Synthesis and Characterizations of Block Copolymer of Poly(*n*-butyl acrylate) and Gradient Poly(methyl methacrylate-*co*-*N*,*N*-dimethyl acrylamide) Made via Nitroxide-Mediated Controlled Radical Polymerization

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ABSTRACT: Methyl methacrylate (MMA)/*N*,*N*-dimethyl acrylamide (DMA) gradient copolymers with various chemical composition were synthesized by nitroxide-mediated controlled radical polymerization (NMP). Molecular weight (MW) characterization via gel permeation chromatography demonstrated that these materials were made in a "controlled" manner. The reactivity ratios values r_1(MMA) = 2.36 and r_2(DMA) = 0.33 were experimentally determined using the linear least-squares numerical method, results in good agreement with the literature. Characterization of the glass transition temperature, T_g, by differential scanning calorimetry (DSC) of gradient copolymers exhibited one T_g, with a value intermediate to the T_g of pure poly(methyl methacrylate) (PMMA) and poly(*N*,*N*-dimethyl acrylamide) (PDMA). In contrast, di- and triblock copolymers made of poly(*n*-butyl acrylate) (PBA) as central block and PMMA/PDMA gradient copolymer as external block yielded two T_g, one corresponding to the T_g of PBA and the other intermediate to the T_g of PMMA and PDMA, indicating microphase separation which was confirmed by dynamic mechanical analysis and TEM observations of films of di- and triblock copolymers showing lamellae structure.

Introduction

Block copolymers, because of their very nature, self-assemble into well-ordered nanoscale structure, which makes them of importance in many technological areas. Indeed, they can be used to obtain low dielectric constant film for microelectronic industry,[1] transparent materials with high refractive index for optical applications,[2] or toughened polymer networks.[3] The nanostruration of block copolymers in the solid state or in selective solvents results from the competition between chain connectivity and blocks immiscibility. The block copolymer must have an amphiphilic character, i.e., it must have two or more blocks of different chemical structure.

The self-assembling power of block copolymers is also retained in their mixtures with numerous homopolymers.[4−7] Block copolymers in this respect appear as promising materials in the development of new formulation methods. This property of block copolymers, triblock copolymers in particular, is exploited in SBM (polystyrene-*b*-polybutadiene-*b*-poly(methyl methacrylate) triblock copolymers[8,9] and SBG (polystyrene-*b*-polybutadiene-*b*-poly(glycidyl methacrylate) triblock copolymers)[10] reinforced materials. Ideal blending conditions are fulfilled when the homopolymer is compatible with one of the copolymer's blocks.

A case of particular interest is the blend of block copolymers with epoxy thermosets.[8,11−15] Because of the miscibility criteria, in most cases, a given block copolymer is efficient in only one or few systems. Ideal is finding a block copolymer, having one block copolymer able to nanostructure several thermoset systems up to the end of the reaction. We aimed to develop the block copolymers AB and BAB, which remain miscible as long as the reaction and the nanostruration is preserved in two model epoxy systems. These two epoxies are constituted of the same epoxy prepolymer, diglycidylether of bisphenol A (DGEBA) and the 4,4′-methylenebis(3-chloro-2,6-diethylaniline (MCDEA) or 4,4′-diaminodiphenylsulfone (DDS) as hardeners, two diamines with very different reactivity and solubility parameters.

Starting from the previous studies,[8,9] the choice of A, the immiscible soft block, is pure poly(*n*-butyl acrylate) (PBA) and B block is poly(methyl methacrylate-*co*-*N*,*N*-dimethyl acrylamide) (P(MMA-*co*-DMA) random copolymer, where DMA is a monomer more polar than MMA.

The efficient control of the structure and the architecture of block copolymers could be obtained through controlled/living radical polymerization (LRP). LRP covers different techniques including atom transfer radical polymerization (ATRP),[16−19] nitroxide mediated polymerization (NMP),[20−22] and reversible addition fragmentation chain transfer (RAFT).[23,24] These different methods are usually used in research laboratories for the synthesis of many well-defined polymer architectures with targeted molecular weight and narrow molecular weight distribution but not extrapolated into the industrial scale.

In the present work, first, we investigated on the synthesis of random copolymers of MMA and DMA using NMP method and the determination of their reactivity ratios. Up to day, the polymerization of MMA monomer by NMP method led to a no controlled polymerization. However, the copolymerization of MMA and a comonomer, which is well controlled by NMP

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Scheme 1. Mediated Radical and Alkoxyamines

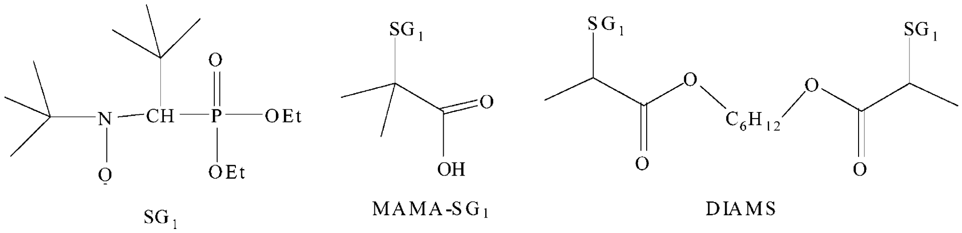

Table 1. Copolymerization Data for Gradient Copolymerization of MMA and DMA in 1,4-Dioxane at 100 °C

sample	MMA, g	DMA, g	$(f_{\mathrm{MMA}})_{\mathrm{o}}$	F_{MMA}	convn, %	$M_{\mathrm{n,SEC}}$	$M_{\mathrm{w}}/M_{\mathrm{n}}$
MMA/DMA1	18.21	2.02	0.899	0.931	64	26 700	1.38
MMA/DMA2	16.21	4.00	0.800	0.862	61	24 400	1.36
MMA/DMA3	14.22	6.01	0.701	0.784	65	25 600	1.32
MMA/DMA4	11.22	9.00	0.552	0.662	66	25 200	1.30
MMA/DMA5	8.22	12.02	0.404	0.508	59	17 300	1.25

