Copolymerization of *N*,*N*-Dimethylacrylamide with *n*-Butyl Acrylate via Atom Transfer Radical Polymerization

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ABSTRACT: The (co)polymerization of *N*,*N*-dimethylacrylamide (DMAA) was performed by atom transfer radical polymerization (ATRP). Using methyl 2-chloropropionate/CuCl/Me_6TREN as the initiating/catalyst system in toluene solution, at room temperature, high molecular weight homopolymers (M_n up to 50 000) with narrow molecular weight distribution (M_w/M_n = 1.05−1.13) were prepared. The controlled polymerization of DMAA has been extended to simultaneous copolymerization with *n*-butyl acrylate (*n*BA), which resulted in a comparable rate of conversion for each monomer, indicating formation of a nearly random copolymer. The reactivity ratios of DMAA and *n*BA in ATRP are similar: $r_{DMAA} = 1.16$ and $r_{nBA} = 1.01$. Block copolymers of *n*BA and DMAA, with two different polymerization degrees of the second block (DP_{DMAA} = 65 and 100), were synthesized using a well-defined P*n*BA-Br (DP_{nBA} = 140) macroinitiator. The other approach to block copolymer formation using extension of PDMAA-Cl (DP_{DMAA} = 160) with *n*BA was used, and block copolymers with DP_{nBA} = 50 and 100 were prepared.

Introduction

Polyacrylamides found numerous applications because of their biocompatibility and hydrophilic/water-soluble properties.[1,2] They were synthesized using ionic (which is limited to N,N-disubstituted acrylamides) and free radical polymerization (FRP). Conventional FRP of acrylamides yields poorly defined polymers, but recently, a range of well-defined polyacrylamides have been prepared by different controlled/living radical polymerization (CRP) methods. Although nitroxide-mediated radical polymerization with TEMPO failed,[3] polymerizations conducted with more reactive alkoxyamines were successful.[4] Atom transfer radical polymerization (ATRP)[5−8] of substituted acrylamides has been reported with both copper-[9−11] and ruthenium-based catalysts[12] as well as a surface-initiated polymerization from silica.[13−15] Additionally, reversible addition−fragmentation chain transfer (RAFT) polymerization of acrylamides has been described.[16−19]

The ATRP polymerization of *N*,*N*-dimethylacrylamide (DMAA) with catalysts prepared from copper halides complexed with linear amines or bipyridine based ligands yielded low conversion of monomer to polymer in either bulk or solution.[9] However, well-controlled ATRP of DMAA, and other acrylamides, has been achieved using methyl 2-chloropropionate as initiator, and CuCl complexed with Me_6TREN as catalyst, in toluene at room temperature, but the synthesis provided a polymer with limited molecular weight, $M_n \sim 10\,000$, despite a low polydispersity $M_w/M_n < 1.2$ being attained.[10]

Amphiphilic or double hydrophilic block copolymers with a PDMAA block can reversibly change their solubility in water depending on temperature or pH. These block copolymers are of commercial interest and such materials have been prepared. One of them was synthesized using a potassium PDMAA macroinitiator to initiate the anionic living polymerization of styrene and butadiene.[20] DMAA has been copolymerized with methyl methacrylate to form both random and block copolymers using a Ru(II)-based catalyst.[21] Block copolymers of DMAA with 4-vinylpyridine[22] and with *N*-hexadecyl-4-vinylpyridinium bromide[23] have been prepared by nitroxide-mediated radical polymerization. Another block copolymer with poly(*n*-butyl acrylate) was synthesized by ATRP using *N*-(2-hydroxypropyl)methacrylamide.[24]

In this paper, we report the synthesis of PDMAA using the initiating system methyl 2-chloropionate/CuCl/Me_6TREN to produce polymers with degrees of polymerization significantly higher than previously reported. By adjusting the initial reaction conditions, we were able to extend homopolymerization of DMAA to polymers with molecular weight $M_n \sim 50\,000$ while retaining low polydispersity (M_w/M_n = 1.12). These conditions also allowed to prepare both random and block copolymers of DMAA and *n*BA.

