Synthesis of Highly Branched Cationic Polyelectrolytes via Self-Condensing Atom Transfer Radical Copolymerization with 2-(Diethylamino)ethyl Methacrylate

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ABSTRACT: Randomly branched (arborescent) cationic polyelectrolytes were synthesized by self-condensing vinyl copolymerization (SCVCP) of a methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), with (diethylamino)ethyl methacrylate (DEAEMA) via atom transfer radical polymerization (ATRP), followed by quaternization. Homopolymerization of DEAEMA with the CuBr/hexamethyltriethylenetetramine (HMTETA) catalyst system gave a linear polymer having controlled molecular weights and narrow molecular weight distribution, which were evaluated by conventional GPC, GPC−viscosity, and MALDI−TOF mass spectrometry. The catalyst system could be applied to self-condensing vinyl polymerization (homo-SCVP) of BIEM in bulk and in solution to provide hyperbranched architectures, as confirmed by ^{1}H and ^{13}C NMR and GPC−viscosity measurements. SCVCP with CuBr/HMTETA in solution gave a series of tertiary amine methacrylate-based branched polymers, in which the molecular weights, the composition of the DEAEMA segment, and the branched structure can be adjusted by an appropriate choice of the comonomer composition, γ. Quaternization reaction of the branched poly(DEAEMA)s with methyl iodide led to water-soluble cationic polyelectrolytes with branched structures.

Introduction

Branched polyelectrolytes have become of special interest because of their industrial importance and scientifically interesting properties.[1,2] Poly(ethylenimine), which is important in various industrial applications, can provide an excellent example: branched and linear polyelectrolytes have quite different properties due to both the different topologies.[3−5] However, the correlation between topology and properties of branched polyelectrolytes has not been studied very much experimentally because of difficulties in the synthesis of well-defined branched polymers with ionic or ionizable groups. One challenge in this field is, therefore, to produce randomly or regularly branched polyelectrolytes, which are suitable for various applications as well as for quantitative analysis of the relation between properties and architectures.

In recent years, much interest has been devoted to water-soluble cationic polymers, such as poly(L-lysine),[6,7] derivatized chitosan,[8,9] 2-(dimethylamino)ethyl methacrylate-based,[10−14] and 2-(diethylamino)ethyl methacrylate (DEAEMA)-based[15−19] (co)polymers that can be used as DNA binding agents in nonviral gene delivery systems. Recent development in this field has also revealed that poly(ethylenimine),[20,21] poly(amidoamine) dendrimers,[22,23] and hyperbranched poly(amidoester)s[24,25] are effective gene transfer molecules. It is generally accepted that the high transfection efficiency of poly(ethylenimine) and poly(amidoamine) dendrimers compared to that of other cationic polymers is due to the “endosome buffering” or “proton sponge” effect of the polymers. Lim et al. demonstrated that tertiary amines in the interior of these highly branched polymers are protonated at acidic endosomal pH and disrupt the endosome, and therefore cationic polymers with three-dimensional structure and interior tertiary amine groups would be a nontoxic and efficient gene carrier through the endosome buffering effect.[24] Water-soluble cationic polyelectrolytes also have a wide range of commercial applications in paper making, mineral processing, and wastewater treatment.[3,26,27]

Poly((dialkylamino)ethyl methacrylate) and their quaternized products have attracted much attention in recent years as water-soluble polymers due to various potential applications, such as environmental protection and drug delivery systems. Poly(DEAEMA) homopolymer is soluble in acidic solution as a weak cationic polyelectrolyte because of protonation of the tertiary amine residues but precipitates from solution at around neutral pH. In contrast, poly((dimethylamino)ethyl methacrylate) has a characteristic temperature-sensitive solubility (lower critical solution temperature, LCST) in water.[15,28] Recently, (dimethylamino)ethyl methacrylate has been polymerized in a controlled fashion via living anionic polymerization,[29] group transfer polymerization,[30] and atom transfer radical polymerization (ATRP).[31−33] A variety of amphiphilic block copolymers containing poly(DEAEMA)[34−37] and/or poly((dimethylamino)ethyl methacrylate)[38−41] segments have been also synthesized by several research groups using such polymerization techniques.

This paper reports on the synthesis of randomly branched (arborescent) cationic polyelectrolytes by self-condensing vinyl copolymerization (SCVCP) of a methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), with DEAEMA via ATRP. The synthetic route to branched poly(DEAEMA) is outlined in Scheme

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† Dedicated to the memory of Dr. Michael G. Lanzendörfer.

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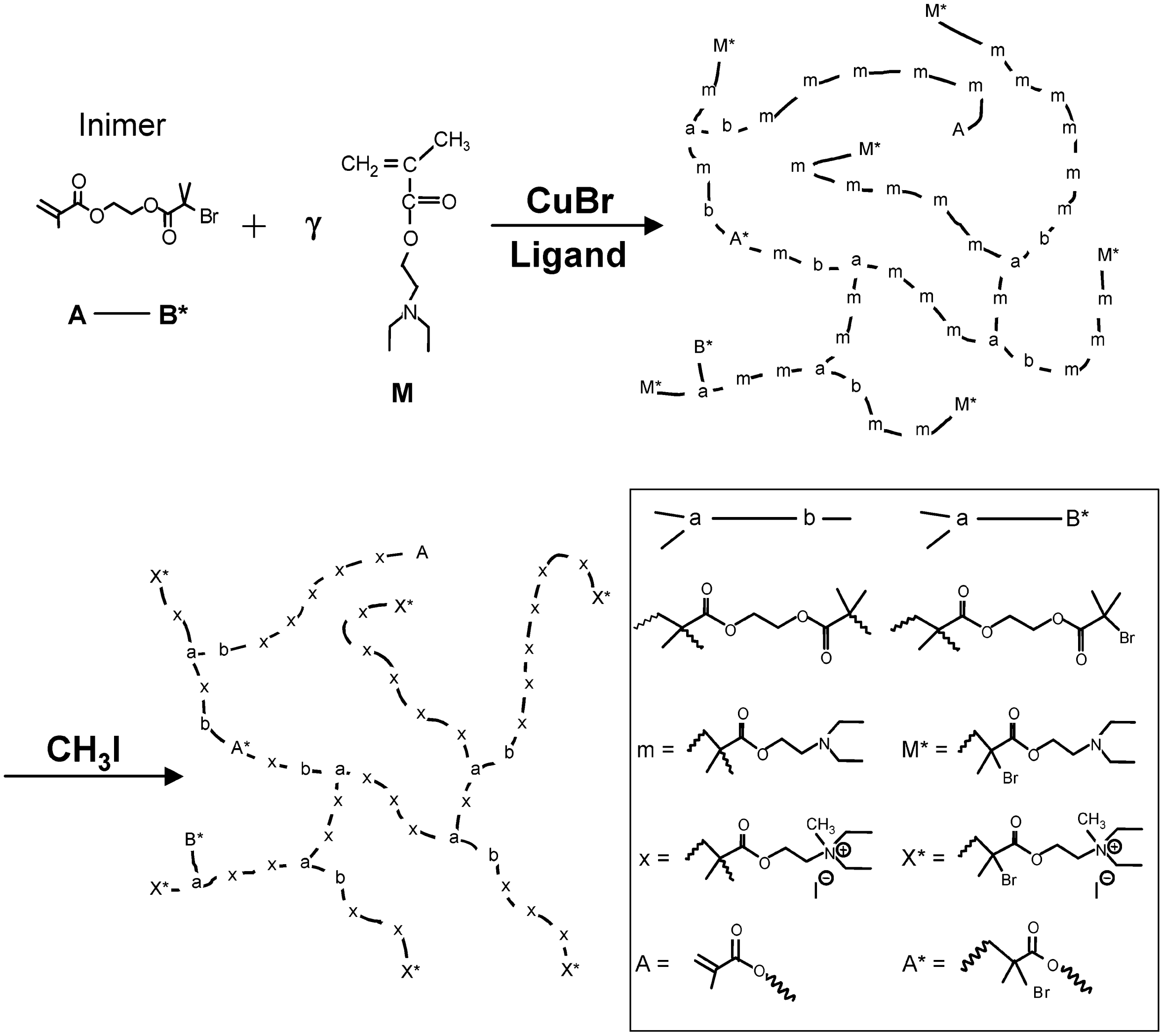
Scheme 1. General Route to Branched Cationic Polyelectrolyte via Self-Condensing Vinyl Copolymerization, Followed by Quaternization with Methyl Iodide



1. The curved lines represent polymer chains. A*, B*, and M* are active units, whereas a, b, and m are reacted ones. A is a methacryloyl group. M and m stand for DEAEMA units at the chain end and in the linear segment, respectively. X* and x stand for quaternized DEAEMA units obtained after quaternization with methyl iodide. SCVCP of AB* inimers with conventional monomers is a facile approach to obtain functional branched polymers because different types of functional groups can be incorporated into a polymer, depending on the chemical nature of the comonomer.[42−47] In a previous paper, we demonstrated the synthesis of randomly branched poly(acrylic acid) by SCVCP of *tert*-butyl acrylate with an acrylate-type inimer via ATRP, followed by hydrolysis of the *tert*-butyl groups.[46] In the approach reported here, cationic branched polymers containing quaternized amine functionalities are derived from nonquaternized monomer units (DEAEMA). In an ideal SCVCP process, living polymerization systems are preferred in order to avoid cross-linking reactions and gelation caused by chain transfer or recombination reactions. Hence, a key criterion for synthesis of highly branched poly(DEAEMA)s with well-defined architectures is to find suitable conditions where both homopolymerization of DEAEMA and homo-SCVP of the inmer can proceed in a controlled/“living” process.