can lead to a controlled polymerization of MMA. This copolymerization method using styrene as comonomer was applied experimentally by Benoit[25] and Miura[26] and theoretically investigated by Fischer.[27] Even though some improvements could be observed, no clear control was reached. Charleux et al.[28,29] was the first to demonstrate that the nitroxide-mediated polymerization of methyl methacrylate using the alkoxyamine based on the *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide (named SG1) can be achieved at 90 °C with high conversion, high quality of control and high degree of livingness by introducing a small amount (8.8%) of styrene. The resulting random copolymer was used to reinitiate the polymerization of styrene and *n*-butyl acrylate with success leading to the formation of block copolymers. In a recent study, Dufils[30] showed that the copolymerization of MMA/BA system with SG1-based alkoxyamine derived from methacrylic acid [HO−C(O)−C(CH_3)$_2$−SG1] was also a controlled radical copolymerization within the molar fraction of MMA ≤ 0.7. For our MMA/DMA system, detailed studies concerning the control character of the polymerization will presented.

Second, we prepared the diblock and triblock copolymer using also NMP method. In parallel of the synthesis investigations, the morphological analysis using transmission electronic microscopy (TEM) and the thermal properties characterization via differential scanning calorimetry and rheological measurements were also undertaken.

Experimental Section

Materials. The stable radical *N*-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide, SG1 (85%), and the alkoxyamine mono and bifunctional based on SG1: methyl methacrylic acid−SG1 (MAMA−SG1, >99%) and DIAMS (82%) respectively (Scheme 1) were kindly supplied by Arkema. Methyl methacrylate (MMA, Aldrich, 99%), *N*,*N*-dimethyl acrylamide (DMA, Aldrich, 99%), *n*-butyl acrylate (BA, Aldrich, 99%) were used as received. Deuterated solvents (Eurisotop Laboratories) and all other solvents (1,4-dioxane, diethyl ether, ethanol) were purchased from commercial sources and used without any further purification.

Synthesis of Random Copolymers. Alkoxyamine (MAMA−SG1, 0.5 mmol) and monomers (DMA and MMA) in various mole fraction (total monomer mix = 20 g) were mixed and the copolymerization was carried out in solution using 1,4-dioxane as solvent (see Table 1). The monomers concentration was 50 wt %. Targeted molecular weight was fixed at 40 000 g/mol for all experiments. The solution was purged by bubbling nitrogen for 30 min to remove all dissolved oxygen. The resulting mixture was then introduced into a 100 mL three-neck round-bottom flask heated at 100 °C, immersed in a thermostatically controlled silicone oil bath and fitted with a reflux condenser, a nitrogen inlet, and a thermometer. During the polymerization, samples were taken periodically to analyze conversion by ^{1}H NMR and analyze molecular weight by SEC. The polymers were purified by precipitation in diethyl ether, filtered to remove the volatiles and dried under high vacuum at room temperature to a constant weight. All purified copolymers were bright, white powders.

Synthesis of Mono- and Difunctional PBA Macroinitiator. *n*-Butyl acrylate, SG1 and MAMA−SG1 or DIAMS (the [SG1]/[alkoxyamine] ratio was 0.05) were placed in a three-neck flask equipped with a reflux condenser and a magnetic stir bar. The system was purged with a nitrogen flow at least 30 min at room temperature before starting the polymerization. The reactor was quickly heated to desired temperature, 120 °C. In order to determine the monomers conversion and the molecular weight, samples were withdrawn at time intervals and NMR and SEC were performed. The polymerizations were stopped between 65% and 85% conversion to improve the livingness chain end of PBA macroinitiator. The residual monomers were removed by vacuum distillation (5 mmHg) at 50 °C during 3 h.

Synthesis of PBA-*b*-P(MMA-*co*-DMA) Diblock Copolymer and P(MMA-*co*-DMA)-*b*-PBA-*b*-P(MMA-*co*-DMA) Triblock Copolymer. The preparation of block copolymer based on PBA was performed in the same way that synthesis of gradient copolymer. The resulting PBA−SG1 or SG1−PBA−SG1 was used as a macroinitiator. The copolymerization was performed in 1,4-dioxane at 100 °C. The concentration of monomer plus macroinitiator in the mixture was 50 wt %. Targeted molecular weights of P(MMA-*co*-DMA) part were fixed at 50 000 g/mol for diblock and triblock copolymer. The molar ration of MMA and DMA was 70/30. Polymer was precipitated in ethanol/water mixture (20/80 v/v). The solvent was removed by filtering and copolymer was dried under high vacuum at 40 °C to a constant mass.

Analysis. Monomer conversion and copolymer composition were determined by ^{1}H NMR spectroscopy using a Brüker AV300 MHz spectrometer. Deuterated chloroform ($CDCl_3$) was used as solvent, and tetramethylsilane (TMS) served as internal standard.

Molecular weights were determined on crude samples by size exclusion chromatography (SEC) operated at 30 °C and calibrated with 10 samples of polystyrene standards from Polymer Laboratories. The molecular weight range of these used standards was comprised between 580 g/mol and 377 400 g/mol. SEC was performed with a Waters 515 liquid chromatography pump and two Styragel (HR4 and HR5) columns in series. The length of each column was 300 mm, the diameter 7.8 mm and the diameter of gel particles was 5 μm. Detection systems were a differential refractive index detector (Waters model 410) and a ultraviolet (UV) detector (Waters model 468). The eluent used was tetrahydrofuran with a flow rate of 1.0 mL/min. For poly(butyl acrylate) samples, the reported values are related to the universal calibration referenced against a primary polystyrene calibration with the following Mark−Houwink coefficients: $k_{\mathrm{PS}} = 11.4 \times 10^{-5}$ dL g^{-1} and $\alpha_{\mathrm{PS}} = 0.716$, and $k_{\mathrm{PBA}} = 12.2 \times 10^{-5}$ dL g^{-1} and $\alpha_{\mathrm{PBA}} = 0.700$.[31,32]

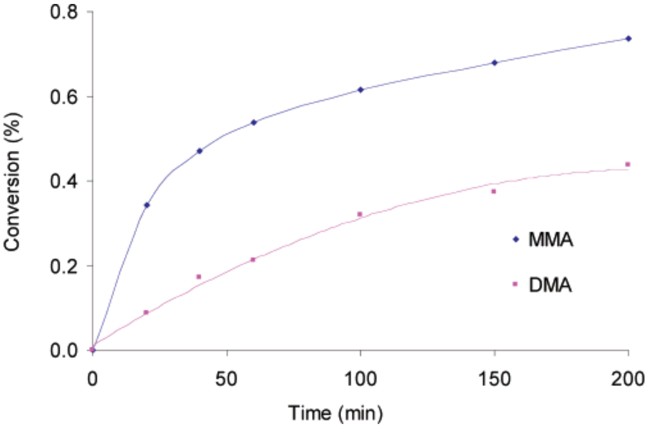

Figure 1. Time−conversion plot of the copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylamide for an initial mole fraction of methyl methacrylate $(f_{MMA})_o = 0.7$.