Experimental Section

N,*N*-Dimethylacrylamide (DMAA, Aldrich 99%) and *n*-butyl acrylate (*n*BA, Aldrich, 98%) were stirred over calcium hydride for 2 h, distilled under vacuum, and stored at −15 °C under an inert gas atmosphere. Methyl 2-chloropropionate (MeClPr, Aldrich, 97%) and ethyl 2-bromopropionate (EtBrPr, Aldrich, 99%) were used as received. Copper(I) chloride (CuCl, Acros, 95%) and copper(I) bromide (CuBr, Aldrich, 98%) were purified by stirring over glacial acetic acid (Fisher Scientific), followed by filtration and washing the remaining solid three times with ethanol and twice with diethyl ether prior to drying under vacuum for 1 day. Tris(2-dimethylaminoethyl)amine (Me_6TREN)[25] and 4,4′-di(5-nonyl)-2,2′-bipyridyne (dNbpy)[26] were prepared as previously described. A stock solution of copper(II) bromide (Aldrich, 99%) complexed by ligand $CuBr_2/(dNbpy)_2$ in butanone was prepared (0.595 g of $CuBr_2$ in 100 g of solution). All solvents and internal standards were used without further purification.

Gel Permeation Chromatography (GPC). Measurements were conducted in DMF (50 °C) using three columns with PSS SDV gel (5 × 10^4, 10^3, 100 Å; Polymer Standards

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Scheme 1. (a) Homopolymerization of DMAA and (b) Copolymerization of DMAA with *n*BA

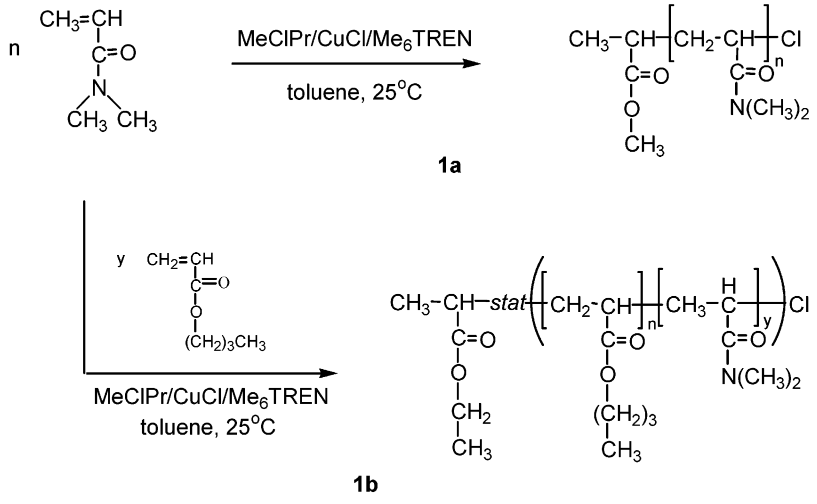

Table 1. Polymerization of DMAA under Different Initial Conditions[a]

no.	$[M]_0$:$[I]_0$:$[CuCl]_0$:$[Me_6TREN]_0$ (M/solvent) (wt/vol); T	time (h)	conv (%)	$M_{n,th}$	$M_{n,GPC}$	M_w/M_n
I	50:1:0.5:0.5 (1/1); 35 °C	55	75.1	3 800	5 000	1.08
II	100:1:2:2 (1/3); 20 °C	2	79.0	7 900	12 300	1.05
III	150:1:2:2 (1/1); 20 °C	4	70.0	10 500	16 200	1.06
IV	250:1:2:2 (1/3); 20 °C	21	58.4	14 600	16 700	1.06
V	500:1:3:3 (1/1); 25 °C	18	70.9	35 400	39 100	1.10
VIA	750:1:3:3 (1/2); 20 °C	72	50.3	37 700	34 600	1.13
VIB	750:1:2:2 (1/1); 20 °C	22	66.8	50 100	52 600	1.12

[a] M = DMAA, I = MeClPr, solvent = toluene.

Service) in series with a Waters 410 differential refractometer and a Waters 515 liquid chromatograph pump (1 mL/min) with toluene as an internal standard. The molecular weights of the copolymers were determined on the basis of use of low-polydispersity poly(methyl methacrylate) (PMMA) standards.

