Macromol. Symp. **2008**, 267, 31–40 DOI: 10.1002/masy.200850706

Tuning the Surface/Bulk Properties by the Control of the Amphiphilic Profile in Gradient Copolymer

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Summary: Nitroxide Mediated Radical Polymerization (NMP) combined with the Semi-Batch process is used for synthesize poly(N,N-Dimethylacrylamide-*grad*-Butyl acrylate), called poly(DMA-*grad*-BuA), in the presence of SG1 as control agent and the alkoxyamine (MAMA) as initiator. The instantaneous composition is used to characterize the gradient copolymers. The variation of the addition rate of DMA influences on the incorporation of DMA in the macromolecular chains. The thermal/rheological properties of gradient copolymers in bulk are also studied and discussed in relation with their local structure.

Keywords: acrylamide; gradient copolymers; semi-batch nitroxide-mediated polymerization

Introduction

Poly(acrylamide) and its derivatives are an extremely important class of synthetic polymers widely used in industry.[1] They find numerous applications because of their biocompatibility and hydrophilic/water-soluble properties.[1,2] They are synthesized using ionic and free radical polymerization (FRP). Conventional FRP of acrylamide yields poorly defined polymers,[3,4] but recently, a range of well-defined polyacrylamides have been prepared by different controlled/living radical polymerization (CRP) methods as: Nitroxide mediated-radical polymerization (NMP),[5] atom transfer radical polymerization (ATRP)[6–12] and reversible addition-fragmentation chain transfer (RAFT).[13–16]

NMP is one of the oldest methods, and remains increasingly interesting because the range of polymerizable monomers still broadens. In NMP, a growing polymer chain is reversibly terminated by a Nitroxide (e.g. TEMPO, SG1). The CRP of DMA and acrylamido monomers in general, has proven to be challenging using NMP. Indeed, Li et Brittain reported the polymerization of DMA by NMP using the TEMPO as counter radical and AIBN as initiator, but the process was not controlled.[17] Diaz et al. have synthesized PDMA and poly(4 VinylPyridine-*b*-N,N-DimethylAcrylamide) in controlled manner using a β-phosphonylated nitroxide, commonly designated as SG1 as a counter agent and the N-Tertiobutyl-N, 1-diethylphosphono-2, 2-dimethylpropyl-o, 1-phenylethylhydroxyamine (Sty-SG1) as initiator.[18] Recently, Schierholz et al. have shown the synthesis of well defined poly(DMA) and poly(DMA-*b*-BuA) in the presence of SG1 and the AIBN as initiator. The authors have shown that the free radical polymerization of DMA exhibits a living/controlled character using an excess of nitroxide radical (SG1).[19]

Unlike block and random copolymers, gradient copolymers represent a novel architecture of materials. These copolymers are synthesized by controlling the relative population of first (A) and second (B) monomers during synthesis. Batch and semi-batch copolymerization methods are used to form controlled gradient copolymers in instantaneous composition.[20–28] The method of batch copolymerization is

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not the best synthetic methodology to perform gradient copolymers with a broad variation of the monomers units in the macromolecular structures. To reach higher gradient composition in the macromolecular chain, Nitroxide Mediated Polymerization combined with the forced gradient process can be used to synthesize. The composition of gradient copolymers gradually changes from one end of the polymer chain to the other.

Recently, we have focused our activity on such polymer structure to understand the effect of the synthetic methodology on the molecular architecture and the intrinsic properties of the monomer on their surface structures.[25,28]

The objective of this work consists on the syntheses of gradient copolymers poly(DMA-*grad*-BuA) by coupling a hydrophilic monomer (DMA) with another hydrophobic one (BuA) having a low glass transition temperature (T_g). We report here for the first time the synthesis of gradient copolymers poly(DMA-*grad*-BuA) by Semi-Batch Nitroxide-Mediated Controlled Radical Polymerization using a alkoxyamine (MAMA) as initiator and a excess of SG1 as control agent. We will show the ability of SG1 combined with the MAMA in a process in Semi-Batch Nitroxide-Mediated Polymerization to control the copolymerization of DMA with BuA. These copolymers synthesized by Semi-Batch process are obtained by continuous addition of DMA during the polymerization reaction of BuA. These copolymers will be characterized by various techniques and we will focus on their organizations at the surface and their structure/rheological properties relationship.