In general, Cu-based ATRP was employed for SCV(C)P of acrylate-type inimers having an acrylate (A) and a bromoester group (B*), capable of initiating ATRP.[47] However, methacrylate-type inimers, such as BIEM, could not be successfully polymerized by such Cu-based ATRP despite variations in ligand and temperature.[48] It was speculated that the tertiary radical sites generated from methacrylate moieties (A) and/or the 2-bromoisobutyryloxy moieties (B*) coupled rapidly, forming an excess amount of deactivating Cu(II) species and prevented polymerization. For the preparation of hyperbranched methcrylates via SCVP with BIEM, Cu-based ATRP with addition of zerovalent copper[48] and Ni-based controlled radical polymerization[49] have been employed. In this paper, we describe optimization study of homopolymerization of DEAEMA via ATRP, homo-SCVP of BIEM, and SCVCP of BIEM and DEAEMA. By using the CuBr/hexamethyltriethylenetetramine (HMTETA) catalyst system, we were able to prepare a monodisperse linear poly(DEAEMA) with controlled molecular weights and poly(BIEM) with hyperbranched architectures. The catalyst system also allowed to prepare randomly branched poly(DEAEMA) by SCVCP via ATRP.

Experimental Section

Materials. CuBr (95%, Aldrich) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol and ether and then dried. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) and ethyl 2-bromo-2-isobutyrate (98%, Aldrich) were distilled and degassed. Bipyridine (Bipy, 99%, Aldrich) was recrystallized from ethanol to remove impurities. Bis(triphenylphosphine)nickel(II) bromide ($(PPh_3)_2NiBr_2$, 99%, Aldrich) was used as received. (Diethylamino)ethyl methacrylate (DEAEMA, 99%, Aldrich) was stirred over CaH_2, distilled from CaH_2, and degassed in high vacuum. 1,1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA, 97%, Aldrich) and other reagents were commercially obtained and used without further purification. Synthesis of a methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), was conducted by the reaction of 2-bromo-isobutyryl bromide with 2-hydroxyethyl methacrylate in the presence of pyridine as reported previously.[49,50] The inimer was degassed by three freeze−thaw cycles.

Polymerization. All polymerizations were carried out in a round-bottom flask sealed with a plastic cap. A representative example for copolymerization ($\gamma = [\text{DEAEMA}]_0/[\text{BIEM}]_0 = 10$) is as follows: BIEM (0.301 g, 1.08 mmol) was added to a round-bottom flask containing CuBr(I) (0.0155 g, 0.108 mmol), HMTETA (0.0249 g, 0.108 mmol), DEAEMA (2.01 g, 10.8 mmol), and ethyl acetate (1.04 g, equimolar to DEAEMA + BIEM, which roughly corresponds to 50 vol %). As soon as BIEM was added to the mixture, the color changed into green, indicating the start of the polymerization. The flask was placed in an oil bath at 60 °C for 1.5 h. Conversion of the double bonds, as detected by ^{1}H NMR, was 95%. The content of the flask was completely solidified when the conversion reached a certain level. After the mixture was dissolved in THF, and was subsequently passed through a silica column, the polymer was precipitated from THF into hexane. Then the product was freeze-dried from dioxane and finally dried under vacuum at room temperature. The polymer had $M_n = 28\,300$ and $M_w/M_n = 1.30$ according to GPC/viscosity using universal calibration, and $M_n = 20\,800$ and $M_w/M_n = 1.88$ according to conventional GPC. For the branched poly(DEAEMA) having a higher degree of branching ($\gamma \le 5$), a white powder was obtained after drying under vacuum at room temperature. In contrast, viscous materials were obtained in the cases of lower degree of branching ($\gamma \ge 10$). Note that glass transition temperature (T_g) of linear poly(DEAEMA) is 295 K[51] (289−297 K[52]).

The homopolymerization of DEAEMA was carried out in bulk. In a typical experiment, ethyl 2-bromo-2-isobutyrate (0.0221 g, 0.108 mmol) was added to a round-bottom flask containing CuBr(I) (0.0155 g, 0.108 mmol), HMTETA (0.0249 g, 0.108 mmol), and DEAEMA (2.011 g, 10.8 mmol). The mixture was heated at 60 °C for 20 min. The resulting polymer was purified by passing through a silica column, then freeze-dried from dioxane, and finally dried under vacuum at room temperature to give a viscous product. The conversion was >92%, with $M_n = 24\,500$ and $M_w/M_n = 1.16$ according to GPC/viscosity and $M_n = 22\,500$ and $M_w/M_n = 1.12$ according to conventional GPC.

The homo-SCVP of BIEM was carried out in bulk and solution. For the solution polymerization, distilled and degassed BIEM (1.01 g, 3.62 mmol) was added to a round-bottom flask containing CuBr(I) (0.0051 g, 0.036 mmol) and ethyl acetate (0.314 g, equimolar to BIEM). As soon as HMTETA (0.0083 g, 0.036 mmol) was added, the system became green, indicating the start of the polymerization. The covered flask was allowed to stand at 60 °C, and the characteristic green color solution kept constant during the polymerization without solidification. After 24 h, the polymerization was stopped by cooling. Conversion of the double bonds detected by ^{1}H NMR of the material was 33%. The product, dissolved in THF, was passed through a silica column and then purified by precipitation from THF into methanol. After the product was collected by centrifugation (4000 rpm, 20 min, 20 °C), the polymer was freeze-dried from dioxane and dried under vacuum. The resulting white powder was employed for GPC, GPC−viscosity, and NMR measurements. The polymer had $M_n = 30\,900$ and $M_w/M_n = 1.66$ according to GPC/viscosity and $M_n = 9000$ and $M_w/M_n = 1.32$ according to conventional GPC. The product before precipitation had $M_n = 2700$ and $M_w/M_n = 2.60$ according to conventional GPC. Poly(2-(2-bromoisobutyryloxy)ethyl methacrylate),[53,54] which was prepared by ATRP of 2-hydroxyethyl methacrylate, followed by esterification with α-bromoisobutyryl bromide, was used as a perfectly linear analogue ($M_{n,GPC} = 20\,500$, $M_w/M_n = 1.16$).

Quaternization of Branched Poly(DEAEMA). Quaternization of linear and branched poly(DEAEMA)s was conducted with methyl iodide (MeI) according to a method reported previously.[31] MeI (0.76 g, 0.54 mmol, which correspond to ca. 1.5 molar excess to DEAEMA units) was added to a solution of 0.10 g of branched poly(DEAEMA) ($\gamma = 5$, 0.013 mmol, $M_{n,GPC-VISCO} = 7900$) in 20 mL of acetone. The mixture was magnetically stirred for 24 h at room temperature, and a pale yellow precipitate started to form after ca. 2 h. Then the quaternized product was separated by filtration and washed with acetone, hexane, and THF in order to remove the excess of methyl iodide. The resulting polymer was dried under vacuum at room temperature to give a pale yellow powder (0.155 g). ^{1}H NMR (D_2O/DCl): 0.6−1.1 ($-CH_2-C(CH_3)-COO-$), 1.1−1.4 ($-NCH_3(CH_2CH_3)_2{}^+I^-$), 1.7−2.3 ($-OCO-CBr(CH_3)_2$, $-CH_2-CBr(CH_3)-COO-$, $-CH_2-C(CH_3)-COO-$), 2.8−3.0 ($-NCH_3(CH_2CH_3)_2{}^+I^-$), 3.2−3.4 ($-NCH_3(CH_2CH_3)_2{}^+I^-$), 3.5−3.7 ($-O-CH_2-CH_2-N-$), and 4.1−4.4 ppm ($-O-CH_2-CH_2-N-$). The degree of quaternization was determined by comparing the peak integral of the quaternary methyl proton signal at 2.8−3.0 ppm with that of the oxymethylene proton at 4.1−4.4 ppm.[55]

Characterization. Conventional GPC and GPC/viscosity systems were used in this study to characterize polymers. The linear and branched polymers obtained from DEAEMA were characterized by GPC using THF as eluent at a flow rate of 1.0 mL/min at room temperature. A conventional THF-phase GPC system was used in order to obtain apparent molecular weights. GPC system I; column set: 5 μm PSS SDV gel, 10^2, 10^3, 10^4, 10^5 Å, 30 cm each; detectors: Waters 410 differential refractometer and Waters photodiode array detector operated at 254 nm. Narrow PMMA standards (PSS, Mainz) were used for the calibration of the column set I. Molecular weights of the branched polymers were determined by the universal calibration principle[56] using the viscosity module of the PSS-WinGPC scientific V 6.1 software package. Linear PMMA standards (PSS, Mainz) were used to construct the universal calibration. GPC system II; column set: 5 μm PSS SDV gel, 10^3, 10^5, and 10^6 Å, 30 cm each; detectors: Shodex RI-71 refractive index detector; Jasco Uvidec-100-III UV detector ($\lambda = 254$ nm); Viscotek viscosity detector H 502B.

MALDI−TOF mass spectrometry was performed on a Bruker Reflex III equipped with a 337 nm N_2 laser in the reflector mode and 20 kV acceleration voltage. Dithranol (Aldrich, 97%) was used as matrix. Sodium trifluoroacetate (Fluka, 99.5%) was added for ion formation. Samples were prepared from THF solution by mixing matrix (20 mg/mL), polymer (10 mg/mL), and salt (10 mg/mL) in a ratio of 10:1:1. The number-average molecular weights, M_n, of the polymer sample were determined in the linear mode.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC-250. The elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kulmbach).