Gas Chromatography (GC). The conversion of monomer was measured using a Shimadzu GC-14A gas chromatograph (GC) equipped with a wide-bore capillary column (30 m, DB-Wax, J&W Sci.) and a FID detector. Toluene or butanone was used as internal standard. Conditions: injector and detector temperature, 250 °C; initial column temperature, 40 °C; isotherm, 0 min; heating, 20 °C/min; final column temperature, 190 °C; isotherm, 3 min.

Homopolymerization—Synthesis of PDMAA. DMAA, toluene, and copper(I) chloride were added to a 10 mL Schlenk flask and degassed by three freeze−pump−thaw cycles. After stirring the mixture at room temperature for 0.5 h, Me_6TREN was added and the flask was placed in a thermostated bath for 10 min. Finally, the initiator, MeClPr, was added to start the reaction. The polymerization was stopped by opening the flask and exposing the catalyst to air. The reaction mixture was then diluted in methylene chloride and passed through a column filled with neutral alumina to remove the copper complex. The solvent and monomer were removed by distillation under high vacuum at room temperature until the residue attained constant weight.

Random Copolymerization—Synthesis of P(DMAA-*co*-*n*BA). Equimolar amounts of DMAA (1.8 mL, 13.2 mmol) and *n*BA (1.2 mL, 13.2 mmol), toluene (3 mL), and CuCl (5.25 mg, 0.05 mmol) were added to a 10 mL Schlenk flask and then degassed by three freeze−pump−thaw cycles. After stirring for 0.5 h at room temperature, Me_6TREN (13.75 μL, 0.05 mmol) was added, and the flask was placed in a thermostated bath for 10 min to complete formation of the catalyst complex. Finally, MeClPr (6 μL, 0.05 mmol) was added, and the polymerization was conducted at 25 °C. The same purification procedure described above was then applied. Other statistical copolymerizations were performed at higher temperature, 50 °C, using 4 times higher concentrations of CuCl and ligand.

To determine the monomer reactivity ratios, two experiments were performed: one with initial ratio of the comonomers $[DMAA]_0$:$[nBA]_0$ = 0.95:0.05 and the other 0.05:0.95.

Block Copolymerization—Synthesis of P*n*BA-*b*-PDMAA. The P*n*BA macroinitiators were prepared under the following typical ATRP conditions: CuBr (0.037 g, 0.26 mmol), dNbpy (0.212 g, 0.52 mmol), $CuBr_2$ stock solution (0.4158 g, 5% of Cu(II)), butanone (0.6 mL, 10 vol %), *n*BA (5.59 mL, 39.0 mmol), and EtBrPr (0.047 mL, 0.26 mmol) were added to a 25 mL Schlenk flask and degassed by three freeze−pump−thaw cycles. The polymerization was conducted under stirring the reaction at 80 °C and was terminated after 18 h by exposing the reaction to air (after 63.3% of monomer conversion). The polymer was recovered after filtration through an alumina column to remove the catalyst by addition to methanol.

The macroinitiator (0.31 g, 0.0186 mmol; M_n = 17 500; DP_n = 140, M_w/M_n = 1.12) was dissolved in toluene (1.0 mL). DMAA (0.5 mL, 4.65 mmol) and Me_6TREN (14.7 μL, 0.0558 mmol) were added, and the mixture degassed by three freeze−pump−thaw cycles. Then CuCl (5.5 mg, 0.0558 mmol) was added to start the reaction. The reaction temperature was either 25 or 50 °C.

Block Copolymerization—Synthesis of PDMAA-*b*-P*n*BA. PDMAA (synthesis described above) used as the macroinitiator (0.32 g, 0.0192 mmol) was dissolved in butanone (0.7 mL). *n*BA (0.7 mL, 4.8 mmol) and dNbpy (15.7 mg, 0.0384 mmol) were then added to the solution, and the mixture was degassed by three freeze−pump−thaw cycles. CuCl (1.9 mg, 0.0192 mmol) was added before starting the reaction by heating to 80 °C.

Results and Discussion

Homopolymerization—Synthesis of PDMAA. A series of polymerizations of DMAA were performed according to Scheme 1a, using different monomer/initiator/catalyst (DMAA/MeClPr/CuCl) ratios and different amounts of solvent (toluene). The conditions are summarized in Table 1.

