polymerization at 90°C. The powders recovered from the reacting mixture were characterized by ¹H-NMR. The result indicated that the SCATRP of DMEAB failed to proceed as expected. Such a result might be attributed to the competitive coordination of CuBr to DMF.³⁴

The control experiments were also performed in H₂O/ethanol or H₂O/THF at different temperatures. In general, significant viscosification of the polymerizing mixtures was unambiguously observed, suggesting the occurrence of the SCATRP. On the other hand, the products collected from the reacting mixtures were characterized by ¹H-NMR and the corresponding results were summarized in Table I. It was easy to note that the SCATRP of DMEAB could steadily proceed in both H₂O/ethanol and H₂O/

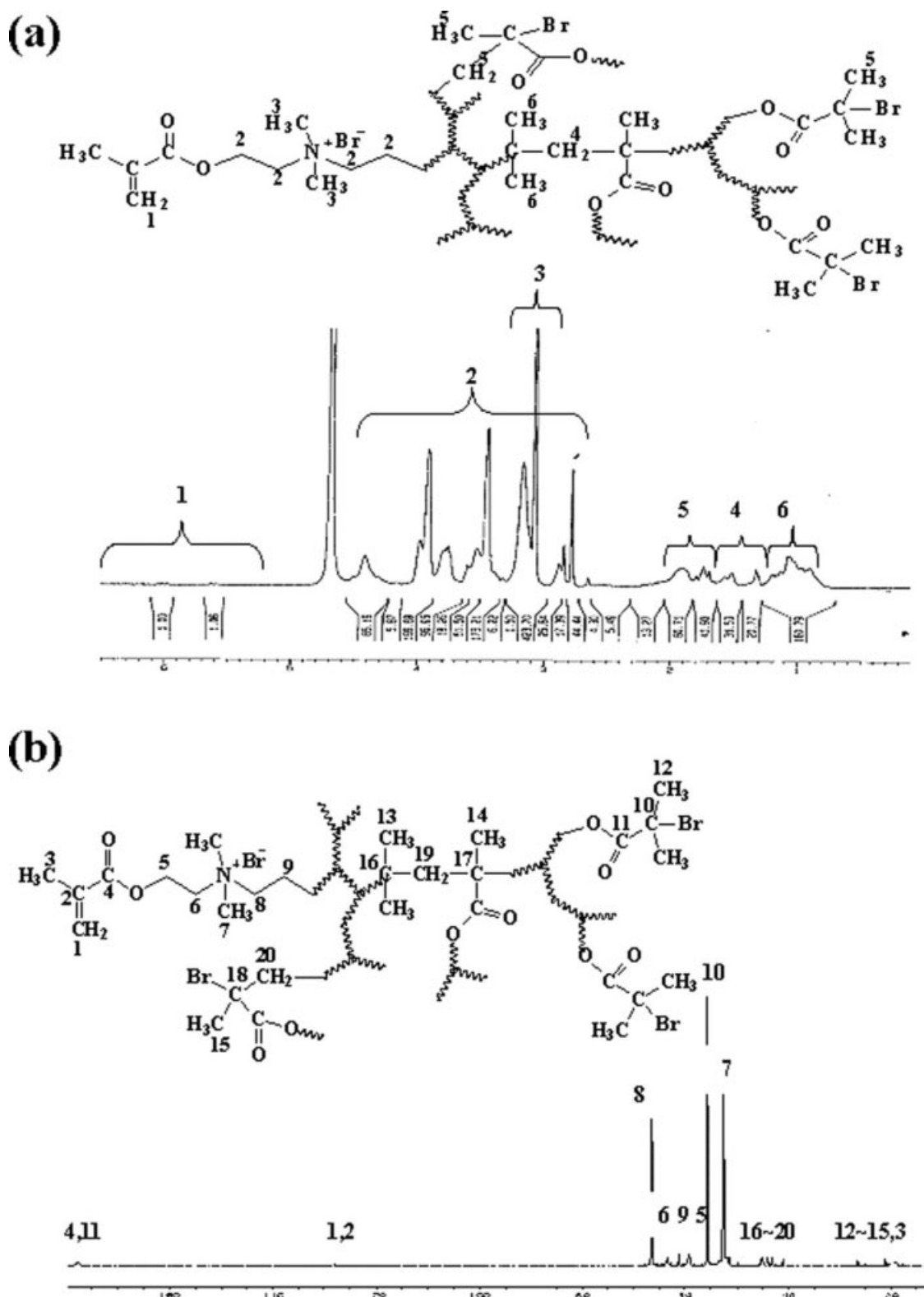


Figure 2 (a) ¹H-NMR and (b) ¹³C-NMR spectra of the hyperbranched PDMEAB.

THF to produce high-MW PDMEAB (the MW determination would be discussed later). As a result, it was inferred that H₂O/ethanol and H₂O/THF were the appropriate solvents for the SCATRP of DMEAB (Table I).

Structure of PDMEAB *via* aqueous SCATRP

The CuBr/bPy-catalyzed SCATRP of DMEAB was conducted in H₂O/ethanol at 90°C, and the [DMEAB] : [CuBr] : [bPy] ratio was fixed at 100 : 1 : 2. After the reaction and polymer recovery, the

TABLE II
Assignment to Structural Elements of the Corresponding Regions of the $^1\text{H-NMR}$ Spectra of Hyperbranched PDMEAB

Region	Peak assignment	Region	Peak assignment
1		4	
2		5	
3		6	

structure of the so-obtained PDMEAB (MW, MWD, and DB, etc.) was tentatively analyzed by NMR spectroscopy and aqueous gel-permeation chromatography.