The DSC studies were carried out using a TA Instruments 2920 Modulated DSC. The modulation conditions include period of 60 s, and modulation amplitudes of ±0.8 °C. Cooling was accomplished with a Refrigerated Cooling system. Typical sample masses for modulated DSC were 3−5 mg. The samples were first heated to 180 °C and keep at this temperature for 5 min to erase any prior thermal history. Then the sample was cool to either room temperature for random copolymers or −100 °C for block copolymers to set the structure and analyzed by subsequent heating to 150 °C. The scanning rate was 3 °C/min. Multiple measurements (≥ 5) were made on all samples. The glass transition temperature (T_g) was chosen at the 50% change of the heat capacity which is close to the point of inflection.

The dynamic viscoelastic storage modulus (E') and loss tangent $= \tan \delta = E''/E'$ (E'' is the loss modulus) vs temperature (T) curves for the diblock and triblock copolymers were generated using a DMA Rheometrics Solid analyzer RSAII. Rectangular bars of the dimension 10 mm × 5 mm were sectioned from compression molded copolymer plaques. Sample thickness was approximately 0.5 mm. All samples were run in tensile mode with a heating rate and frequency of 2 °C/min and 1 Hz, respectively.

Transmission electron microscopy (TEM) analysis was used to examine the morphology of these materials. TEM micrographs were obtained by means of a Philips CM120 microscope utilizing 80 keV accelerating voltage. All specimens were sectioned with a diamond knife using a Reicherd-Jung Ultracut E microtome at −70 °C. Each section was then transferred from the edge of the diamond knife to a 600 hexagonal mesh copper grid. The thickness of the sections was about 70 nm. Electron density contrast between the soft and hard block domains was imparted through staining the sections with ruthenium tetroxide (RuO_4).

Results and Discussion

A. Copolymerization of MMA and DMA. A.1. Reactivity Ratios. A series of copolymers were prepared by nitroxide mediated polymerization of MMA and DMA with different feed composition using a SG1-based alkoxyamine derived from methacrylic acid [HO−C(O)−C(CH_3)$_2$−SG1] as initiator. The reactions were run up to conversion 59−65% yielding copolymers with $M_w/M_n = 1.25-1.40$. The molar fraction of monomer units incorporated in the copolymer was determined from the ^{1}H NMR spectra of copolymer samples prepared with different monomer feeds. The results for obtained copolymers are presented in Table 1.

The MMA/DMA copolymerization is a methacrylate/acrylamide system, difference reactivity ratios were expected. Most existing procedures for calculating reactivity ratios such as those proposed by Finneman and Ross[33] and by Kelen and Tüdös[34] can only be applied to experimental data at sufficiently low conversion, because calculation is based on the differential copolymerization equation.[35,36] The only exception is the extended Kelen−Tüdös method which involves a rather more complex calculation and it can be applied to medium conversion experimental data (in most cases, conversion can be as high as 40−50%).[37] With regard to high conversion of our copolymerization, we used a linear least-squares procedure proposed by Mao and Huglin[38] based on the integrated copolymerization equations developed by Lowry and Meyer.[39] This method is a numerical method to determine the reactivity ratios, which involves the values of conversion in the calculation and is applicable to very high values of conversion.[40−42] Use of this analysis procedure yielded:

$$r_1(\text{MMA}) = 2.36$$

$$r_2(\text{DMA}) = 0.33$$

The present findings are in good accord with literature values for this system at high conversion data.[43] The high value of r_{MMA} indicates that the probability of MMA entering the copolymer chain is much higher than that of DMA. In such system, where $r_1 \gg r_2$, a spontaneous gradient copolymer were formed, with densely MMA segments incorporated at the beginning of the copolymerization. Gradient copolymers possess a well-defined structure intermediate to that of block and random copolymer. They have a composition which changes gradually from predominantly sequences of one comonomer to the other as a fraction of the copolymer chain length.[44]

A.2. Copolymerization Kinetics. The nitroxide mediated polymerization of MMA and DMA was conducted in solvent medium at 100 °C for a targeted molecular weight of 40 000 g/mol. Time−conversion plots (Figure 1) reveal that MMA consumed at a faster rate than DMA, which was observed in each experiment. The different initial comonomers ratios lead to polymers with composition of MMA in the copolymer increasing with proportion of added MMA (Table 1).

To describe the copolymerization kinetic of MMA and DMA, we directly used the equation $\ln([M_0])/([M]) = (3/2)k_p((K[I_0])/(3k_t))^{1/3}t^{2/3}$ established by Fischer,[45] usually used to study the polymerization of monomer in the presence of nitroxide. Parts a and b of Figure 2 show kinetic data for five different feed ratios of MMA. The first-order kinetic plots of the gradient copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylamide, displayed in Figure 2a,b exhibit a linear increase of $\ln([M]_0/[M])$ vs $t^{2/3}$, indicating that the polymerizations of monomers pairs MMA/DMA obey a first-order dependence on monomer concentration.