Table 2. Synthesis of Random Copolymer P(DMAA-*co*-*n*BA)[a]

no.	$[DMAA]_0:[nBA]_0:[I]_0:[CuCl]_0:[Me_6TREN]_0$ monomer/solvent (wt/vol); T	time (h)	conv (%) nBA	conv (%) DMAA	$M_{n,GPC}$	M_w/M_n
VIIA	250:250:1:1:1 (1/1); 50 °C	10	15.8	20.0	9 800	1.12
VIIB	250:250:1:4:4 (1/1); 25 °C	3.5	46.6	55.6	23 100	1.34
VIIC	475:25:1:1:1 (1/1); 25 °C	24	25.6	29.2	15 600	1.22
VIID	25:475:1:1:1 (1/1); 25 °C	24	25.7	25.3	12 800	1.18

[a] I = MeClPr, solvent = toluene.

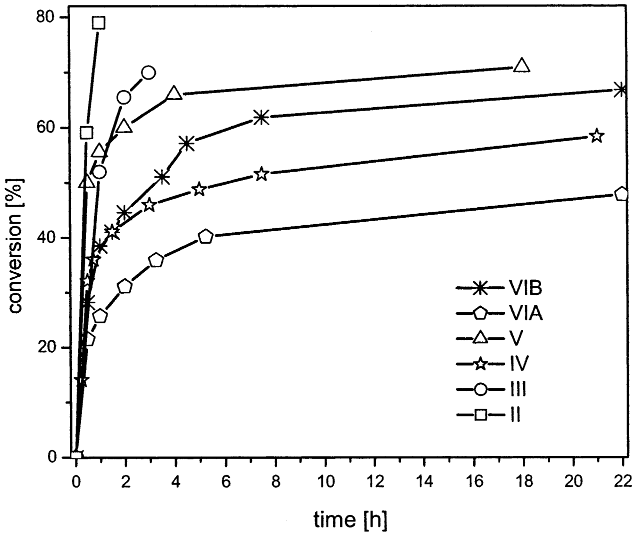

Figure 1. Conversion vs time curves for polymerization of DMAA. Initial conditions presented in Table 1.

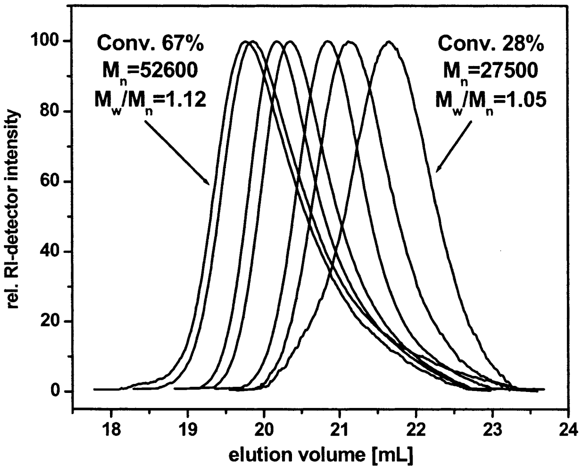

Figure 2. GPC traces of PDMAA (VIB). Conditions: $[DMAA]_0$:$[MeClPr]_0$:$[CuCl]_0$:$[Me_6TREN]_0$ = 750:1:2:2; DMAA:solvent = 1:1 (w/v); solvent = toluene, T = 20 °C.

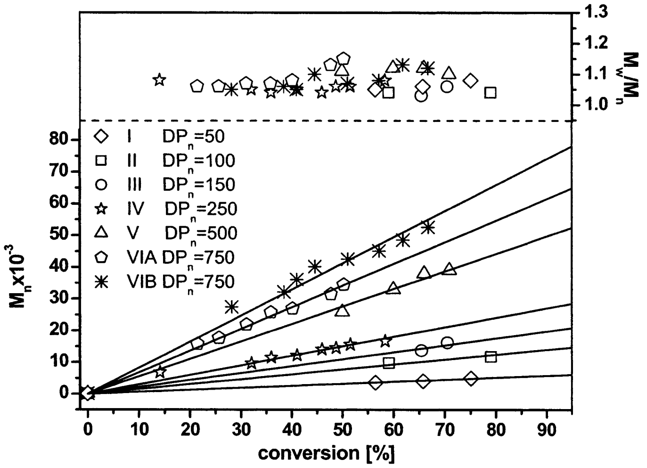

Figure 3. Dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on monomer conversion for the polymerization of DMAA. Initial conditions presented in Table 1.