Results and Discussion

Effect of Catalyst System on Homopolymerization of DEAEMA. To find a suitable catalyst system for the synthesis of highly branched cationic polyelectrolytes by SCVCP via ATRP, we initially investigated the influence of the catalyst system (Cu- and Ni-based catalysts) on the homopolymerization of DEAEMA. The bulk polymerization of DEAEMA with CuBr was conducted using ethyl 2-bromo-2-isobutyrate, which has the same initiating group as in the methacrylic inimer (BIEM). Three different nitrogen-based ligands, hexamethyltriethylenetetramine (HTMTETA), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), and 2,2′-bipyridine (Bipy), were employed as ligands to complex

Table 1. Homopolymerization of 2-(Diethylamino)ethyl Methacrylate (DEAEMA)[a]

catalyst/ligand	$[M]_0:[I]_0:[Cat.]_0:[Lig]_0$	temp (°C)	time (h)	conv[b] (%)	$M_{n,calc}$[c]	$M_{n,GPC}$[d] (M_w/M_n)
CuBr/PMDETA	100:1:1:1	60	0.5	100	18 700	24 000 (1.26)
CuBr/HMTETA	100:1:1:1	60	0.3	92	17 200	22 500 (1.12)
CuBr/Bipy	100:1:1.3:2.6	60	3.5	81	15 200	53 800 (1.70)
$(PPh_3)_2NiBr_2$	100:1:1	100	8	80	15 100	

[a] Bulk polymerization with ethyl 2-bromo-2-isobutyrate. [b] Conversion of the double bonds as determined by ^{1}H NMR. [c] Theoretical number-average molecular weight was calculated from the monomer conversion. [d] Determined by GPC using THF as eluent with PMMA standards.

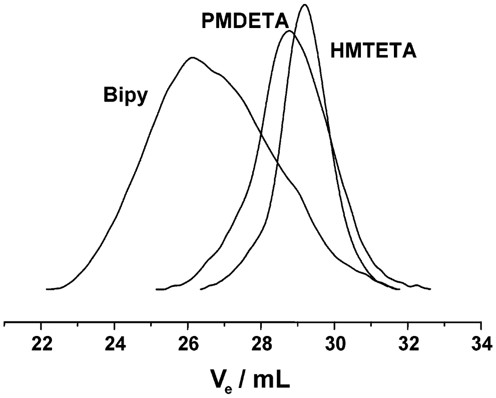


Figure 1. GPC traces of linear poly(DEAEMA)s prepared by CuBr with various ligands. See Table 1 for detailed polymerization conditions.

copper ions. The results are summarized in Table 1 and Figure 1. When DEAEMA was polymerized using CuBr/HMTETA at 60 °C, almost full conversion (>90% determined by ^{1}H NMR) was reached after 20 min, and a viscous polymer was obtained. The number-average molecular weight of the poly(DEAEMA), measured by a conventional GPC using PMMA standards, was $M_n = 22\,500$, which is slightly higher than the theoretical value ($M_n = 17\,200$), and the polydispersity index was $M_w/M_n = 1.12$. The polymer obtained using PMDETA has a slightly broader molecular weight distribution than in the case of HMTETA. In contrast, the polymerization with Bipy shows low initiator efficiency and leads to a broad molecular weight distribution. Such a tendency is similar to the results reported in Cu-based ATRP of (dimethylamino)ethyl methacrylate.[32] Homopolymerization of DEAEMA with $(PPh_3)_2NiBr_2$ at 100 °C, which was successfully employed for the synthesis of hyperbranched polymers by a homo-SCVP of BIEM,[49] provided an insoluble product, suggesting that the Ni-based catalyst is not suitable for the polymerization of DEAEMA.

In this study, the linear and branched polymers obtained from DEAEMA were evaluated by conventional GPC and GPC/viscosity systems using THF as eluent. The determination of the molecular weight of branched polymers is complicated by the fact that the hydrodynamic volume for a given molecular weight differs significantly from that of a linear sample. Therefore, GPC with a mass-sensitive on-line detector, such as a viscosity detector using the universal calibration principle,[56,57] is required for the determination of molecular weights of branched poly(DEAEMA)s. It must be also noted that GPC characterization of linear poly((dialkylamino)ethyl methacrylate)s may possibly involve several problems. For example, adsorption of poly((dimethylamino)ethyl methacrylate) on GPC columns has been reported by several research groups.[29,58] To minimize such effect, some GPC measurements were conducted in THF with 1−2% of triethylamine.[29,31] However, these molecular weights are not accurate due to usage of PMMA or PSt linear polymers as calibration standards. Bütün et al. reported that the molecular weights of poly((dimethylamino)ethyl methacrylate)s and poly(DEAEMA)s synthesized by GTP ($M_w/M_n < 1.2$) are observed by GPC using two PLgel columns in THF, and the values are higher than the theoretical ones due to results of different hydrodynamic volumes.[15] Zhang et al. demonstrated that GPC traces in DMF of poly((dimethylamino)ethyl methacrylate)s prepared by ATRP show a small tailing toward the low molecular weights ($M_w/M_n = 1.12-1.26$) due to the adsorption of the polymers on the GPC column.[32]

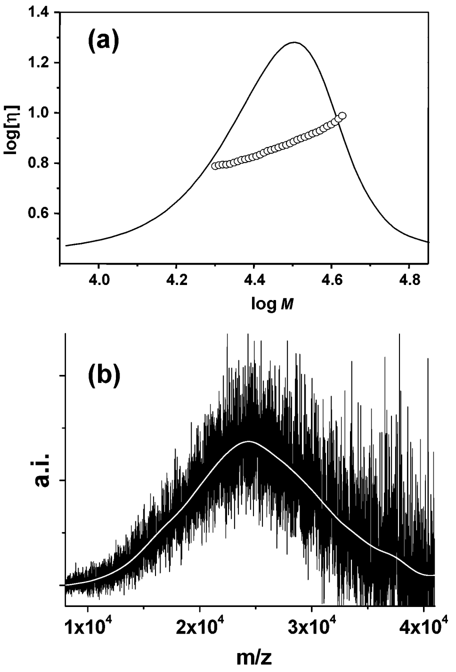


Figure 2. (a) Mark−Houwink plot and RI signal and (b) MALDI−TOF mass spectrum (linear mode) of linear poly(DEAEMA) obtained by CuBr/HMTETA. See Table 1 for detailed polymerization conditions.

To make clarify these points, a linear poly(DEAEMA) obtained by CuBr/HMTETA was characterized by GPC/viscosity using THF and MALDI−TOF mass spectrometry (MS). As can be seen in Figure 2, both GPC/viscosity trace and MALDI−TOF MS spectrum show unimodal peaks with low polydispersity, and the molecular weights and molecular weight distributions obtained from MALDI−TOF MS ($M_n = 21\,000$, $M_w/M_n = 1.08$) are in fair agreement with those from GPC/viscosity ($M_n = 24\,500$, $M_w/M_n = 1.16$). This is an indication that the influence of the adsorption of poly(DEAEMA) on the GPC columns (PSS SDV gel columns) is negligible, and GPC/viscosity measurement in THF can provide reliable information on the molecular weights of linear and branched poly(DEAEMA)s. It is assumed that bulky alkyl groups in DEAEMA, com-

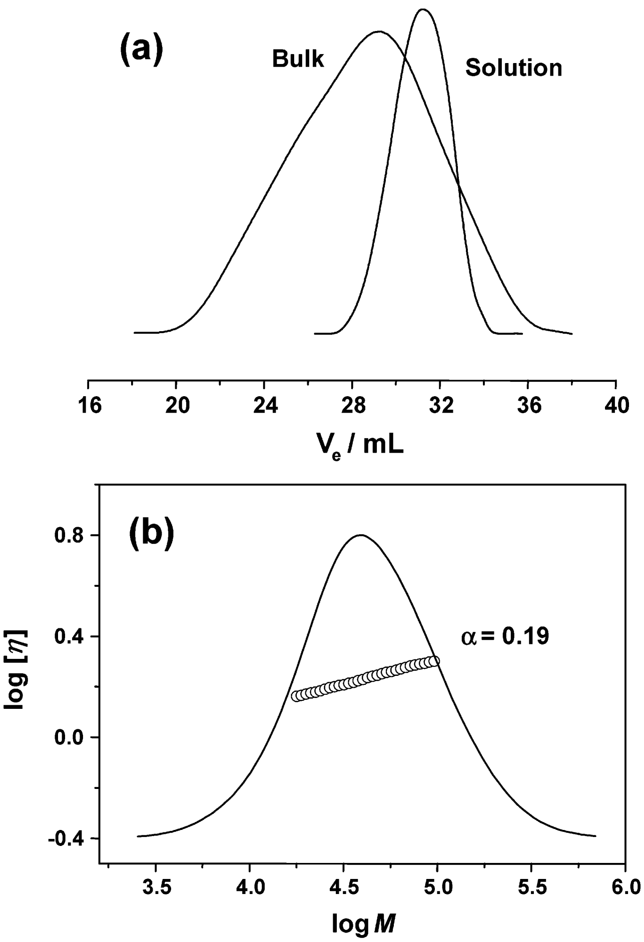


Figure 3. (a) GPC traces of polymers obtained by homo-SCVP of BIEM in bulk and solution and (b) Mark−Houwink plot and RI signal of poly(BIEM) obtained in solution. Conditions: $[BIEM]_0$:$[CuBr]_0$:$[HMTETA]_0$ = 100:1:1, temperature = 60 °C.

pared to (dimethylamino)ethyl methacrylate, may help to prevent the adsorption on the GPC columns. To our knowledge, this is the first MALDI−TOF analysis of poly((dialkylamino)ethyl methacrylate). Further characterization of tertiary amine-based cationic polyelectrolytes and their quaternized products using MALDI−TOF MS will be reported in a forthcoming paper.