Figure 2(a) shows the $^1\text{H-NMR}$ spectrum of a typical PDMEAB prepared via the CuBr/bPy-catalyzed SCATRP of DMEAB in $\text{H}_2\text{O}/\text{ethanol}$. Because the structure of the hyperbranched PDMEAB macromolecules was rather complicated, the peak assignment was tabulated in Table II.^{24,25} For the linear PDMEAB prepared via the conventional free radical polymerization in which the bromoisobutyrate moieties were not involved in the chain initiation, the integral ratio of the peaks associated with the $-\text{OOC}(\text{CH}_3)_2\text{Br}$ moiety to those associated with the $-\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2-$ moiety was about 2 : 1, similar to that of DMEAB.

However, during the course of the SCATRP of DMEAB, because the bromoisobutyryloxy moieties gradually underwent the CuBr/bPy-catalyzed redox process and transformed into the isobutyryloxy radicals, which added to the (2-methacryloyloxy)ethyl moiety for the chain propagation. Thus, the corresponding integral ratio of the peaks associated with the Region 5 to those associated with the Region 6 ought to be much lower than 2 : 1. For the $^1\text{H-NMR}$ spectrum in Figure 2(a), the ratio was estimated to be about 1 : 1.4, suggesting that most bromoisobutyryloxy moieties were involved in the chain initiation (transferred from the Region 5 to the Region 6). The appearance of Region 4 further confirmed that the bromoisobutyryloxy moieties initiated the chain prop-

agation and resulted in a hyperbranched topology.^{24,25} Figure 2(b) shows the corresponding $^{13}\text{C-NMR}$ spectrum and the peak assignment of the hyperbranched PDMEAB sample. Both the $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectroscopy confirmed that the aqueous SCATRP of DMEAB gave rise to the hyperbranched PDMEABs.