Initially, conditions that allowed the synthesis of PDMAA with a lower degree of polymerization, DP_n = 50−100 (I and II in Table 1), were determined. Higher molecular weight PDMAA was then prepared by increasing the monomer/initiator ratio. The reaction was driven to higher conversion by increasing the ratio of catalyst to initiator and reducing the amount of solvent. The polymerization (III) had both high reaction rate and high monomer conversion. When conducting the polymerization at an even higher ratio of monomer/initiator, in more diluted system (IV), rate of polymerization slowed down. In the next reaction (V), using both higher ratio monomer/initiator and higher amount of catalyst, but reduced amount of solvent, a monomer conversion of 71% was reached within 18 h. A further increase in monomer/initiator ratio (750:1, VIA) produced higher molecular weight polymer. To reduce the viscosity, the reaction mixture was diluted with more toluene, resulting in a slower reaction; only 50% DMAA was converted into polymer after 3 days. Smaller amounts of toluene led to higher conversion (67%) within a shorter time 22 h (VIB) and provided a high molecular weight PDMAA (M_n ∼ 50 000).

These results confirmed the earlier observations[10] on limited conversion of monomer to polymer (Figure 1), indicating the occurrence of termination reactions or loss of the catalyst. However, the limited conversion cannot be explained by a total decomposition of the growing centers, since this would provide polymers with much higher polydispersity. The lower molecular weight tailing in the GPC chromatogram (Figure 2) suggests chain-breaking reactions, but the GPC traces are still monomodal with relatively narrow MWD, indicating significant control over DMAA polymerization. The molecular weights increased linearly with conversion, and the overall polydispersity remained low throughout the polymerization (Figure 3). In almost all cases (especially at higher molar masses), the values of M_n measured vs linear PMMA standards were in a fair agreement with the theoretical values (Table 1).

Random Copolymerization—Synthesis of P(DMAA-*co*-*n*BA). DMAA was copolymerized with nBA (Scheme 1b) using the same catalyst system (MeClPr/CuCl/Me_6TREN) described above for DMAA homopolymerization (Table 2).

Copolymers (VIIA,B) with different degrees of polymerization were synthesized by adjusting the reaction conditions. Higher catalyst levels and higher reaction temperature lead to faster reactions and higher conversion (VIIB). The molecular weights increased linearly with conversion, but some tailing in GPC traces was noticed (Figure 4). Similar control was observed for

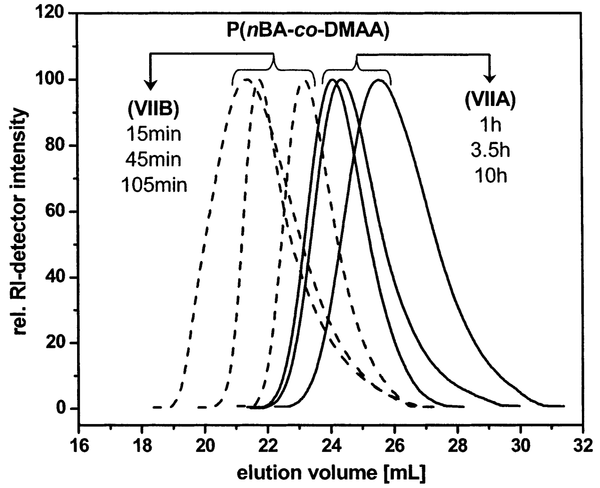

Figure 4. GPC traces of random copolymers PDMAA-*co*-P*n*BA (VIIA,B). Initial conditions presented in Table 2.