Experimental Part

Materials

N,N-DimethylAcrylamide (DMA, 99%), Butyl Acrylate (BuA, 99%) were used as received from Aldrich. The alkoxyamine, 2-méthylaminoxypropionic-SG1, (MAMA, 99%), as the initiator, N-tert-Butyl-(1-diethyl-phosphono-2,2-dimethylpropyl) nitroxide (SG1, 88%), as the counter radical, were provided by Arkema Chemicals. All solvents and reagents were used as received without further purification.

Homopolymerization of DMA

Before the copolymerization study of DMA with BuA, we would like to ensure the possibility to control the polymerization of DMA with SG1 using the MAMA as alkoxyamine. For that, the kinetics of polymerization of DMA was achieved in order to demonstrate the ability of MAMA to control the polymerization of DMA. In a 50 ml round flask, MAMA (0.077 g, $2.021 \cdot 10^{-4}$ mol), SG1 (0.004 g, $1.26 \cdot 10^{-5}$ mol), DMA (10 g, 0.101 mol) ($[SG1]/[MAMA] = 6\%$), were dissolved in 23 ml of toluene. The mixture was degassed by bubbling with nitrogen gas for 30 minutes. The flask was placed into an oil bath at 112 °C. Aliquots were sampled to determine conversion by ^1H NMR and molecular weight by SEC. After 3 h 10 min, the flask was cooled down room temperature and exposed to air: 43% conversion (^1H NMR); $M_n = 13300$ g/mole and $I_p = 1.4$. The polymer was precipitated in hexane, the resulting solid was isolated by vacuum filtration and dried 48 hours under vacuum. The plots linearity of the logarithmic change of the monomer concentration with time indicated not only a first order with respect to the monomer but that the growing radical concentration remained constant. This aspect was ratified by the linear dependence of M_n with conversion. This behavior was characteristic of a well controlled Nitroxide Mediated Polymerization and has be used to pattern gradient compositions in the macromolecular chains.[29] After 3 h 10 min the reaction was stopped at 43% monomer conversion with a molecular weight $M_n = 13300$ g/mole and $I_p = 1.4$.

Semi-Batch Copolymerization of DMA with BuA by NMP

a-Synthesis of Gradient Copolymer A (G_A)

The synthesis of this copolymer was prepared by Semi-Batch Nitroxide-Mediated copolymerization. Indeed, into a first round flask, BuA (12.8 g, 0.1 mol) and 2-methylaminoxypropionic-SG1 (MAMA) (0.151 g, $3.96 \cdot 10^{-4}$ mole) as initiator, an excess of SG1, [SG1]/[MAMA] $\approx$ 6% and 19 mL of toluene were introduced, [BuA] $\approx$ 5.2 mole/L. The initiator was solubilized by stirring. The solution was degassed by nitrogen bubbling for 30 minutes. In another round flask, we introduced N, N-DimethyAcrylamide monomer (9.7 g, 0.098 mole). The N, N-DimethyAcrylamide monomer was degassed by nitrogen bubbling for 30 minutes. After, DMA was transferred into an syringe. The first round flask (BuA solution) was placed in an oil bath at 112 °C; then as soon as the reaction temperature was reached, DMA was added (considered as $t = 0$ minute). The Semi-Batch polymerization was performed by addition of DMA using a pump with a rate of 1.4 mL/h. After 7 h 10 min, the DMA addition was complete, whereas the reaction is stopped after 7 h 20 min (10 minutes after end of DMA addition). From these experimental values, the classical ratio has been calculated [DMA-BuA]/[MAMA] $\approx$ 500.

Samples of the copolymerization mixture were withdrawn at periodic intervals, and conversion was determined by ^{1}H NMR spectroscopy while molecular weights were determined by SEC. The final polymer obtained was soluble in the THF, precipitated in hexane and the resulting solid was isolated by vacuum filtration and dried 48 hours under vacuum. Monomer conversion was found to be 76% DMA and 88% BuA (from ^{1}H NMR). Average molecular weight and molecular weight distribution were measured using SEC, at final stage ($M_n = 33000$ g/mole; $I_p = 1.28$).

b-Synthesis of Gradient Copolymer B (G_B)