The MW, MWD, and DB of the PDMEAB were preliminarily determined by multiangle laser light scattering-gel permeation chromatography (MALLS-GPC). Because PDMEAB cannot be dissolved in THF, water was selected as the mobile phase and NaNO_3 was added to adjust the ionic strength from 0 to 0.2 mol/L. However, in most cases, the RI detector failed to give the concentration signals, and thus, we obtained only very few credible results from the aqueous MALLS-GPC measurement. Figure 3 shows the MALLS-GPC elutogram of a hyperbranched PDMEAB, which was carried out on a modular system consisting of a Postnova pump (PN1011), a mixed bead column (Polymer Laboratory, 5 μm), and a PD2100 detector system (Precision Detector, including a two-angle laser light scattering detector at 15° and 90° , a dynamic light scattering detector and a differential refractive detector), with water as eluent at a flow rate of 0.5 mL/min at 30°C .³⁵ The MALLS-GPC measurement gave a M_n of 1.72×10^5 and a M_w of 2.18×10^5 , leading to a MWD of 1.26.

We first attributed such a failure in the MALLS-GPC measurement to a very low differential refractive indices (dn/dc values) of the aqueous PDMEAB solutions. Thus, the dn/dc values of the aqueous

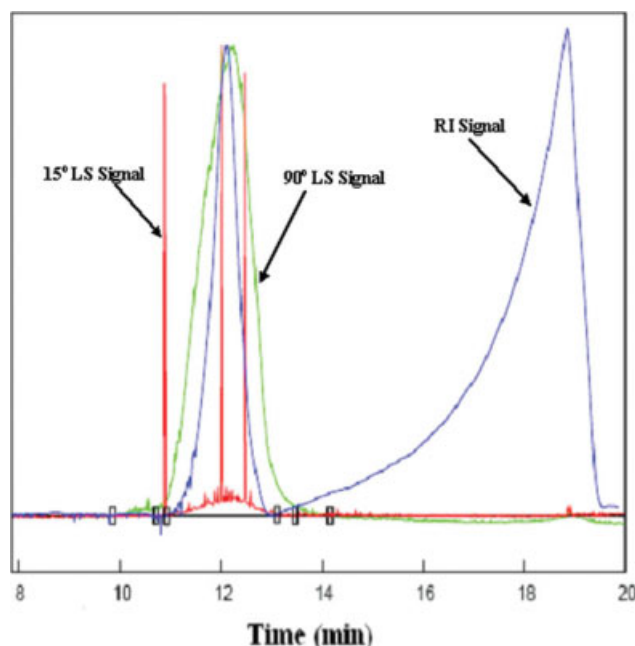


Figure 3 MALLS-GPC elutogram of the hyperbranched PDMEAB. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PDMEAB solutions with different ionic strength adjusted by NaNO_3 was measured on a Wyatt Optilab differential refractometer ($\lambda = 690 \text{ nm}$), as shown in Figure 4. It was clear that the dn/dc values under different ionic strength were generally comparable with that of PS /THF (0.185 mL/g).^{36,37} Therefore, it was believed that such a failure was due to the significant adsorption of the PDMEAB to the filler surfaces of the aqueous GPC columns, which has been well noted in literature.^{6,8,38,39}

Thus, the $^1\text{H-NMR}$ spectroscopy was also used to calculate the DP_n because it was generally accepted that each hyperbranched macromolecule prepared via SCVP contains an unreacted double bond,^{17,24–26} so the DP_n of the hyperbranched PDMEAB was estimated from the following formula:

$$\text{DP}_n = \frac{S_3}{3S_1}$$

where S_3 and S_1 represented the peak integrals of the $-\text{N}^+(\text{CH}_3)_2-$ (Region 3) and $\text{CH}_2=$ (Region 1) moieties, respectively. The Factor 3 was introduced to account for the fact that one quaternary ammonium contains six methyl protons whereas one double bond contains two.

On the other hand, for the determination of DB, although Hawker proposed several approaches,^{40,41} it remained a challenge in characterizing hyperbranched polymers. Fréchet demonstrated that a comparison between the GPC derived apparent M_w ($M_{w,\text{GPC}}$) and MALLS-derived actual M_w ($M_{w,\text{MALLS}}$)

could qualitatively confirm the hyperbranched architecture, because highly branched or hyperbranched macromolecules would have a $M_{w,\text{GPC}}$ much lower than the corresponding $M_{w,\text{MALLS}}$.¹⁷ Jiang used the $M_{w,\text{MALLS}}/M_{w,\text{GPC}}$ ratio as indicator for the DB.⁴² Matyjaszewski, in the SCATRP of 4-chloromethylstyrene to prepare highly branched PS, adopted the following equation to qualitatively estimate the extent of branching (EB)²⁶:

$$\text{EB} = \frac{b}{b + B^*}$$

where b and B^* were the integral areas of the peaks associated with the pendant protons and those associated with the protons neighboring to C-Cl , respectively. It has to be noted that because the calculation of DB was based on the linear, branched, and terminal repeat units, and the estimation of EB was based on the various protons, there would be great discrepancy between them. In this work, because we failed to carry out the MALLS-GPC measurement, and performed only $^1\text{H-NMR}$ spectroscopy to characterize the structure of the hyperbranched PDMEAB, the Matyjaszewski's method was used, where b and B^* were the integral areas of the Region 6 and 5, or S_6 and S_5 , respectively.

SCATRP kinetics

The kinetic study of the CuBr/bPy -catalyzed SCATRP of DMEAB was carried out by taking the aliquots from the polymerizing mixture at different time intervals. After precipitation in acetone and drying in vacuum, the hyperbranched PDMEAB was characterized by $^1\text{H-NMR}$ spectroscopy. Their DP_n

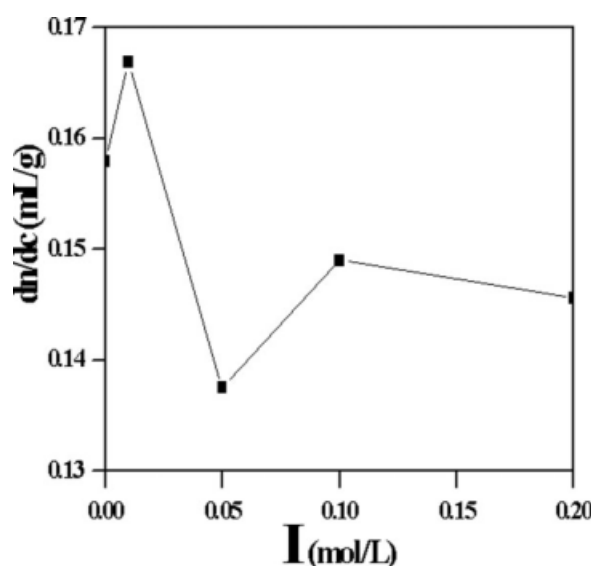


Figure 4 dn/dc values of aqueous PDMEAB solutions with different $[\text{NaNO}_3]$.