Figure 3 plots M_n, $M_{n,th}$ and M_w/M_n vs conversion for gradient copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylate. Results show here are typical for all experiments studied in this paper. Figure 3 shows that measured molecular weights in copolymerization increase linearly with monomers conversion and are very close to theoretical values, which were calculated from the relation $M_{n,th} = M_{n,targeted}[\text{convn}_{DMA}(f_{DMA})_o + \text{convn}_{MMA}(f_{MMA})_o]$. However, we noted a slight difference between measured M_n and $M_{n,th}$ when $(f_{MMA})_o < (f_{DMA})_o$ (experiment 5, Table 1) as shown in Figure 4. This disagreement was attributed to differences in hydrodynamic volumes between the polystyrene standards and the gradient copolymer which contains more DMA segments than other ones. Figure 3 and 4 also show M_w/M_n vs conversion. Polydispersity index in these experiments decrease with conversion and remain quite low. These results are also typical for all copolymerizations studied in this work.

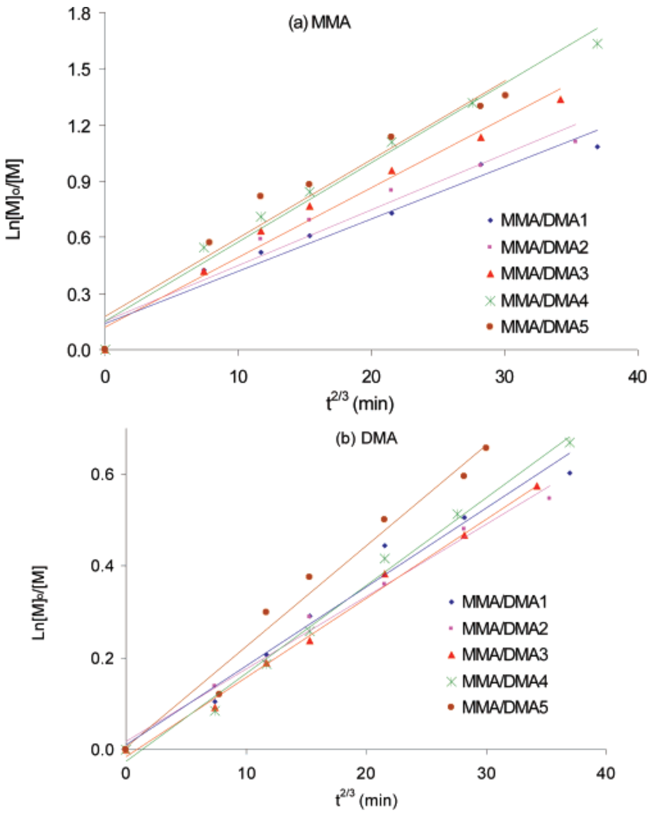

Figure 2. First-order plot of monomer consumption vs time for the copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylamide for different initial mole fractions of methyl methacrylate $(f_{\mathrm{MMA}})_o$. Experiment numbers listed in the legend correspond to conditions in Table 1.

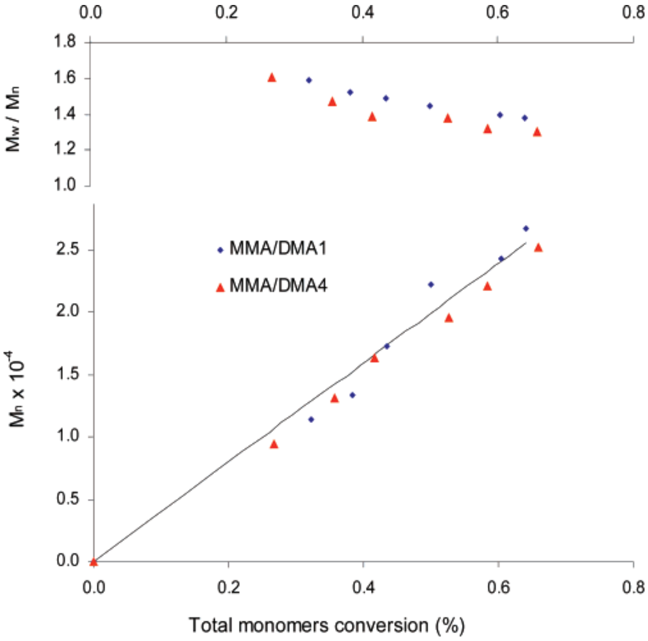

Figure 3. $M_{n,th}$; M_n and M_w/M_n vs conversion for the simultaneous copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylamide. Experiment numbers listed in the legend correspond to those in Table 1.

The copolymerization of MMA and DMA proceeded smoothly and exhibited a "living"/controlled character: indeed, the two criteria of control, which are a linear increase of $\ln([M]_0/[M])$ with time or $t^{2/3}$ and a linear evolution of M_n with monomers conversion, are satisfied (Figures 3 and 4).

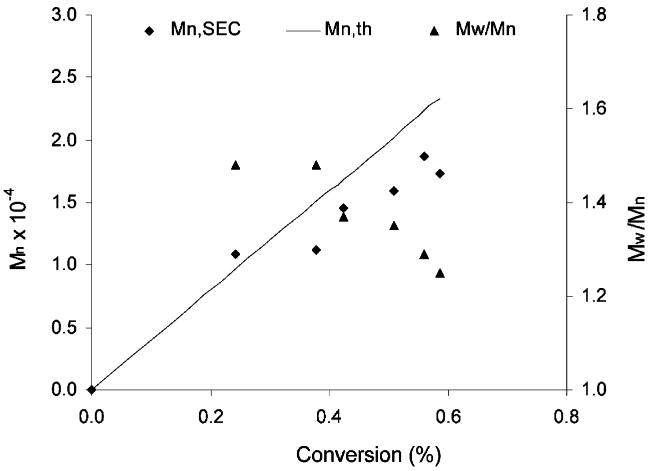

Figure 4. $M_{n,th}$; M_n and M_w/M_n vs conversion for the simultaneous copolymerization of methyl methacrylate and *N*,*N*-dimethyl acrylamide with initial molar fraction of methyl methacrylate $(f_{\mathrm{MMA}})_o = 0.4$ (experiment 5).