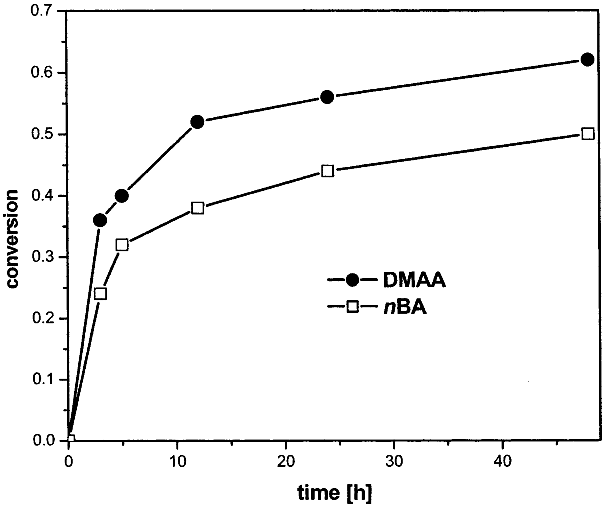

Figure 5. Time–conversion plot of the copolymerization of DMAA and *n*BA (VIIB). Conditions: $[\mathrm{DMAA}]_0$:$[n\mathrm{BA}]_0$:$[\mathrm{MeClPr}]_0$:$[\mathrm{CuCl}]_0$:$[\mathrm{Me_6TREN}]_0$ = 250:250:1:4:4; monomer:solvent = 1:1 (w/v); solvent = toluene, T = 50 °C.

reactions using excess of either DMAA or *n*BA (VIIC,D).

Time–conversion plots indicate slightly faster incorporation of DMAA than *n*BA into the copolymer when an equimolar ratio of monomers was used (Figure 5). In the literature, the copolymerization reactivity ratios of DMAA with some acrylates were reported for conventional copolymerization. The systems DMAA/2-methoxyethyl acrylate ($r_1 = 1.11$, $r_2 = 0.63$)[27] and DMAA/2-(*N*-ethylperfluorooctanesulfonamido)ethyl acrylate ($r_1 = 1.22$, $r_2 = 0.63$)[28] indicated higher reactivity of DMMA monomer, whereas the copolymerization of DMAA with ethyl acrylate or 2-ethylhexyl acrylate resulted in random composition of copolymers.[29] The monomer reactivity ratios, for system presented in this paper, were estimated by the Jaacks method[30] at high and low monomer feed ratios ($[\mathrm{DMAA}]_0$:$[n\mathrm{BA}]_0$ = 19 and 0.05, VIIC and VIID, respectively). Their values were calculated from the Jaacks plots: $-\ln(1 - x_{\mathrm{DMAA}}) = r_{\mathrm{DMAA}} \times -\ln(1 - x_{n\mathrm{BA}})$, yielding $r_{\mathrm{DMAA}} = 1.16 \pm 0.03$ (Figure 6a) and $-\ln(1 - x_{n\mathrm{BA}}) = r_{n\mathrm{BA}} \times -\ln(1 - x_{\mathrm{DMAA}})$, yielding $r_{n\mathrm{BA}} = 1.01 \pm 0.03$ (Figure 6b). These values indicate formation of a nearly random copolymer.

Block Copolymerization—Synthesis of P*n*BA-*b*-PDMAA and PDMAA-*b*-P*n*BA. Block copolymers were synthesized by two different procedures. In the first approach, DMAA was polymerized from a well-defined P*n*BA-Br (M_n = 17 500; DP = 140, M_w/M_n = 1.12) macroinitiator (Scheme 2a). Two P*n*BA-*b*-PDMAA block copolymers with different degrees of polymerization for the second block were prepared: one with $\mathrm{DP_{DMAA}}$ = 100 (VIIIA) and one with $\mathrm{DP_{DMAA}}$ = 65 (VIIIB) (Table 3). Both have low polydispersity (M_w/M_n < 1.2) and monomodal GPC traces (Figure 7).