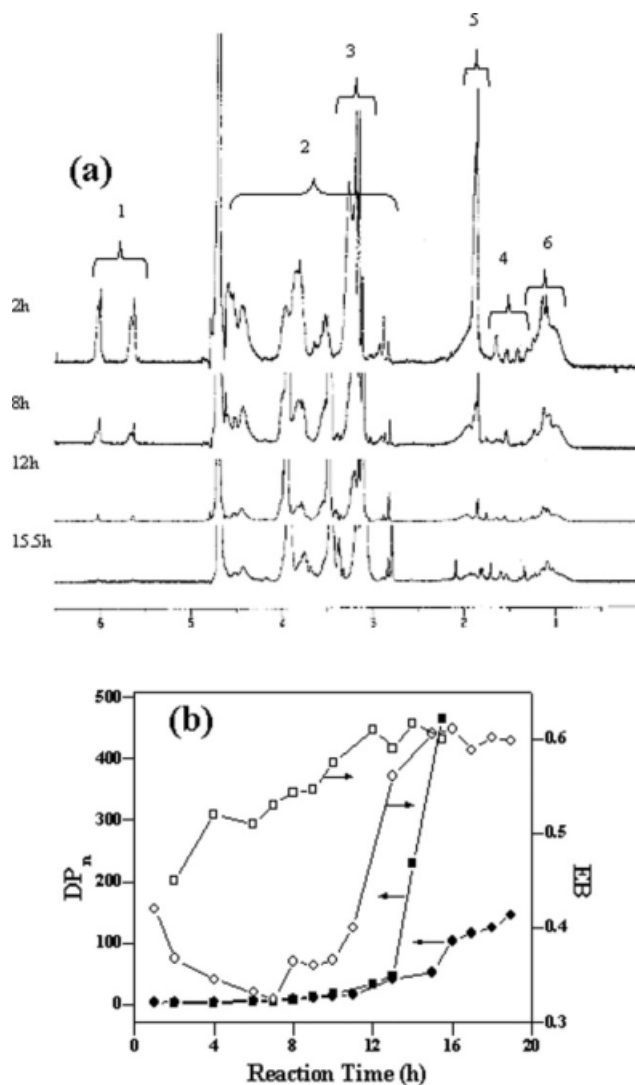


Figure 5 (a) $^1\text{H-NMR}$ spectra of the hyperbranched PDMEAB at different time intervals ($[\text{DMEAB}] : [\text{CuBr}] : [\text{bPy}] = 100 : 1 : 2$, reaction temperature: 90°C); (b) dependence of DP_n and EB of the hyperbranched PDMEAB on the reaction time ($[\text{DMEAB}] : [\text{CuBr}] : [\text{ligand}] = 100 : 1 : 2$, ligand = bPy for \blacksquare \square and PMDETA for \bullet \circ ; reaction temperature: 90°C).

and EB were estimated by the above equations from the corresponding $^1\text{H-NMR}$ spectra.

Figure 5(a) shows the respective $^1\text{H-NMR}$ spectra of the hyperbranched PDMEAB recovered from the mixture ($[\text{DMEAB}] : [\text{CuBr}] : [\text{bPy}] = 100 : 1 : 2$, reaction temperature: 90°C) at different time intervals. It was evident that the peak integrals associated with the $\text{CH}_2=$ (Region 1) and $-\text{OCC}(\text{CH}_3)_2\text{Br}$ groups (region 5), compared with that of the $-\text{N}^+(\text{CH}_3)_2-$ moieties (Region 3), were reduced gradually with the reaction time. Because the amount of the $-\text{N}^+(\text{CH}_3)_2-$ moieties maintained constant throughout the reaction, Figure 5(a) confirmed that the $\text{CH}_2=$ and $-\text{OCC}(\text{CH}_3)_2\text{Br}$ moieties were involved in the chain propagation and chain

initiation, respectively. Figure 5(b) shows the dependence of the DP_n and EB of the hyperbranched PDMEAB on the reaction time ($[\text{DMEAB}] : [\text{CuBr}] : [\text{ligand}] = 100 : 1 : 2$, ligand = bPy or PMDETA, reaction temperature: 90°C). It was clear that the DP_n grew very slowly at the initial stage and increased approximately in an exponential pattern at the later stage, similar to the SCVP and polycondensations.⁴³ In particular, the DP_n of the hyperbranched PDMEAB obtained from the CuBr/PMDETA-catalyzed SCATRP was about 6, 15, and 124, after a reaction for 6, 11, and 18 h, respectively. Figure 5(b) also shows that the CuBr/bPy complex exhibited a higher catalytic activity than the CuBr/PMDETA complex in this work. For example, the DP_n of the hyperbranched PDMEAB obtained from the CuBr/bPy-catalyzed SCATRP was about 3, 33, and 466, after a reaction for 6, 12, and 15 h, respectively. A further extension of the reaction time could definitely enhance the DP_n , but the NMR signals associated with the $\text{CH}_2=$ diminished gradually so that it cannot be clearly detected.²⁵

The effect of reaction temperature on the SCATRP kinetics was also investigated. Figure 6 shows the dependence of the DP_n and EB of the hyperbranched PDMEAB on the reaction time ($[\text{DMEAB}] : [\text{CuBr}] : [\text{bPy}] = 100 : 1 : 2$, reaction temperature 70°C). It was certain that the polymerization rate at 70°C was much lower than that at 90°C .