Effect of Polymerization Conditions on SCVP of BIEM. To get further insights into the influence of the polymerization conditions, homo-SCVP of a methacrylic AB* inimer, 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), was conducted with the CuBr/HMTETA catalyst system. When the reaction was performed at a ratio $[BIEM]_0$:$[CuBr]_0$ = 100 in bulk, after 15 min at 60 °C, a solid polymer with apparent number-average molecular weight M_n = 14 800 and polydispersity index M_w/M_n = 5.51 (as determined by conventional GPC, Figure 3a) was obtained with high conversion (>85%). On the other hand, the fluid reaction mixture did not solidify during the polymerization in ethyl acetate, and the conversion was still low (ca. 30%) even after 24 h. The behavior is quite reasonable on the basis of the consideration that the lower inimer concentration favors a shift of the equilibrium toward the dormant sites, leading to a lower concentration of radicals. It means that the overall polymerization rate can be controlled by the dilution of the reaction with solvent. As can be seen in Figure 3, the polymer obtained after precipitation shows a unimodal peak with M_n = 30 900 and M_w/M_n = 1.66 (as determined by GPC/viscosity using universal calibration), compared to M_n = 9000 and M_w/M_n = 1.32 (as determined by conventional GPC). The ratio of $M_{n,GPC-VISCO}$ to $M_{n,GPC}$ (4.0) is close to the value (5.2) of the hyperbranched polyacrylate ($M_{n,GPC-VISCO}$ = 23 800, degree of branching = 0.43) obtained by a homo-SCVP of an acrylic AB* inimer, 2-(2-bromopropionyloxy)ethyl acrylate.[46] The molecular weight estimated roughly by ^1H NMR ($M_{n,NMR} \approx 25\ 000$), assuming one double bond per macromolecule, was 2−3 times higher than that determined by GPC. The difference in the molecular weights indicates the formation of the branched structure, as branched polymers have smaller hydrodynamic volumes than their linear analogues. The low value of the Mark−Houwink exponent of the poly(BIEM) (α = 0.19) also suggests a highly branched architecture. These results indicate that homo-SCVP of BIEM proceed smoothly with the CuBr/HMTETA catalyst system both in bulk and in solution, allowing for the synthesis of soluble poly(BIEM) without cross-linking process derived from radical−radical combination. In this study, the molecular weights were established by GPC/viscosity using universal calibration, as the relation between molecular weight and hydrodynamic volume of branched polymers differs substantially from linear ones. For the determination of the absolute molecular weights, evaluation using a static light scattering or GPC−multiangle light scattering is required. However, it was difficult due to low molecular weights of the products.

From the theoretical point of view, the polydispersity index of hyperbranched polymers obtained by SCVP at different conversion (x = conversion of double bonds) is given as[59]

$$\frac{P_w}{P_n} = \frac{1}{1-x} = P_n \tag{1}$$

If the contribution of unreacted inimer is excluded from the various moments, the expression of the polydispersity can be written as[59]

$$\frac{P_w}{P_n} = \frac{(1-e^{-x})[1-(1-x)^3 e^{-x}]}{(1-x)[1-(1-x)e^{-x}]^2} \tag{2}$$

The polydispersities calculated from eq 2 are 1.22 (x = 0.33) and 4.35 (x = 0.85). These values are comparable to the observed values of the polymers obtained by SCVP of BIEM with CuBr/HMTETA (M_w/M_n = 1.32 and 5.51, as determined by conventional GPC, in solution and bulk polymerization, respectively). Note that these observed values come from the polymers purified by precipitation, where low-molecular-weight products may be removed with the unreacted inimer. Actually, the higher polydispersity was observed for the intact polymer before the purification.

According to the theory of SCVP, the conversion of double bonds, x, can be related to the degree of branching. Assuming that A* and B* centers have equal reactivities ($k_A = k_B$), the degree of branching obtained from the theory, DB_{theo}, at different conversion can be represented as[60]

$$DB = \frac{2(1-e^{-x})(x-1+e^{-x})}{1-(1-x)(2-e^{-x})} \tag{3}$$

From this approach, DB_{theo} = 0.41 and 0.19 can be

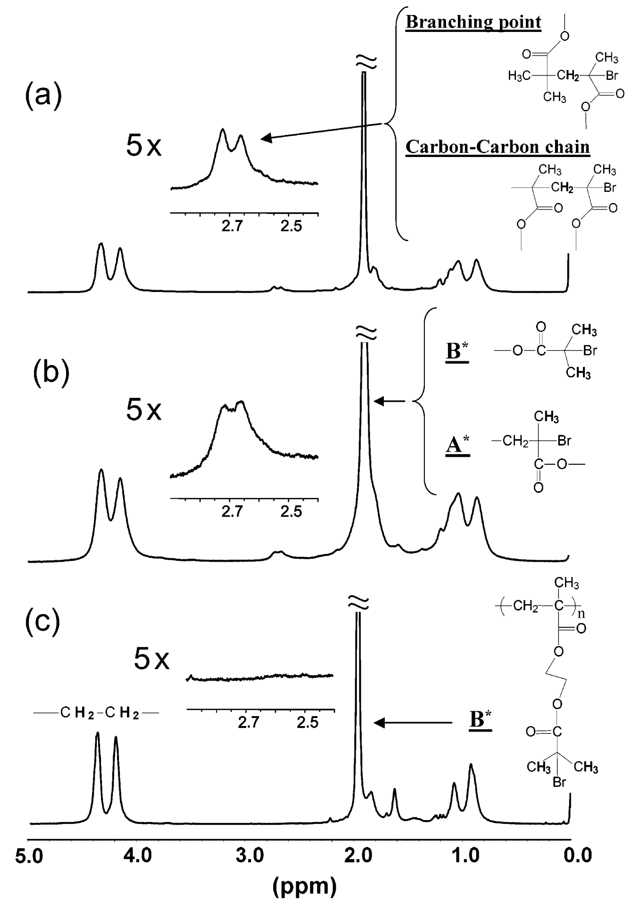


Figure 4. ^{1}H NMR spectra (CDCl$_3$) of the polymers obtained by homo-SCVP of BIEM in bulk (a) and solution (b) and a linear analogue, poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (c). Conditions for homo-SCVP of BIEM: see Figure 3. Synthetic procedure for the linear analogue: see refs 53 and 54.

expected for bulk and in solution polymerization, respectively. These values represent a rough estimate, as they are calculated on the basis of the assumption of equal rate constants for polymerization. When the reactivities of the active centers are not equal, the dependences are more complex and the degree of branching may be higher or lower, depending upon the systems.

The structures of the poly(BIEM)s obtained by homo-SCVP in bulk and in solution were compared with a perfectly linear analogue, poly(2-(2-bromoisobutyryloxy)ethyl methacrylate),[53,54] which was prepared by ATRP of 2-hydroxyethyl methacrylate, followed by esterification with α-bromoisobutyryl bromide. As can be seen in Figure 4a,b, the poly(BIEM)s obtained by homo-SCVP show the peaks at 2.5−3.0 ppm, which are attributed to the methylene protons geminal to a bromine atom. The peak is formed by activation of the 2-bromoisobutyryloxy moieties (B*) and subsequent addition of BIEM to form one A* (corresponding to an end group in the branching point) and by subsequent addition of BIEM to A* to form new A* (corresponding to an end group in the carbon−carbon chain). The peak could not be observed in the linear analogue (Figure 4c), suggesting that the branched architecture was obtained by the homo-SCVP of BIEM with CuBr/HMTETA. The integral ratio for the peaks at 2.5−3.0 ppm to peaks at 4.0−4.5 ppm, which corresponds to the ethylene protons in the ethylene glycol spacer and is independent of the degree of branching, is 0.072 in the case of the poly(BIEM) obtained by bulk. The ratio is almost the same to that (peaks at 2.5−3.0 ppm over peaks at 4.0−4.5 ppm = 0.056) of the poly(BIEM) obtained in solution. This is an indication that the peak at 2.5−3.0 ppm is independent of the molecular weights of the polymer and is therefore attributed mainly to an end group in the branching point. The results support the formation of the branched structures by bulk and solution polymerizations but provide no quantitative information on the degree of branching. The broad peaks at 0.7−1.5 ppm are attributed to the methyl group in the backbone. The methylene protons in the backbone observed at 1.5−2.2 ppm is overlapped by the strong peak at 2.0 ppm, which is assigned to methyl protons adjacent to a bromine atom (A* and B*). Note that subsequent addition of BIEM to A* or B* forms the next carbon−carbon bond, and the methyl protons incorporated in the chain (corresponding to reacted units, a and b) should be shifted to upfield and are overlapped by the methacrylic backbone. Hence, the sum of methyl protons of the geminal to bromine at 2.0 ppm and methylene protons at 1.5−2.2 ppm corresponds to eight protons in a perfect linear polymer, but the value decreases with increasing degree of branching. The consideration is consistent with the result of ^{1}H NMR analysis: (sum of protons at 1.5−2.2 ppm)/(protons of the ethylene glycol linkage) ≈ 2.0 for the linear analogue, whereas it is 1.7 and 1.6 for the poly(BIEM)s obtained by homo-SCVP in bulk and in solution, respectively. These results also support the formation of the branched structure by homo-SCVP. Unfortunately the proportion of B* and b could not be determined by this method because of an overlap of the peak of the b group, which is formed by activation of B* and subsequent addition of monomer, with a signal of methyl protons in the polymer backbone. Hence, it was impossible to determine the degree of branching quantitatively via ^{1}H NMR analysis. Alternatively, we employed the two independent integral ratios; the ratio of the peaks at 2.5−3.0 ppm and to the peaks at 4.0−4.5 ppm, and the ratio of sum of protons at 1.5−2.2 ppm to protons of the ethylene glycol linkage, to provide the information on the branched architectures. As mentioned above, the theoretical calculation suggests that the degree of branching of the polymer obtained in solution is lower than that in bulk. However, the two integral ratios were observed to be similar (0.072 vs 0.056 and 1.7 vs 1.6, respectively), even if the two different polymerizations showed a large difference in the conversion. It means that the integral ratios are useful to distinguish between the branched polymers and a linear analogue, but the measurement may be not sensitive enough to evaluate the difference quantitatively in the branched architectures between the polymers obtained by different conditions. Also, the influences of the different reactivity ratios, intramolecular cyclization, and purification procedures on the degree of branching cannot be ruled out.