The experimental conditions were the same for this copolymerization except the addition rate of DMA, which is 2.8 mL/h. After 3 h 35 min, the DMA addition was complete, whereas the reaction is stopped after 4 h. Monomer conversion was found to be 48% DMA and 62% BuA (^{1}H NMR). Average molecular weight and molecular weight distribution were measured using SEC, at final stage ($M_n = 24000$ g/mole; $I_p = 1.24$).

c-Gradient Copolymer C (G_C)

As described above for the two first gradient copolymers, the experimental conditions were the same for this copolymerization except the addition rate of DMA, which is 0.8 mL/h. After 13 h, the DMA addition was complete, whereas the reaction is stopped after 13 h 20 min. Monomer conversion was found to be 69% DMA and 98% BuA (^{1}H NMR). Average molecular weight and molecular weight distribution were measured using SEC, at final stage ($M_n = 35000$ g/mole; $I_p = 1.48$).

Results and Discussion

In a previous work, we have synthesized and characterized gradient copolymers (S/BuA) by different synthetic methodologies using an alkoxyamine (MAMA) as initiator. Even if these polymers were not amphiphilic, the used synthetic methodologies were very important to well-understand the formation of the gradient profile inside the macromolecular chains. These copolymers have shown controlled characters for the molecular weight (M_n) and for the polymolecularity index. We noticed that the Semi-Batch Nitroxide Mediated Polymerization process was a fine way to obtain gradient copolymers for monomers which did not present a broad difference between their reactivity ratios and which were difficult to obtain using the Batch Nitroxide Mediated Polymerization. Finally, the synthetic methodologies has showed that the different way/rate of the monomer addition can tuned the incorporation of monomer in the copolymer and consequently on the molecular structure of the soft polymeric materials.

Gradient Copolymerization: Synthesis of poly(DMA-*grad*-BuA)

Considering our interest in gradient copolymer by coupling antagonist intrinsic properties of two different monomers, i.e.

medium/high[25] or low/high[28] glass transition temperature, we have selected extremely polar and apolar monomers, i.e. a hydrophilic monomer (DMA) and a hydrophobic monomer (BuA), to synthesize a range of gradient copolymers. The synthesis of gradient copolymers has been carried out by semi-batch nitroxide mediated polymerization using MAMA as initiator and SG1 as radical counter.

Continuously adding one monomer during a copolymerization reaction is an interesting way to form a more significant compositional gradient along the chain. Using this method, we force the incorporation of the added monomer in the macromolecular chains. The nature as well as the structure of the gradient obtained is strictly related to the addition rate, in other terms, it is related to the change of the molar fractions of the monomeric units in the mixture feed. This synthetic methodology has previously been used to create a strong gradient composition in monomer units in an elastomer-thermoplastic copolymer.[28]

The choice of this technique for the preparation of gradient copolymers is based on the close values of the reactivity ratio between the two monomers, $r_{BuA} = 1.01 \pm 0.03$ and $r_{DMA} = 1.16 \pm 0.03$.[14] The batch copolymerization by ATRP for these monomers, indicates the formation of random copolymers. For that, Nitroxide Mediated Polymerization combined with the forced gradient mode is used to synthesize poly(DMA-*grad*-BuA). This technique of polymerization is based on the continuous addition of DMA during the polymerization of BuA.

The composition gradient of the copolymers can be characterized through the copolymerization kinetics. Conversions of DMA and BuA as well as M_n and I_p are measured as a function of polymerization time. The DMA and BuA conversions are obtained by ^{1}H NMR versus time for three copolymerization reactions with three different additions rates.

For the gradient copolymers G_A, G_B and G_C, the reaction is stopped at 86/76%, 62/48% and 98/69% % conversion for BuA/DMA, respectively. The final average molecular weight and molecular weight distribution are: $M_n = 33000$ g/mole; $I_p = 1.28$ for the gradient copolymer (G_A), $M_n = 24000$ g/mole; $I_p = 1.24$ for gradient copolymer (G_B) and $M_n = 35000$ g/mole; $I_p = 1.48$ for gradient copolymer (G_C).

For all copolymers, the instantaneous composition is used to describe the profile of gradient copolymers. It is calculated by monitoring the conversion by ^{1}H NMR of each component during the copolymerization. This instantaneous composition is determined from the relative area of the dimethyl protons resonance of DMA ($\delta = 2.9$–3.1 ppm) and those of O-CH_2 ($\delta = 4.05$ ppm) protons corresponding to BuA units.