Physical properties of hyperbranched PDMEAB

The physical properties of hyperbranched polymers were significantly different from their linear counterparts.^{10,13–16,44,45} The segmental motion of the hyperbranched polymers was subject to various factors, viz. branched site, terminal functionality, imperfect spherical conformation, and reduced chain

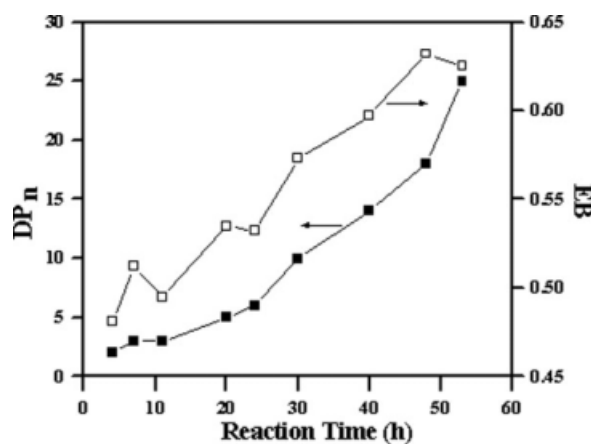


Figure 6 Dependence of DP_n and EB of the hyperbranched PDMEAB on the reaction time ($[\text{DMEAB}] : [\text{CuBr}] : [\text{bPy}] = 100 : 1 : 2$, reaction temperature: 70°C).

entanglement, which would lead to a glass transition pattern different from their linear analogues. Figure 7 shows the differential scanning calorimetry (DSC) thermograms of the linear PDMEAB and two hyperbranched PDMEAB samples ($DP_n = 10$, $EB = 0.4$ for PDMEAB^I; $DP_n = 124$, $EB = 0.61$ for PDMEAB^{II}). The T_g of the linear PDMEAB was evidently observed to be about 120°C, and that of the PDMEAB^I was noted at 70°C. However, the T_g of the PDMEAB^{II} appeared to be below 50°C. Such a result suggested that the hyperbranched structure would considerably reduce the T_g and a higher DP_n would further decrease the T_g .

The rheological behaviors of aqueous solutions of the linear NaPAAC, and linear PDMEAB and hyperbranched PDMEAB were also studied. For most linear polymers in semidilute or concentrated solutions, the chains presumed a considerable extent of chain entanglement. Polymer chains underwent significant de-entanglement under vigorous shearing, giving rise to a shear-thinning phenomenon. However, due to the spherical conformation, the solutions of hyperbranched macromolecules were reported to be in a Newtonian behavior.¹⁶

Figure 8(a) shows the shear rate-shear viscosity (related to water) curves of the aqueous solutions of the linear NaPAAC, linear PDMEAB, and hyperbranched PDMEAB ($DP_n = 145$, $EB = 0.60$ for PDMEAB^{III}). The solutions of the linear NaPAAC and linear PDMEAB underwent a typical shear-thinning process, as the high shear rate triggered the interchain de-entanglement. However, the shear-thinning effect for the solutions of the PDMEAB^{III} was less pronounced to a certain extent, attributable to the spherical structure. On the other hand, Figure 8(b) shows the corresponding shear rate-relative shear viscosity of the aqueous solutions with NaCl

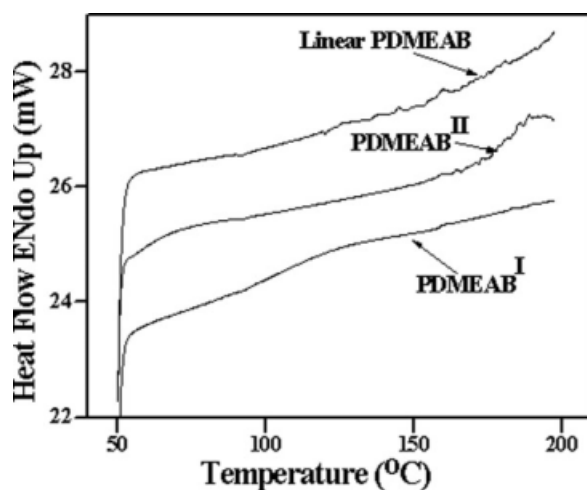


Figure 7 DSC thermograms of (a) the linear PDMEAB, (b) PDMEAB^I ($DP_n = 10$, $EB = 0.4$), and (c) PDMEAB^{II} ($DP_n = 124$, $EB = 0.61$).