^{13}C NMR measurements were also used for the characterization of the resulting branched architectures. As can be seen in Figure 5a, characteristic peaks at 177.5, 177.2, 176.3 (d), 171.7 (g), 63.5 (e), 62.9 (f), 55.9 (h), 54.4 (a), 45.5, 45.1 (b), 31.1 (i), and 19.3, 17.6 (c) ppm are seen in the linear analogue, poly(2-(2-bromoisobutyryloxy)ethyl methacrylate), which correspond reasonably to the linear structure. In addition to these peaks, a quarternary carbon peak at 40.6 ppm (h′) is

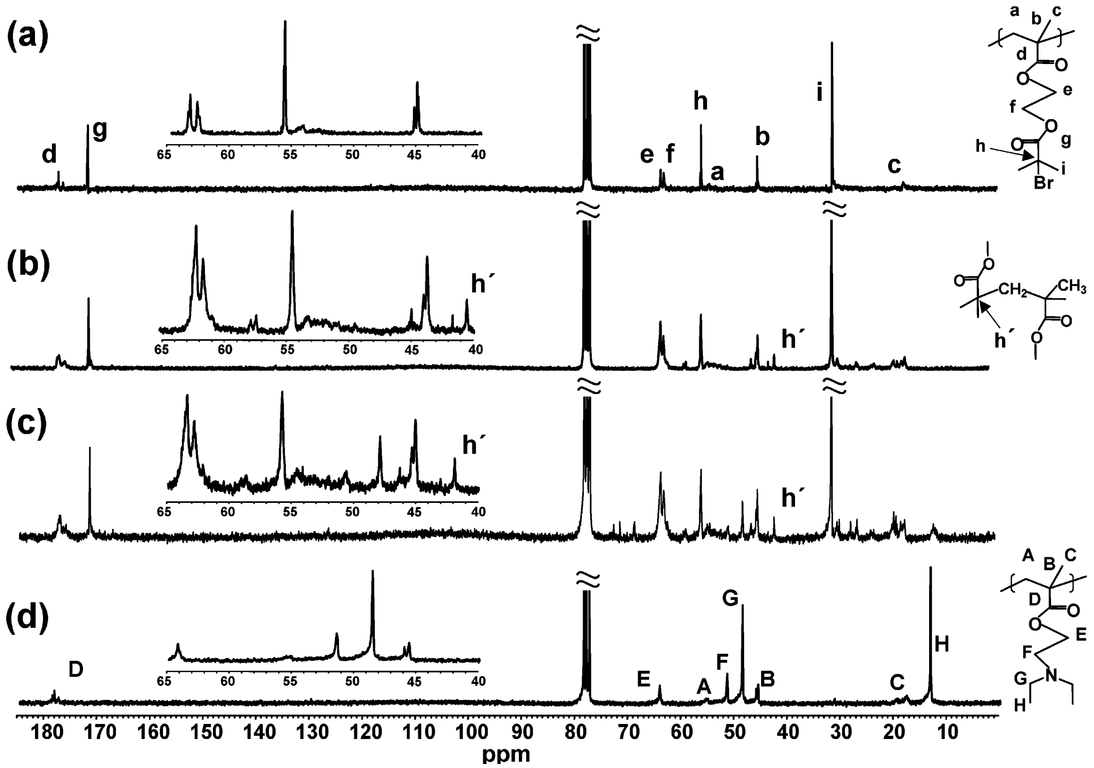


Figure 5. ^{13}C NMR spectra ($CDCl_3$) of poly(2-(2-bromoisobutyryloxy)ethyl methacrylate) (a), the polymers obtained by homo-SCVP of BIEM in solution (b) and by SCVCP of BIEM and DEAEMA at $\gamma = 1$ (c), and linear poly(DEAEMA) (d). Samples for (a) and (b): see Figure 4. Samples for (c) and (d): see Table 3 and Table 1, respectively.

Table 2. Self-Condensing Vinyl Copolymerization of BIEM and DEAEMA under Various Conditions[a]

catalyst/ligand	solvent[b]	temp (°C)	time (h)	conv[c] (%)	$M_{n,GPC}$[d] (M_w/M_n)	$M_{n,GPC-VISCO}$[e] (M_w/M_n)
CuBr/HMTETA		60	0.5	100	gel	
CuBr/HMTETA	ethyl acetate	60	1.5	95	20 800 (1.88)[f] 14 800 (2.10)[g]	28 300 (1.30)[f]
CuBr/PMDETA	ethyl acetate	60	24	67	6 800 (2.00)[g]	13 100 (1.36)[g]
$(PPh_3)_2NiBr_2$		100	8	45	gel	
$(PPh_3)_2NiBr_2$	DMF	100	24		gel	

[a] Copolymerization at a constant comonomer ratio, $\gamma = [\text{DEAEMA}]_0/[\text{BIEM}]_0 = 10$, and a constant comonomer-to-catalyst ratio, $\mu = ([\text{DEAEMA}]_0 + [\text{BIEM}]_0)/[\text{CuBr}]_0 = 100$. [b] Ethyl acetate or *N*,*N*-dimethylformamide (equimolar to DEAEMA + BIEM) was used as a solvent. [c] Conversion of double bonds as determined by ^{1}H NMR. [d] Determined by GPC using THF as eluent with PMMA standards. [e] Determined by GPC/viscosity measurement. [f] Purified by column filtration, followed by precipitation from THF into hexane. [g] Purified by column filtration, followed by precipitation from THF into water.

clearly observed in the polymer obtained by SCVP of BIEM (Figure 5b), which is assigned to b formed by activation of the 2-bromoisobutyryloxy moieties (B*) and subsequent addition of BIEM. The peak should be attributed to the branching points, suggesting the formation of branched polymers by the homo-SCVP.

Effect of Polymerization Conditions on SCVCP of BIEM with DEAEMA. A series of copolymerizations of BIEM with DEAEMA were carried out under various conditions. To compare the catalyst systems, the polymerization was conducted at 60 °C at a constant comonomer ratio, $\gamma = [\text{DEAEMA}]_0/[\text{BIEM}]_0 = 10$, and a constant comonomer-to-catalyst ratio, $\mu = ([\text{DEAEMA}]_0 + [\text{BIEM}]_0)/[\text{CuBr}]_0 = 100$, where $[\text{DEAEMA}]_0$, $[\text{BIEM}]_0$, and $[\text{CuBr}]_0$ represent the initial concentration of comonomer, inimer, and catalyst, respectively. The results are summarized in Table 2. Initial attempts to synthesize branched poly(DEAEMA) were carried out by bulk polymerization, which were mainly employed for the homopolymerization of DEAEMA described above as well as a homo-SCVP of BIEM. In all cases, the bulk polymerization generated only insoluble products, which may be due to unfavorable cross-linking reactions and gelation caused by chain transfer or recombination reactions. In contrast, the polymerization in ethyl acetate (equimolar to DEAEMA + BIEM) with CuBr/HMTETA proceeded smoothly up to 95% conversion without cross-linking. The viscous reaction mixture was soluble in THF at ambient temperature. The polymer obtained after precipitation into hexane had $M_n = 28\,300$ and $M_w/M_n = 1.30$ (as determined by GPC/viscosity using universal calibration), compared to $M_n = 20\,800$ and $M_w/M_n = 1.88$ (as determined by conventional GPC). The higher molecular weights determined by GPC−viscosity compared with apparent ones obtained by GPC indicate branched structures. The Mark−Houwink exponent of the branched polymers is apparently lower ($\alpha = 0.49$) compared to that for linear poly(DEAEMA) ($\alpha = 0.60$). These results suggest that the addition of solvent suppresses the polymerization rate by lowering the radical concentration, allowing for the synthesis of soluble branched poly(DEAEMA). Obviously, the polymerization mixture prior to precipitation, which includes a certain amount of inimer, comonomer, and low-molecular-weight products, showed broader molecular weight distributions and lower molecular

Table 3. Self-Condensing Vinyl Copolymerization of BIEM and DEAEMA at Different Comonomer Ratios γ^a