Table 2. Glass Transition Temperature for the Five MMA/DMA Gradient Copolymers

	composition (mol %)			
sample	MMA	DMA	T_g (°C) expt	T_g (°C) calcd
MMA/DMA1	93	7	114.1	112.8
MMA/DMA2	86	14	109.7	110.6
MMA/DMA3	78	22	107.6	108.2
MMA/DMA4	66	34	93.3	104.2
MMA/DMA5	50.8	49.2	95.9	100.6

Up to now, the polymerization of methyl methacrylate by NMP is a noncontrolled polymerization and conduces to "dead" polymers. However, as demonstrated again in this work, the incorporation of small proportion of DMA (10 mol %, experiment 1, Table 1), which can be polymerized with good control under comparables condition,[46] allowed us to control the polymerization of MMA by the NMP method.

A.3. Glass Transition Temperature. There has been limited experimental study[44,47−50] of the properties of gradient copolymers. These studies have demonstrated that copolymers with weak composition gradients along the chain exhibited a single glass transition temperature, T_g. In contrast, with copolymers exhibiting stronger composition gradients, they presented a microphase separation. Buzin et al.[44] noted that gradient copolymers exhibit unusual or unique thermal properties relative to conventional random copolymers because of their composition distribution, "the repulsive interchain interactions are varying smoothly along the chain". This prediction was demonstrated through the systems where block copolymers with one of the block itself was a copolymer exhibiting a small gradient in composition, resulting in experimental measured thermal properties relatively similar to those of block copolymers. Recently, Gray et al.[48] discovered significant differences in the enthalpy recovery behavior of styrene/4-methylstyrene random and gradient copolymers of similar overall composition, confirming the prediction of Buzin et al.[44]

All DSC measurements were recorded in the temperatures range from 50 to 150 °C for the five MMA/DMA gradient copolymers after cooling from the melt. The T_g for the MMA/DMA gradient copolymers are shown in Table 2. All samples exhibit single T_g falling not far from the T_g of pure PMMA (115 °C)[44] and PDMA (89 °C).[51] In the sample riche in MMA content (M/AM1, Table 2), the T_g is close to that of pure PMMA, with increase in the content of DMA in copolymer, T_g shifts to the region of lower temperature, toward the T_g of

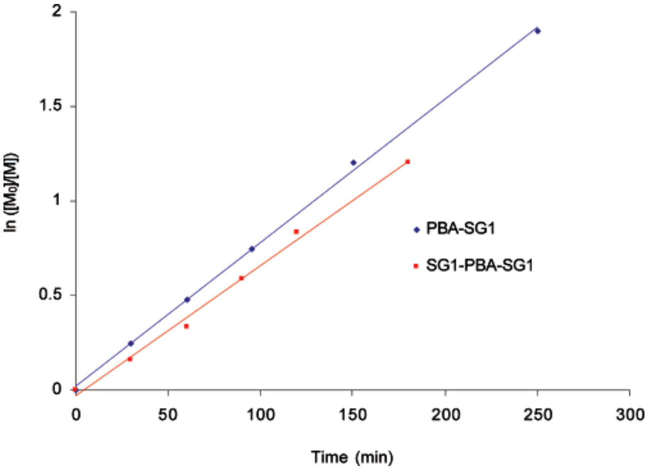

Figure 5. Kinetic plots for the polymerization of *n*-butyl acrylate in bulk at 120 °C with alkoxyamine MAMA−SG1 (PBA−SG1) or DIAMS (SG1−PBA−SG1).

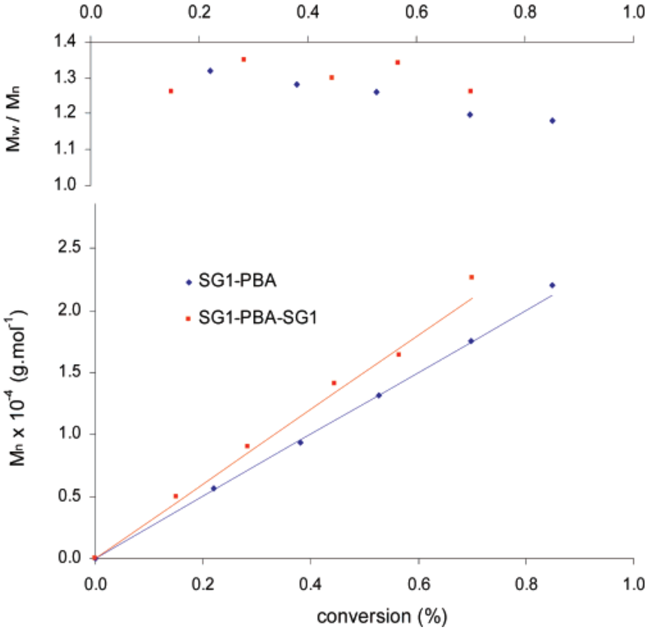

Figure 6. $M_{n,th}$ (line); M_n (symbol) and M_w/M_n vs conversion for the controlled radical polymerization of *n*-butyl acrylate in bulk at 120 °C with alkoxyamine MAMA−SG1 (PBA−SG1) and DIAMS (SG1−PBA−SG1).

PDMA. It is strange that when the DMA content becomes equal to that of PMMA, the T_g of copolymers shifts again to higher temperature.

The glass transition temperature of statistic copolymers can be calculated by Fox's equation:[52]

$$1/T_g = w_{MMA}/T_{gPMMA} + w_{DMA}/T_{gPDMA}$$

Here T_g, T_{gPMMA}, and T_{gPDMA} are the transition temperatures of statistic copolymer, PMMA homopolymers, and PDMA homopolymers respectively; w_{MMA} and w_{MDA} are the weight fractions of MMA and DMA monomers in copolymer. The calculated T_g of different copolymers according to Fox's equation is listed in Table 2. Almost obtained T_g by DSC is close enough to the calculated value except for samples MMA/DMA4 and MMA/DMA5.

While the single T_g of the MMA/DMA gradient copolymers suggested either the T_{gPMMA} and T_{gPDMA} are close or these materials were not microphase separated as observed by Gray et al.[47] for styrene/4-acetoxystyrene system or by Farcet et al.[49] for styrene/*n*-butyl acrylate system with $M_w < 50\,000$ g/mol, which have a weak composition gradients along the chain.