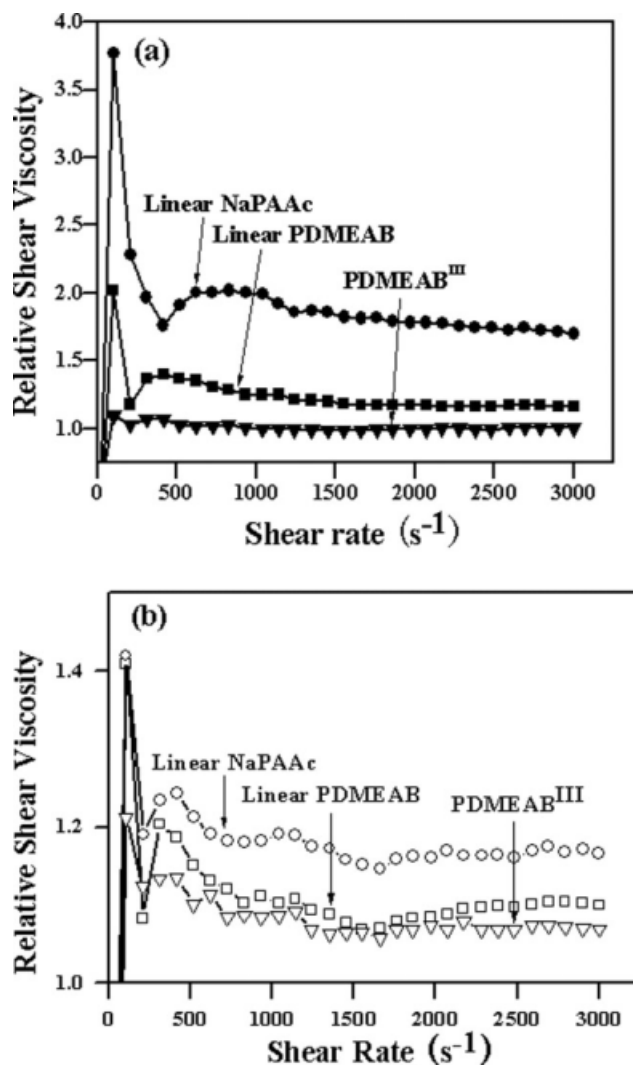


Figure 8 Shear rate–relative shear viscosity curves of aqueous solutions of the linear NaPAAC, linear PDMEAB, and PDMEAB^{III} ($DP_n = 145$, $EB = 0.60$). The concentration was fixed at 3 g/L.

added (1.0M). The shear viscosity of the aqueous solutions of the linear NaPAAC and linear PDMEAB was reduced remarkably due to the polyelectrolyte effect. However, this effect for the hyperbranched PDMEAB was much less obvious, resulting from the size-persistent spherical conformation.

CONCLUSIONS

With the molecular design of the first water-soluble and positively charged inimer, DMEAB, the truly hyperbranched cationic polyelectrolytes, PDMEAB, was directly prepared via the aqueous SCATRP, which showed a methodological advantage over the strategies reported previously. The hyperbranched architecture was verified by NMR spectroscopy and the kinetic study confirmed the DP_n of the hyperbranched PDMEAB grew in a similar manner to

typical SCVPs. DSC results confirmed that the hyperbranched architecture gave rise to a lower glass transition temperature than the linear analogue. In comparison with those of linear polyelectrolytes, the aqueous solutions of the hyperbranched PDMEAB approximately behaved in a Newtonian fashion, and the shear viscosity almost maintained constant with the addition of NaCl.

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