					BIEM ratio in polymer		
γ^b	conv^c (%)	$M_{n,GPC}{}^d$ (M_w/M_n)	$M_{n,GPC-VISCO}{}^e$ (M_w/M_n)	α^f	calcd^g	obsd (NMR)^h	obsd (EA)^i
1	65	3600 (1.76)	6300 (2.75)	0.21	0.50	0.55	0.61
2.5	72	4500 (1.58)	6200 (2.80)	0.27	0.29	0.23	0.35
5	82	5700 (1.88)	7900 (3.90)	0.31	0.17	0.22	0.24
10	95	20800 (1.88)	28300 (1.30)	0.49	0.09	0.08	0.12
25	96	30100 (1.70)	35600 (1.21)	0.51	0.04	0.01	0.06

[a] Copolymerization at 60 °C for 1.5−2 h with CuBr/HMTETA at a constant comonomer-to-catalyst ratio, $\mu = ([\mathrm{DEAEMA}]_0 + [\mathrm{BIEM}]_0)/[\mathrm{catalyst}]_0) = 100$ in the presence of ethyl acetate (equimolar to DEAEMA + BIEM). [b] $\gamma = [\mathrm{DEAEMA}]_0/[\mathrm{BIEM}]_0$. [c] Conversion of double bonds as determined by ^{1}H NMR. [d] Determined by GPC using THF as eluent with PMMA standards. [e] Determined by GPC/viscosity measurement. [f] Mark−Houwink exponent as determined by GPC/viscosity measurement. [g] Calculated from the composition in feed. [h] Determined by ^{1}H NMR. [i] Determined from the elemental analysis using the nitrogen content.

weights. As shown in Table 2, the precipitation of the polymer mixture from THF into hexane or water yields fractions with substantially different molecular weights, which may come mainly from the difference in the amounts of low-molecular-weight products removed during the purification process. There is no significant difference in the chemical composition of the two materials: the inimer composition determined by elemental analysis was 0.12 and 0.14 for hexane and water, respectively. For GPC/viscosity measurements, purified polymer samples are required in order to avoid the influence of residual monomers and solvent. The solution copolymerization with CuBr/PMDETA also gave a soluble product. However, homo-SCVP of BIEM under the same condition showed no activity, suggesting that the CuBr/PMDETA catalyst system is not applicable for synthesis of highly branched poly(DEAEMA) by SCVCP. This agrees with general tendency that tridentate nitrogen-based ligand, like PMDETA, shows less activity than tetradentate one, such as HMTETA. SCVCP with the Ni-based catalyst provided insoluble products, although the SCVCP of BIEM with methyl methacrylate gave branched polymers without cross-linking under the same condition,[49] suggesting that the tertiary nitrogen atom in DEAEMA has some influence on the polymerization behavior.

As mentioned above, the nature of ligand used to complex copper ions was found to play an important role in the determination of the activity, molecular weights, molecular weight distribution, and branched architectures of polymers obtained by homopolymerization of DEAEMA, homo-SCVP of BIEM, and SCVCP of BIEM and DEAEMA. The behavior is mainly related to the activation and deactivation rate constants in ATRP equilibrium. Additionally other factors, such as polarity of both the monomers and reaction medium, may also have an influence on the equilibrium. In this copolymerization system, BIEM used as an AB* inimer contains the methacryl and bromoisobutyryloxy groups, both of which form tertiary halides, which are known to produce higher concentration of radicals than secondary active sites.[48] DEAEMA used as a comonomer also generates a tertiary radical. The tertiary α-bromoester dormant species (A* and M*) formed during the reaction should have a reactivity similar to the bromoisobutyryloxy group (B*) found on the AB* inimer. Hence, the difference in the rate constants for the six possible propagation reactions of the different centers is considered to be small. For homo-SCVP, the inherently high initiator (inimer) concentration favors a shift of the equilibrium toward the active radicals, and the initial rate of radical formation is faster than that in conventional ATRP. The higher concentration of radicals leads to an increased amount of termination, leaving an excess of Cu(II). For a successful SCV(C)P via ATRP, a sufficient proportion of Cu(II) relative to Cu(I) should be maintained throughout the polymerization in order to keep a low concentration of monomeric and polymeric radicals. The concentration of the initiator (bromoester group) during SCVCP is basically dependent upon the comonomer ratio, γ, in the feed. The catalyst concentration is also one of the key factors to control the topological structures as well as the molecular parameters. In this system, the comonomer-to-catalyst ratio was kept at a constant value of $\mu = ([\mathrm{DEAEMA}]_0 + [\mathrm{BIEM}]_0)/[\mathrm{CuBr}]_0 = 100$, and actual $[\mathrm{BIEM}]_0$:$[\mathrm{CuBr}]_0$ is about 9 in the case of $\gamma = 10$. As can be seen in the next section, the branched poly(DEAEMA)s could be obtained in the range of $\gamma = 1-25$, which correspond to $[\mathrm{BIEM}]_0$:$[\mathrm{CuBr}]_0 = 50-3.8$. Under the copolymerization conditions in solution, the initial rate of radical formation should be lower than in the synthesis of the branched poly(BIEM) by homo-SCVP, leading to depressions of radical concentration and termination reactions.

Effect of the Comonomer Ratio on SCVCP of BIEM with DEAEMA. Influence of the comonomer ratio on SCVCP of BIEM with DEAEMA was investigated with CuBr/HMTETA in ethyl acetate. The polymerization was conducted at 60 °C at different comonomer ratios, $\gamma = [\mathrm{DEAEMA}]_0/[\mathrm{BIEM}]_0$ between 1 and 25, keeping the comonomer-to-catalyst ratio at a constant value of $\mu = ([\mathrm{DEAEMA}]_0 + [\mathrm{BIEM}]_0)/[\mathrm{CuBr}]_0 = 100$. Under that condition, almost full conversion was reached within 2 h in the cases of higher γ values ($\gamma > 10$), while the conversion decreases slightly with decreasing γ value. The products obtained in the range of $\gamma = 1-25$ are easily soluble in THF, whereas the product produced at $\gamma = 100$ is hard to dissolve completely in THF. The molecular weights and molecular weight distribution of the copolymers were characterized by GPC/viscosity using universal calibration and conventional GPC. The results are given in Table 3. In all samples, the molecular weights determined by GPC−viscosity are higher than the apparent ones obtained by GPC, indicating highly branched structures. The ratios of $M_{n,GPC-VISCO}$ to $M_{n,GPC}$ of the copolymers are 1.1−1.8, suggesting that a suitable amount of AB* inimer, BIEM, in the feed leads to a considerably compact structure, and the difference in the amount has an influence on the molecular weights and compact structure in solution. All samples show relatively low polydispersities. For SCVCP, the molecular weight distribution is decreased in proportion to the comonomer ratio, $\gamma = [\mathrm{M}]_0/[\mathrm{I}]_0$:

$$M_w/M_n = 1 + P_n/(\gamma + 1) \qquad (4)$$

for $\gamma \gg 1$.[44] Hence, higher γ values and/or intermediate

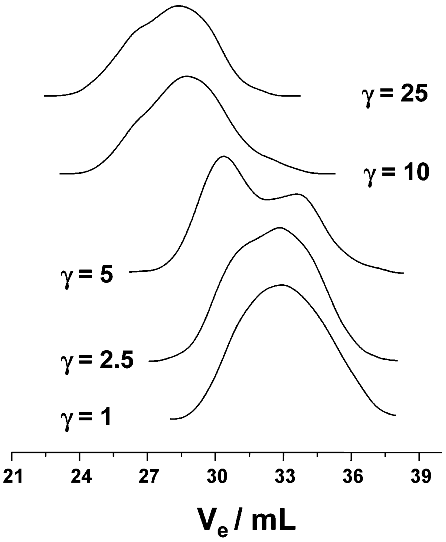


Figure 6. GPC traces of branched copolymers obtained by SCVCP of BIEM and DEAEMA at different comonomer ratios, γ = [DEAEMA]$_0$/[BIEM]$_0$. See Table 3 for detailed polymerization conditions.

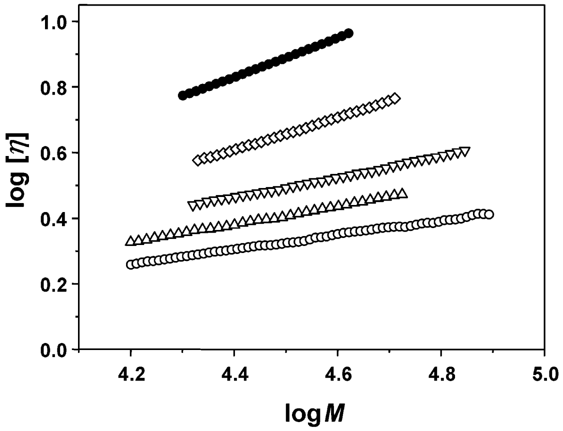


Figure 7. Mark−Houwink plots for the polymers obtained by copolymerizations of BIEM and DEAEMA: γ = 1 (○), 2.5 (△), 5 (▽), and 10 (◇). Samples: see Table 3. The intrinsic viscosity of a linear poly(DEAEMA) (●) is given for comparison.

conversion (conversion = 65−82%), in addition to the polymer purification process by the precipitation, may contribute to obtain copolymers having relatively narrow polydispersities. For example, the polymer obtained at $\gamma = 5$ had $M_{n,GPC} = 1900$ ($M_w/M_n = 4.35$) and $M_{n,GPC} = 5700$ ($M_w/M_n = 1.88$) before and after the precipitation in hexane. As can be seen in Figure 6, the elution curves shift toward higher molecular weights with increasing comomer ratio, γ. Number-average molecular weights of the copolymers consistently increase with γ, and molecular weights up to $M_{n,GPC-VISCO} = 35\,600$ could be obtained at $\gamma = 25$. The same tendency was observed in SCVCP of *tert*-butyl acrylate with an acrylate-type inimer via ATRP[46] as well as SCVCP of methyl methacrylate with a methacrylate-type inimer having a silylketene acetal group via group transfer polymerization.[45] These results suggest that the relationship between the molecular weights and γ is independent of the polymerization and catalyst systems, and may be attributed to an inherent tendency for cyclization in SCVCP process.