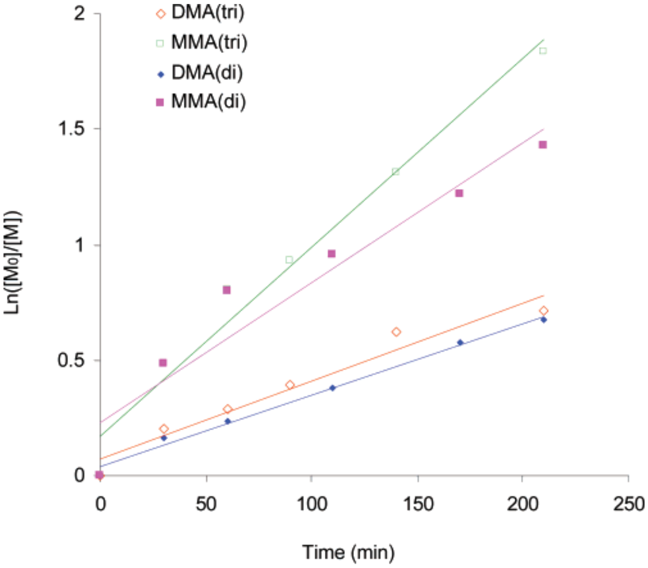

Figure 7. First-order plot of monomer consumption vs time for the copolymerization of MMA and DMA using PBA−SG1 and SG1−PBA−SG1 macroalkoxyamines. The synthesis was performed in dioxane at 100 °C.

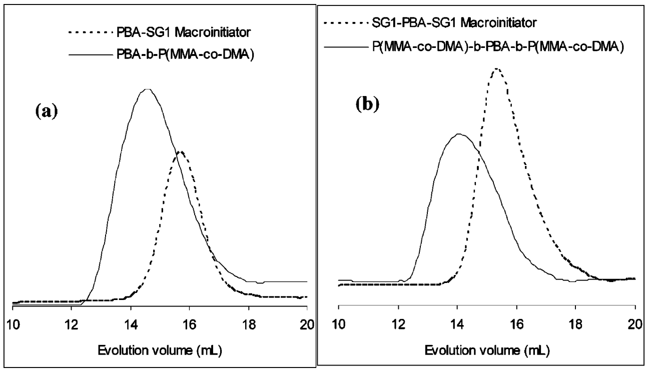

Figure 8. Relative refractive index traces from size exclusion chromatography for (a) a poly(*n*-butyl acrylate) macroalkoxyamine [PBA−SG1; M_n = 22 000 g/mol; M_w/M_n = 1,18] and the resulting poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate-*co*-*N*,*N*-dimethyl acrylamide) diblock copolymer [PBA-*b*-P(MMA-*co*-DMA; M_n = 47 100 g/mol; M_w/M_n = 1.48] and for (b) a poly(*n*-butyl acrylate) macroalkoxyamine [SG1−PBA−SG1; M_n = 22 500 g/mol; M_w/M_n = 1,28] and the resulting poly(methyl methacrylate-*co*-*N*,*N*-dimethyl acrylamide)-*b*-poly(*n*-butyl acrylate)-*b*-poly(methyl methacrylate-*co*-*N*,*N*-dimethyl acrylamide) triblock copolymer [P(MMA-*co*-DMA)-*b*-PBA-*b*-P(MMA-*co*-DMA; M_n = 50 000 g/mol; M_w/M_n = 1.35].

B. Di- and Triblock Copolymers. B.1. Homopolymerization of *n*-Butyl Acrylate. The bulk polymerization of *n*-butyl acrylate at 120 °C mediated by alkoxyamines MAMA−SG1 or DIAMS was characterized by following the evolution of the conversion index by ^{1}H NMR and the molecular weight by SEC. A small excess of nitroxide SG1, typically 5 mol % relative to alkoxyamine concentration, was added to the polymerization of *n*-butyl acrylate in purpose to improve livingness and having better polymerization control.

In agreement with other reports,[53−55] the *n*-butyl acrylate polymerization showed linear kinetics, the molecular weight increased with conversion and polydispersity remained low. The semilogarithmic kinetic plots of ln([M]$_0$/[M]) vs times for two experiments (Figure 5) showed that, in the presence of excess SG1, the rate of *n*-butyl acrylate polymerization with DIAMS

Table 3. Experimental Conditions for the Synthesis of M/AM−A Diblock and M/AM−A−M/AM Triblock Copolymers Using PBA−SG1 ($M_{n,SEC}$ = 22 000, M_w/M_n = 1.18) and SG1−PBA−SG1 ($M_{n,SEC}$ = 22 500, M_w/M_n = 1.26) as Macroinitiator[a]

sample	conditions [MMA]:[DMA]:[I]	time (min)	total convern	composition (mol %) PBA:P(MMA/DMA)	$M_{n,SEC}$ (g mol^{-1})	$M_{n,RMN}$ (g mol^{-1})	M_w/M_n
diblock	10:4.2:0.03	210	68.1	35.6 : (77.2/22.8)	47 100	52 600	1.48
triblock	10:4.2:0.03	210	74.2	34.4 : (76.5/23.5)	50 000	55 400	1.35

[a] The targeted molecular weight of MMA/DMA block was fixed at 50000 g mol^{-1}.

Table 4. Glass Transition Temperatures Observed by DMA and DSC for the PBA and PMMA/PDMA Block Domains in Diblock and Triblock Copolymers

	PBA block		P(MMA/DMA) block	
sample	T_α (°C)	T_g (°C)	T_α (°C)	T_g (°C)
diblock	−32	−49	120	107
triblock	−33	−49	113	102

was slower than that of *n*-butyl acrylate polymerization with MAMA−SG1 in spite of same targeted molecular weight. The evolution of molecular weight with conversion as well as the polydispersity index during the reaction are shown in Figure 6. A linear relationship between molecular weight and conversion was obtained with a good linearity; moreover, the polydispersity index was relatively low, typically about 1.2 for PBA−SG1 and 1.3 for SG1−PBA−SG1.