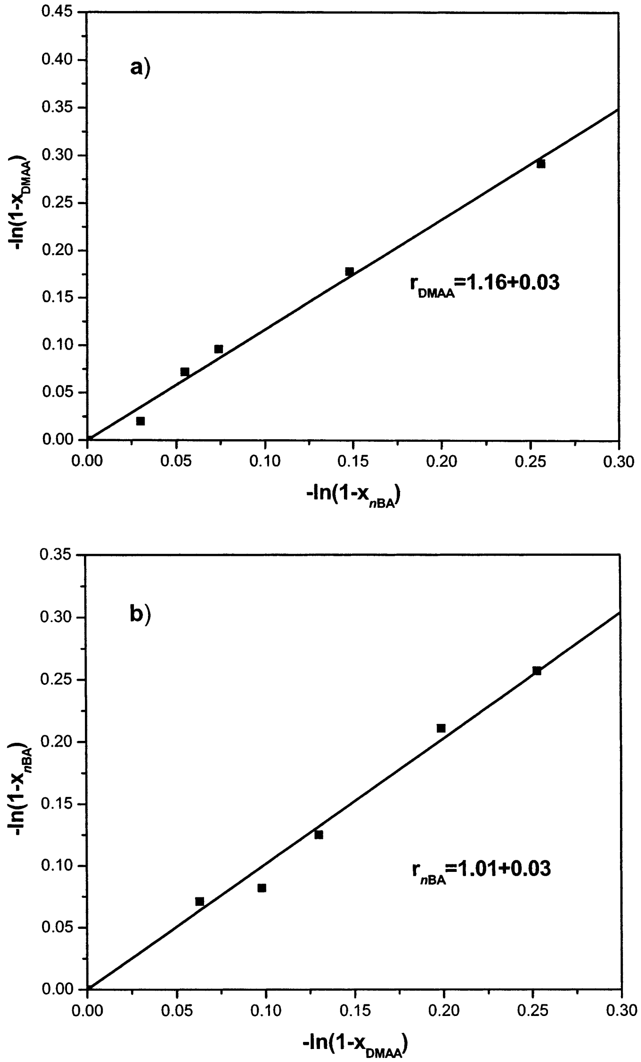

Figure 6. Jaacks plots of the ATRP at comonomers ratio (a) $[\mathrm{DMAA}]_0$:$[n\mathrm{BA}]_0$ = 19 and (b) $[\mathrm{DMAA}]_0$:$[n\mathrm{BA}]_0$ = 0.05. Conditions: $[\mathrm{M}]_0$:$[\mathrm{I}]_0$:$[\mathrm{CuCl}]_0$:$[\mathrm{Me_6TREN}]_0$ = 500:1:1:1; monomer: solvent = 1:1 (w/v); solvent = toluene, T = 25 °C.

The other approach to prepare block copolymers, presented in Scheme 2b, is chain extension from PDMAA-Cl (III) (M_n = 16 200; DP = 160, M_w/M_n = 1.06) with *n*BA. This approach also yielded block copolymers PDMAA-*b*-P*n*BA (IXA, $\mathrm{DP}_{n\mathrm{BA}}$ = 50; IXB, $\mathrm{DP}_{n\mathrm{BA}}$ = 100) with monomodal molecular weight distribution (Figure 8) and values of polydispersity around 1.25 (Table 3). The GPC traces of both block copolymers, P*n*BA-*b*-PDMAA and PDMAA-*b*-P*n*BA, show quantitative initiation of the second block.

Conclusions

Well-defined PDMAA homopolymers with high degrees of polymerization ($\mathrm{DP_n}$ = 120–530) and low polydispersity (M_w/M_n = 1.05–1.13) were synthesized

Scheme 2. (a) Synthesis of Block Copolymer P*n*BA-*b*-PDMAA and (b) Synthesis of Block Copolymer PDMAA-*b*-P*n*BA

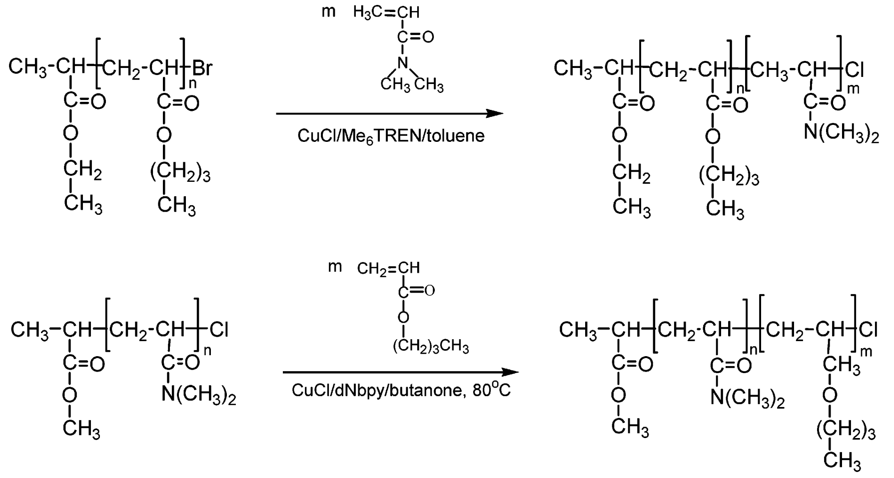

Table 3. Synthesis of Block Copolymer P*n*BA-*b*-PDMAA[a]