Figures 7 and 8 show the Mark−Houwink plots and contraction factors,[61] $g' = [\eta]_{branched}/[\eta]_{linear}$, as a function of the molecular weight for representative branched

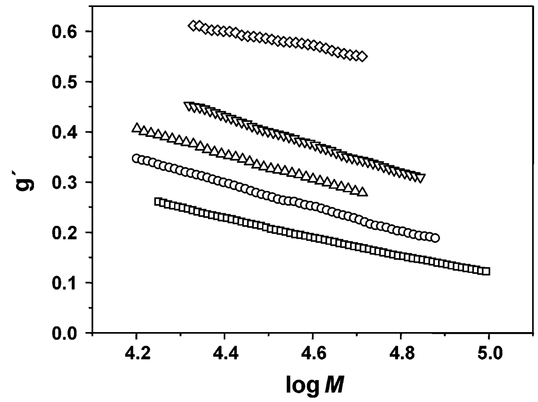


Figure 8. Contraction factors, $g' = [\eta]_{branched}/[\eta]_{linear}$, for the polymers obtained by SCVP of BIEM (□) and by copolymerizations: γ = [DEAEMA]$_0$/[BIEM]$_0$ = 1 (○), 2.5 (△), 5 (▽), and 10 (◇). Samples: see Table 3.

polymers obtained by SCVCP. Plots of a hyperbranched polymer obtained by homo-SCVP of BIEM and a linear poly(DEAEMA) are shown in comparison. The viscosities of the branched poly(DEAEMA)s are significantly lower than those of the linear one and increase with γ. At higher molecular weights (log $M > 4.5$), the intrinsic viscosity of the branched poly(DEAEMA) ($\gamma = 5$) is less than 60% of that of the linear one. As shown in Figure 7, there are only slight differences in the slopes between the branched copolymers, but the values at each molecular weight increase with increasing γ value. The contraction factors for all the branched polymers decrease with increasing molecular weights. The GPC/viscosity measurements of the branched poly(*tert*-butyl acrylate)s obtained by SCVCP with an acrylic-type inimer showed the similar tendency,[46] suggesting the feasibility of the viscosity improvement by the inimer incorporation, regardless of the kinds of inimer and polymer. These results also indicate that GPC/viscosity measurement in THF can provide reliable information on the molecular weights and viscosity of linear and branched poly(DEAEMA)s, even if the comonomer unit contains a tertiary amine group. It must be noted that multimodal GPC traces obtained with γ = 2.5, 5, and 10 (Figure 6) indicate the presence of fractions with different hydrodynamic volumes. The Mark−Houwink plots (Figure 7) of the corresponding polymers, however, are not affected, indicating that the different fractions have similar structure.

The influence of the comonomer ratio, γ, on the Mark−Houwink exponent is shown in Figure 9. In the whole range of γ values, the exponents of the branched polymers are significantly lower (α = 0.2−0.5) compared to that for linear poly(DEAEMA) ($\alpha = 0.60$). Such a systematic decrease in the Mark−Houwink exponent, α, as well as the contraction factor, g', suggests a more compact architecture with an increased number of branches. Particularly, the branched poy(DEAEMA)s obtained at $\gamma = 1$ show an Mark−Houwink exponent ($\alpha = 0.21$) comparable to that of a hyperbranched poly(BIEM) ($\alpha = 0.19$) obtained by a homo-SCVP. The exponent ($\alpha = 0.51$) obtained at $\gamma = 25$ is comparable to that of the branched poly(*tert*-butyl acrylate) obtained by a SCVCP via ATRP ($\alpha = 0.46$ at $\gamma = 25$).[46] At a comonomer ratio of $\gamma = 5$ (corresponding to 20% inimer), the α value is about half of the value of linear poly(DEAEMA). This is an indication that the branching structure induced by the copolymerization with a tiny amount of AB* inimer has a significant influence on

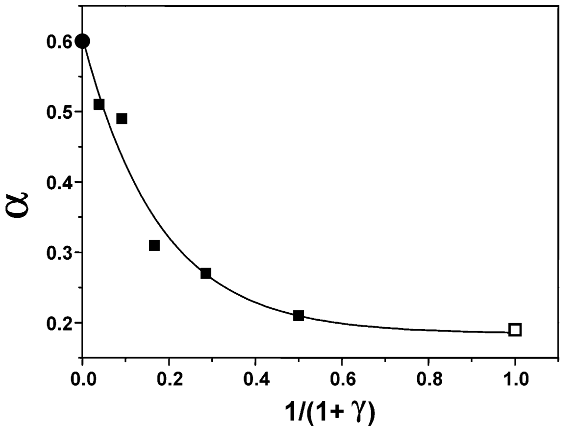


Figure 9. Dependence of the Mark–Houwink exponent, α, on comonomer ratio, γ (■). Linear poly(DEAEMA) (●): α = 0.60. Hyperbranched poly(BIEM)(□): α = 0.19.

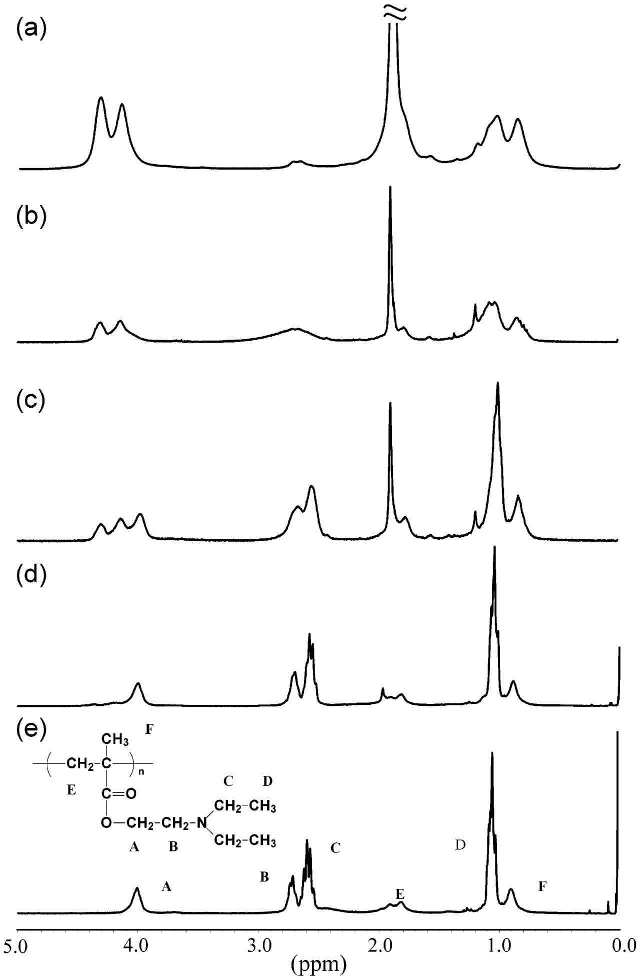


Figure 10. ^{1}H NMR spectra (CDCl$_3$) of the polymers obtained by SCVP of BIEM (a), by SCVCP of BIEM and DEAEMA: γ = 1 (b), 2.5 (c), 10 (d), and by ATRP of DEAEMA (e).

macroscopic (e.g., intrinsic viscosity) and microscopic (e.g., radius of gyration) quantities, even if the degrees of branching of the copolymers are expected to be lower than those of the corresponding hyperbranched polymers obtained by homo-SCVP.

The structure of the branched poly(DEAEMA)s was also confirmed by ^{1}H NMR and elemental analysis. Figure 10 shows the respective ^{1}H NMR spectra of the linear and branched poly(DEAEMA)s obtained by ATRP and SCVCP, respectively. Characteristic peaks at 0.8–1.2, 1.7–2.0, 2.5–2.9, and 3.9–4.2 ppm are clearly seen in the linear poly(DEAEMA), which are suppressed with increasing γ value. Besides the signals of poly(DEAEMA) segment, the BIEM inimer signals appear at 4.1–4.5 and 1.9–2.0 ppm, which correspond to the protons of the ethylene linkage of BIEM and methyl protons adjacent to a bromine atom (A* in the polymer chain end and B* in the 2-bromoisobutyryloxy group), respectively. The BIEM content in the copolymers obtained by SCVCP was roughly determined from ^{1}H NMR spectra by comparing the peaks at 2.5–2.9 ppm due to the six methylene protons (B and C) adjacent to a nitrogen atom in the DEAEMA segment and peaks at 3.9–4.5 ppm attributed to the sum of the protons of the ethylene linkage in BIEM and methylene protons (A) adjacent to the ester oxygen in DEAEMA. The comonomer content determined by ^{1}H NMR is in accord with the comonomer composition in the feed which corresponds to the γ value, as can be seen in Table 3. Obviously, the compositions are rough estimates due to the overlapping methylene protons (C and B) with the peaks of the end groups (2.5–3.0 ppm), which are attributed to the methylene protons geminal to a bromine atom. The deviation should be less significant in the cases of higher γ values because the number of end groups (sum of A* and B*) is proportional to the BIEM content. The comonomer contents could be determined by elemental analysis via nitrogen content (Table 3), which are consistent with the theoretical values within experimental error. The agreements suggest that the difference in the rate constants for the inimer and comonomer is relatively small, and hence the comonomer composition in the intermediate conversion (conversion = 65–82%) is in fair agreement with the composition in the feed. In this copolymerization system, BIEM used as an AB* inimer contains the methacrylate (A*) and bromoisobutyryloxy (B*) groups, both of which form tertiary radicals. The radicals are basically the same radicals generated from tertiary α-bromoester dormant species (M*) in DEAEMA used as a comonomer. Hence, it is reasonable to consider that the difference in the rate constants for the six possible propagation reactions of the different centers is not significant.