B.2. Synthesis of PBA-*b*-P(MMA-*co*-DMA) Diblock and P(MMA-*co*-DMA)-*b*-PBA-*b*-P(MMA-*co*-DMA) Triblock Copolymers. The NMP of MMA and DMA was also conducted using the same conditions as for the synthesis of the MMA/DMA random copolymer. The mono- and difunctional PBA−SG1 and SG1−PBA−SG1 macroalkoxyamines were used as macroinitiator. The targeted molecular weight of MMA/DMA block was fixed at 50 000 g/mol. As expected from the kinetic results in part A, the copolymerization kinetics of MMA/DMA system initiated by the macroinitiators exhibited the similar data than that initiated by MAMA−SG1 (Figure 7). A weak increase of the viscosity of initial mixture due to the presence of macroinitiator did not influence on the kinetic of the polymerization. Figure 7 shows that methacrylate as well as acrylamide comonomer presents kinetic rates slightly faster during the formation of triblock copolymer than that during the formation of diblock copolymer.

The shift of the SEC peaks toward higher molar masses (lower evolution volume) of the kinetics samples taken at various conversions demonstrated that molar mass progressively increased, forming well-defined copolymers. SEC traces of the macroinitiators and the resulting purified diblock and triblock copolymers confirmed relatively high initiation efficiency during the block copolymerization (Figure 8, parts a and b). However, the $M_{n,SEC}$ values were lower than the $M_{n,th}$ values, it is due to the fact that the determination of these $M_{n,SEC}$ values were relatives to polystyrene standards (result not shown). The characteristics of diblock and triblock copolymers are presented in Table 3.

B.3. Morphology of Ultrathin Films. The morphologies of diblock and triblock copolymers films prepared by solvent casting (the block copolymer is dissolved in tetrahydrofuran and placed in flat-bottomed Petri dishes; the solvent evaporates slowly for 1 week and then one night under vacuum) are given in Figure 9a,b. Because of the lack of electronic contrast between poly(methyl methacrylate) and poly(*n*-butyl acrylate) blocks, the blocks are not strongly stained by staining agent and the direct observation of nanophase-separated morphology by TEM is not obvious. On the basis of block copolymers composition (Table 3), the random copolymer P(MMA-*co*-DMA) is the major component in block copolymer. The PBA block represents only about 35 wt % of block copolymer, it is expected to form cylinders in the P(MMA/DMA) phase as observed by Jérôme et al.[56] for ABA triblock copolymers consisting of outer PMMA blocks and inner poly(alkyl acrylate) blocks with about 25−35 wt % of block copolymer. However, as shown in Figure 9, a lamellar morphology was observed for both copolymers. The bright lamellae correspond to the less polar PBA phase. The gray appearing lamellae accord with the P(MMA/DMA) phase. This unusual morphology according to the classical phase diagram of AB diblock and BAB triblock copolymer was already observed by Chauvin[57] in PBA−PMMA diblock copolymer, which was prepared by NMP method. This same author was demonstrated that the variation of phase diagram was due to the large molecular weight distribution of block copolymers, that is also the case of our systems.

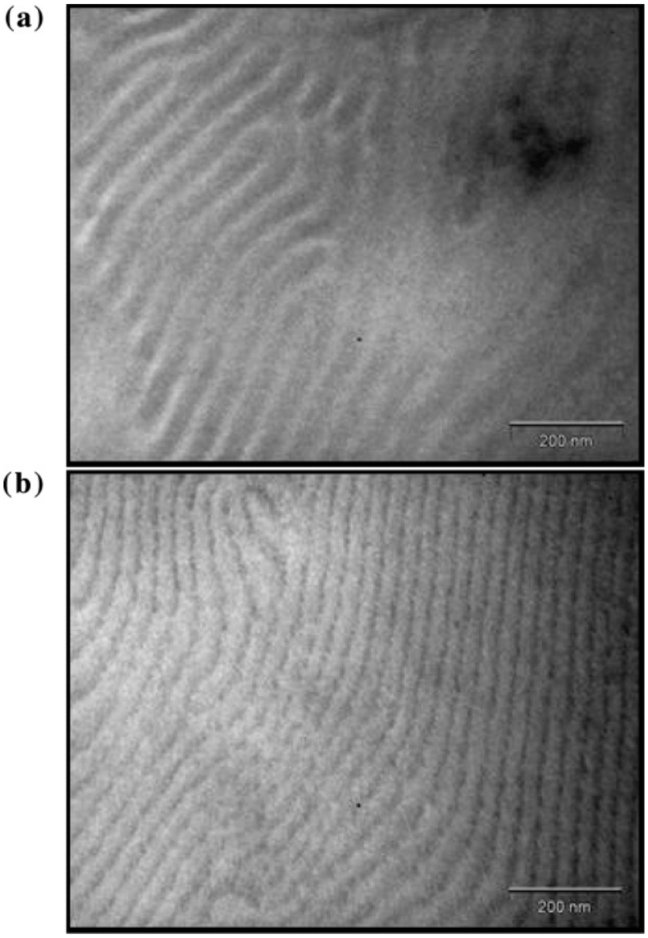

Figure 9. TEM micrographs of (a) PBA-*b*-P(MMA/DMA) diblock and (b) P(MMA/DMA)-*b*-PBA-*b*-P(MMA/DMA) triblock copolymers that illustrate lamellar morphology.

The thickness of the individual lamellae can be estimated directly from the electron micrograph to be L_{PBA} = 23 ± 2 nm for both coplymers, $L_{P(MMA/DMA)}$ = 35 ± 3 nm for diblock copolymer and $L_{P(MMA/DMA)}$ = 13 ± 1 nm for triblock copolymer. The PBA block length is similar in both copolymers, thus their domain size is identical, however, the P(MMA/DMA)