no.	$[M]_0$:$[MI]_0$:$[CuCl]_0$:$[L]_0$ monomer/solvent (wt/vol); *T*	time (h)	conv (%)	$M_{n,GPC}$	M_w/M_n	DP_{nBA}/DP_{DMAA}
VIIIA	250:1:3:3 (1/2); 25 °C	21	51.5	27 600	1.17	140/100
VIIIB	250:1:3:3 (1/2); 50 °C	24	25.6	24 700	1.14	140/65
IXA	250:1:1:2 (1/2); 80 °C	20	19.5	22 300	1.27	50/160
IXB	250:1:1:2 (1/1); 80 °C	24	40.5	25 900	1.25	100/160

[a] VIIIA,B: M = DMAA, MI = P*n*BA-Br (M_n = 17 500, M_w/M_n = 1.12), L = Me_6TREN, solvent = toluene. IXA,B: M = *n*BA, MI = PDMAA-Cl (M_n = 16 200, M_w/M_n = 1.06), L = dNbpy, solvent = butanone.

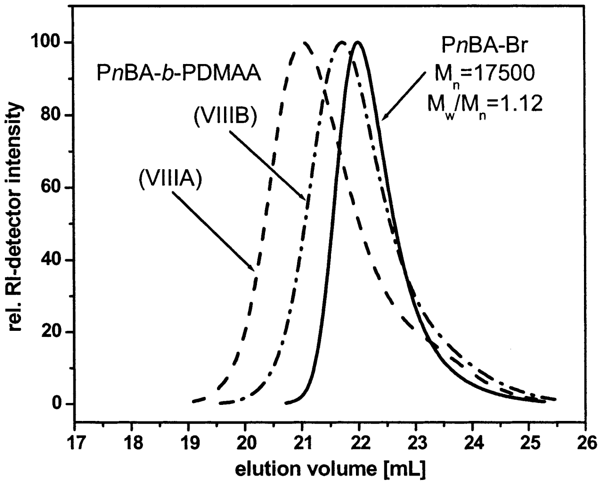

Figure 7. GPC traces of block copolymer P*n*BA-*b*-PDMAA (VIIIA,B). Initial conditions presented in Table 3.

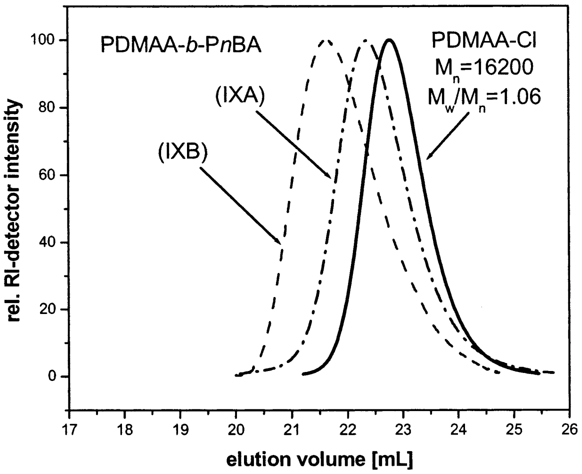

Figure 8. GPC traces of block copolymer PDMAA-*b*-P*n*BA (IXA,B). Initial conditions presented in Table 3.

using MeClPr/CuCl/Me_6TREN as the initiator/catalyst system in an ATRP. Simultaneous copolymerization indicated slightly higher reactivity of DMAA than nBA, leading to the copolymers with a nearly random composition. The reactivity ratios of the comonomers, calculated by the Jaacks method, are $r_{DMAA} = 1.16$ and $r_{nBA} = 1.01$. A P*n*BA-Cl macroinitiator was successfully used for chain extension with DMAA to form a block copolymer. Chain extension of PDMAA with *n*BA in the presence of a CuCl catalyst resulted in the preparation of a block copolymer with a well-defined second block.

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