Parts c and d of Figure 5 show the ^{13}C NMR spectra of the polymer obtained by SCVCP of BIEM and DEAEMA at γ = 1 and linear poly(DEAEMA), respectively. The characteristic peaks at 178.7, 178.3, 177.6 (D), 64.3 (E), 55.5 (A), 51.5 (F), 48.7 (G), 46.1, 45.7 (B), 17.7 (C), and 13.2 (H) ppm are seen in the linear poly(DEAEMA). In addition to these peaks, the signals attributed to the poly(BIEM) segment are observed clearly in the copolymer obtained by SCVCP (Figure 5c). Furthermore, the spectrum of the copolymer shows the quarternary carbon peak at 40.6 ppm (h′), which is assigned to the branching point (b). Hence, the spectrum of the copolymer appears as the superposition of the spectra of the two components, poly(BIEM) and poly(DEAEMA), with additional branching points, suggesting the formation of branched structure by SCVCP.

In the case of ideal SCVCP via ATRP, the resulting branched polymers carry one bromoester function per inimer unit, and the functionality decreases with comonomer (DEAEMA) composition. As can be seen in Figure 11, the bromine contents of the branched polymers are dependent upon the comonomer composition in the feed and are in fair agreement with the calculated

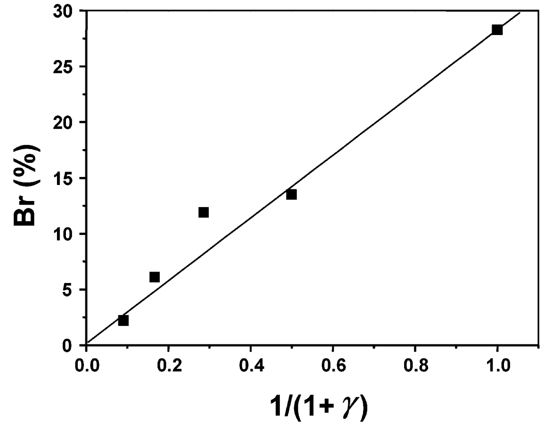


Figure 11. Dependence of bromine contents on $1/(\gamma + 1)$. Samples: see Table 3. The calculated value (—) is given for comparison.

values. This is an indication that unfavorable termination and transfer reactions are essentially negligible under the condition used in this study, and the number of bromoester end groups can be simply determined by the comonomer ratio, γ, in the feed. This result also indicates the feasibility to use the bromoester end groups for further modifications and as the initiating part for polymerization of a second monomer.

Quaternization of Branched Poly(DEAEMA)s. The quaternization reaction was carried out using a 1.5–3-fold molar excess of methyl iodide in acetone at room temperature. In the cases of branched copolymers having higher γ value, the reaction was very fast with precipitation forming within 1–2 h. The pale yellow precipitate started to form after 2–5 h in the case of the copolymer with lower γ value, and the mixture was stirred for 24 h. The extent of quaternization was evaluated using ^{1}H NMR spectroscopy. Figure 12 shows the ^{1}H NMR spectra of the linear and branched poly(DEAEMA)s and their quaternized products in D_2O/DCl (pH ≈ 1). The characteristic methyl protons of the poly(DEAEMA) segment observed at 1.3 ppm decreases with decreasing γ value, whereas the characteristic peak at 1.7–2.2 ppm, which corresponds to methylene protons of the poly(DEAEMA) backbone and methyl protons adjacent to a bromine atom, increases, suggesting the increase of the inimer content. The tendency is the same as that of ^{1}H NMR results in $CDCl_3$. After quaternization of the branched poly(DEAEMA), peaks A, B, and C are shifted downfield from 3.3, 3.6, and 3.9 ppm to 3.5, 3.8, and 4.5 ppm, respectively. Further, a new peak, E, appeared at 3.0–3.2 ppm because of the quaternary methyl group. The same tendency was also observed in the linear poly(DEAEMA), which is in good agreement with the result reported by Bütün et al.[55] The degree of quaternization was determined to be ca. 100% by comparing the integrals of peaks E and A. The difference between the linear and branched poly(DEAEMA)s is seen in the relative intensities of peaks attributed to the backbone and side chains. As can be compared in Figure 11b,d, the relative intensities of the methylene proton at 1.8–2.0 ppm in the branched poly(DEAEMA) are higher than those of linear ones, regardless of before and after quaternization.

As discussed in the previous section, it is possible to control the composition of DEAEMA, which corresponds to the number of charged monomer in the copolymer, the molecular weights, and branched architectures by varying the comonomer composition in the feed during SCVCP. Variation in the branched architectures and charged density provides a facile way to control their physical and solution properties. Similar to linear poly(DEAEMA), the branched poly(DEAEMA)s obtained by SCVCP are water-insoluble at a neutral pH and are only soluble in acidic media (pH ≲ 2) due to protonation of tertiary amine groups. The branched poly(DEAEMA)s are also soluble in many common solvents including THF, acetone, and $CHCl_3$. It must be noted that there is some difference in the solubility between linear and branched polymers. For example, the linear poly(DEAEMA) was dissolved within 5 min in acidic aqueous solution, while pure dissolution was only obtained after >2 h in the cases of the branched poly(DEAEMA)s having lower γ values (for example, more than 5 h for $\gamma = 1$). The branched architectures, molecular weights, and the number of nonpolar BIEM segments in the vicinity of DEAEMA segments should have an influence on the solution properties.

Since quaternization of the amine groups in the poly(DEAEMA) segment yields a strong cationic polyelectrolyte, the resulting branched polymers exhibit greatly

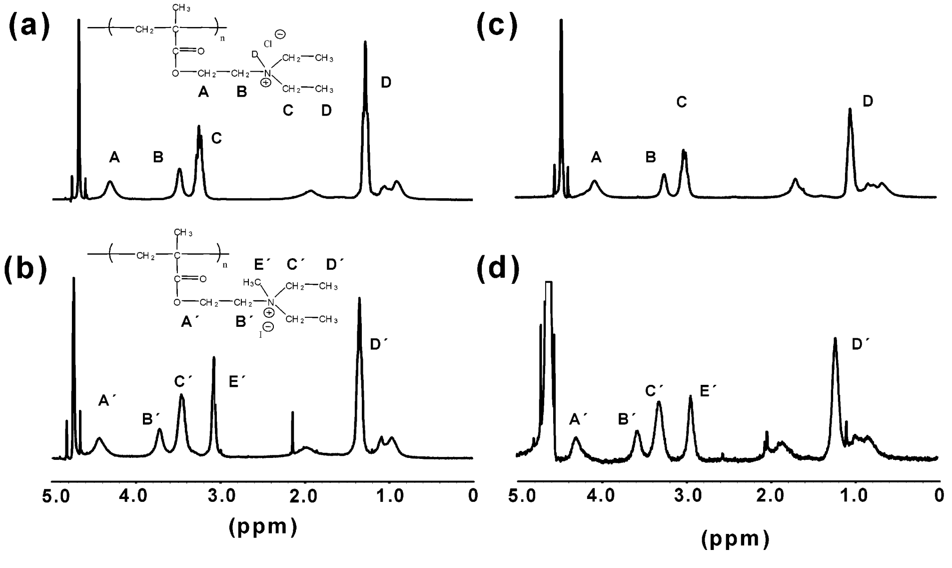


Figure 12. ^{1}H NMR spectra (D_2O/DCl, pH ≈ 1) of linear (a, b) and branched ($\gamma = 5$, c, d) poly(DEAEMA)s: (a, c) before quaternization and (b, d) after quaternization with MeI.

enhanced solubility in aqueous solution compared to the nonquaternized precursors. The quaternized products of the branched poly(DEAEMA)s in the range of $\gamma = 1-25$ are easily soluble in water at room temperature at a neutral pH value as well as in methanol and DMAc, while insoluble in most organic solvents. Further studies on this interesting branched polyelectrolytes, such as the influence of branched architectures on the chain configuration in aqueous solution under various salt concentrations and pHs, as well as interpolyelectrolyte complexation with oppositely charged polymers, such as poly(acrylic acid), will be reported separately.

Conclusions

We have demonstrated that the CuBr/HMTETA catalyst system could be successfully applied for homopolymerization of DEAEMA, homo-SCVP of BIEM, and SCVCP of BIEM and DEAEMA, which provide a monodisperse linear poly(DEAEMA) with controlled molecular weights, poly(BIEM)s with hyperbranched architectures, and randomly branched poly(DEAEMA)s, respectively. By quaternization with MeI, water-soluble cationic polyelectrolytes with controllable branched structures were obtained, which can provide viable tailored materials with unique properties for various applications, such as chemical sensing and gene delivery systems. This work substantially broadens and extends the scope of branched polyelectrolytes, in which the compact structures due to the branched architectures and charge densities can be manipulated simply by the nature and composition of comonomer.

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