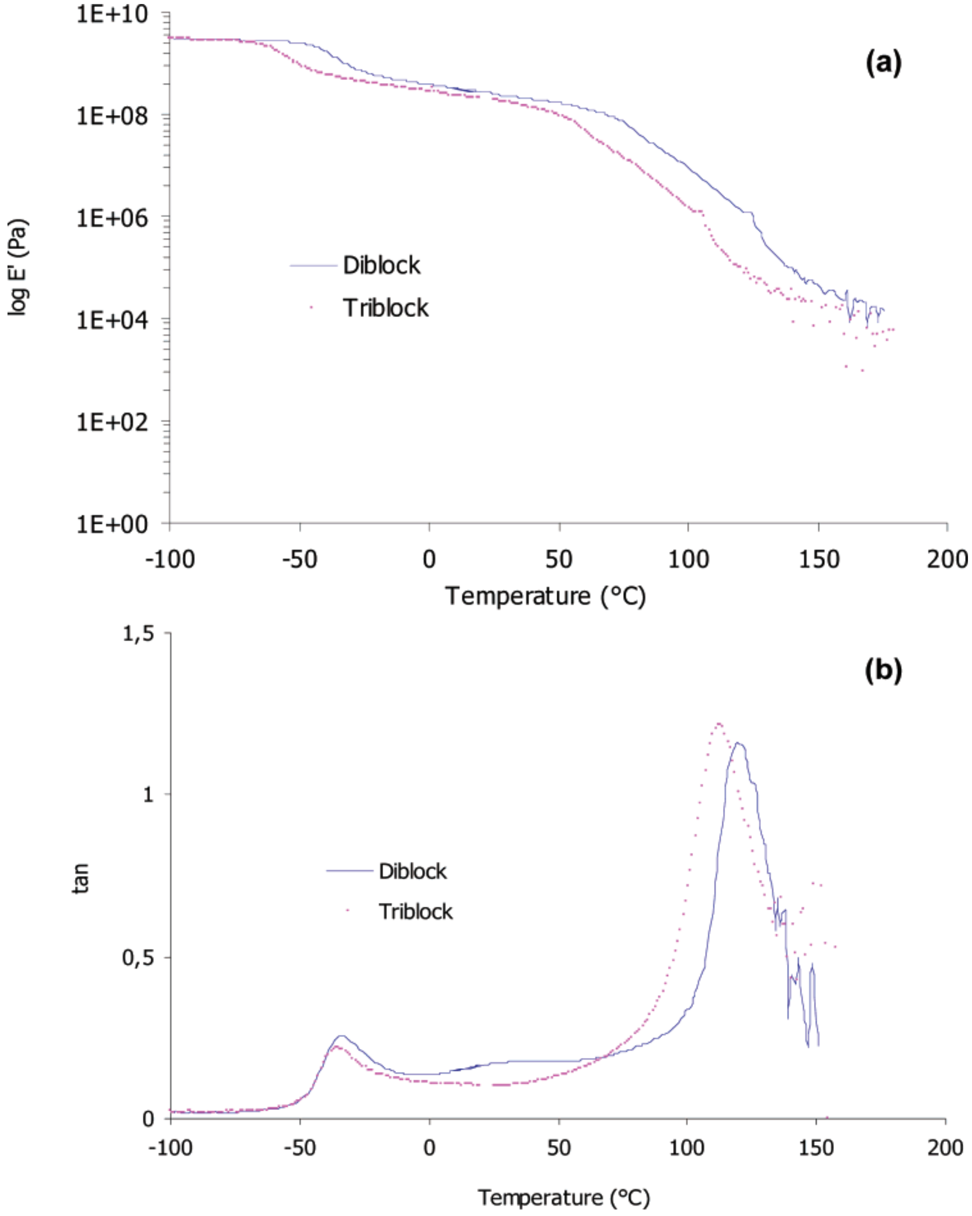

Figure 10. (a) E' and (b) tan δ vs temperature for M/AM−A diblock and M/AM−A−M/AM triblock copolymers having the similar molecular weight and molar composition.

block length of diblock copolymer is twice the size of the P(MMA/DMA) block of triblock copolymer. Of this fact, P(MMA/DMA) lamellae thickness of diblock copolymer is higher the one of triblock copolymer.

B.4. Differential Scanning Calorimetry and Dynamic Mechanical Analysis. To investigate the phase behavior of block copolymers, DMA measurements have been performed. Dynamic mechanical storage modulus, E', and lost tangent, tan $\delta = E''/E'$ vs temperature (T) curves for diblock and triblock copolymers are shown in Figure 10, parts a and b, respectively. Both copolymers shown two sharp α relaxation temperatures, Table 3 lists the temperatures of relaxation observed on these curves as well as the transition temperature detected by DSC measurements.

The first α relaxation temperature at ca. −33 °C (by DMA) can be attributed to the PBA rich phase. Above this temperature, an extended rubber plateau is observed. There is a considerable difference between the value of T_g(PBA) determined by DSC and by DMA. The value obtained by DSC (−49 °C) is very close to that of the PBA homopolymer (−50 °C) newly measured by Buzin et al.[44] The loss tangent plot of diblock copolymer shows a shoulder that appears at approximately 39 °C, which was not observed for triblock copolymer. This relaxation is more obvious for diblock copolymers having higher molecular mass (results not shown). A second α relaxation temperature was observed at ca. 120 °C and 113 °C for diblock and triblock copolymer, respectively as indicated by a drop in E' and a corresponding maximum in tan δ. This second T_α is attributed to the PMMA/PDMA mixed phase.

Conclusion

The nitroxide-mediated polymerization of methyl methacrylate at 100 °C, with SG1 nitroxide as controller agent could be carried out to large conversions by adding even a small proportion of DMA (10 mol %). The polymerization exhibited all the features of a controlled system. In this copolymerization system, the experimental obtained reactivity ratios ($r_1 \gg r_2$) let to think that a spontaneous gradient copolymer should be formed, with densely MMA segments incorporated at the beginning of the copolymerization. However, because of the fact that the T_g of pure PMMA is too close of that of pure

PDMA, the DSC measurements of these systems exhibited only a single T_g, which would not allow us to confirm the formation of a spontaneous gradient copolymer.

Well-defined PBA-*b*-P(MMA-*co*-DMA) diblock and P(MMA-*co*-DMA)-*b*-PBA-*b*-P(MMA-*co*-DMA) triblock copolymers were then synthesized by NMP. Block copolymers were studied by DSC and DMA measurements and TEM observations. Both block copolymers exhibited two T_g, one near the T_g of PBA and the other intermediate to the T_g of PMMA and PDMA. This result indicated a microphase separation of copolymers which was confirmed both by dynamic mechanical analysis and TEM.

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