During the synthesis of gradient copolymers, aliquots are removed throughout the reaction to verify the change in overall fraction of DMA content as a function of chain length. Figure 1 shows the relationship between the instantaneous composition and the apparent normalized chain length. This instantaneous fraction of the DMA increases with apparent normalized chain length for the three copolymers. It corresponds to a variation in the chemical composition in the macromolecular chains. This evolution shows that the composition of the copolymer changes clearly and gradually during copolymerization with the increase of the monomer conversions.

This result confirms that Semi-Batch method yields easily to DMA/BuA gradient copolymers. Moreover, the variation of the instantaneous fraction of DMA in three copolymers is not the same thank to the three copolymers do not have the same composition and consequently the same microstructure along the main chain. Such behavior demonstrates that the addition rate of monomer has a role on the incorporation of monomer in the copolymer and consequently on its micro-structure. By comparison between three copolymers, we can notice an increase in the incorporation of the units of DMA with the increase of addition rate. The final composition of DMA

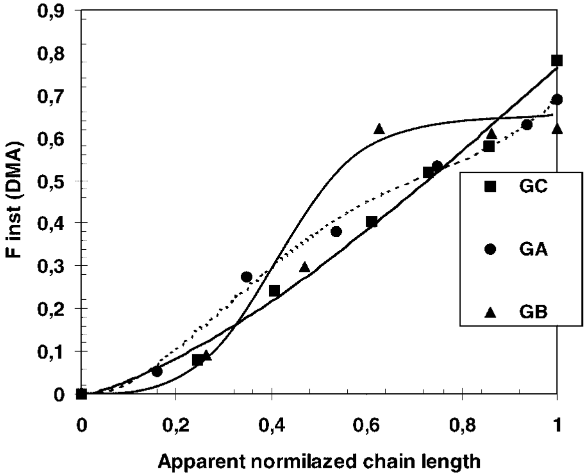

Figure 1.
Evolution of DMA content in gradient copolymers as a function of the apparent normalized chain length.

in the three copolymers is 46, 43 and 40% for G_A, G_B and G_C respectively.

In fact, it is shown in the literature that the DMA is slightly more reactive than BuA,[10] the increase of its concentration in the mixture supports its incorporation compared to the BuA units. These results indicate that three kinds of gradient copolymers composed of the DMA units and BuA units with different gradient shape distribution could be synthesized by controlling of the DMA addition rate.

In fact, for copolymer G_B, a typical "S" curve is obtained as described by Karaky[28] and Matyjaszewski.[30] The DMA gradient increases rapidly for apparent normalized chain lengths between 0.2 up to 0.6 and tends to a plateau characteristic of a blocky structure. This behavior seems to show that copolymer G_B presents a strong gradient which tends to a blocky pattern (three well-defined segments of different length) with a specific monomer unit arrangement from the start to the end of the macromolecular chain. The final composition of the copolymer G_B is 43% of DMA.

On contrary, the synthesis methodology, lower addition rate (1.4 and 0.8 mL/h), used for copolymer G_A and G_C respectively, seems to create a continuous monomer unit gradient in the macromolecular chain. In these cases, a linear increase of DMA units in the molecular structure leads to a more continuous gradient copolymer from more or less exclusively "pure" PBuA richer and richer in DMA up to final composition in DMA of 46 and 40%, for G_A and G_C respectively. This result has been also observed in case of copolymerisation of BuA in presence of Styrene.[28] This study clearly identifies an important parameter of the control of the gradient profile: the addition rate. Indeed, if the addition rate is in the same order of magnitude that the consumption rate of the monomer, the gradient profile increases progressively and linearly, otherwise the reactive media becomes richer and richer in one monomer, leading to a strong increase of its introduction in the macromolecular chain as described in the "S" shape profile.

Thermal/Rheological Properties of Gradient Copolymers

A study of the physical properties is carried out on these copolymers. DSC is used to determine the glass transition temperature T*g* of these gradient copolymers and the thermograms of G_A, G_B and G_C are reported in Figure 2. For the G_C copolymer, two Tg are observed, $Tg_{1C} = -45.1\,°C$ and $Tg_{2C} = 27.5\,°C$. In fact, the presence

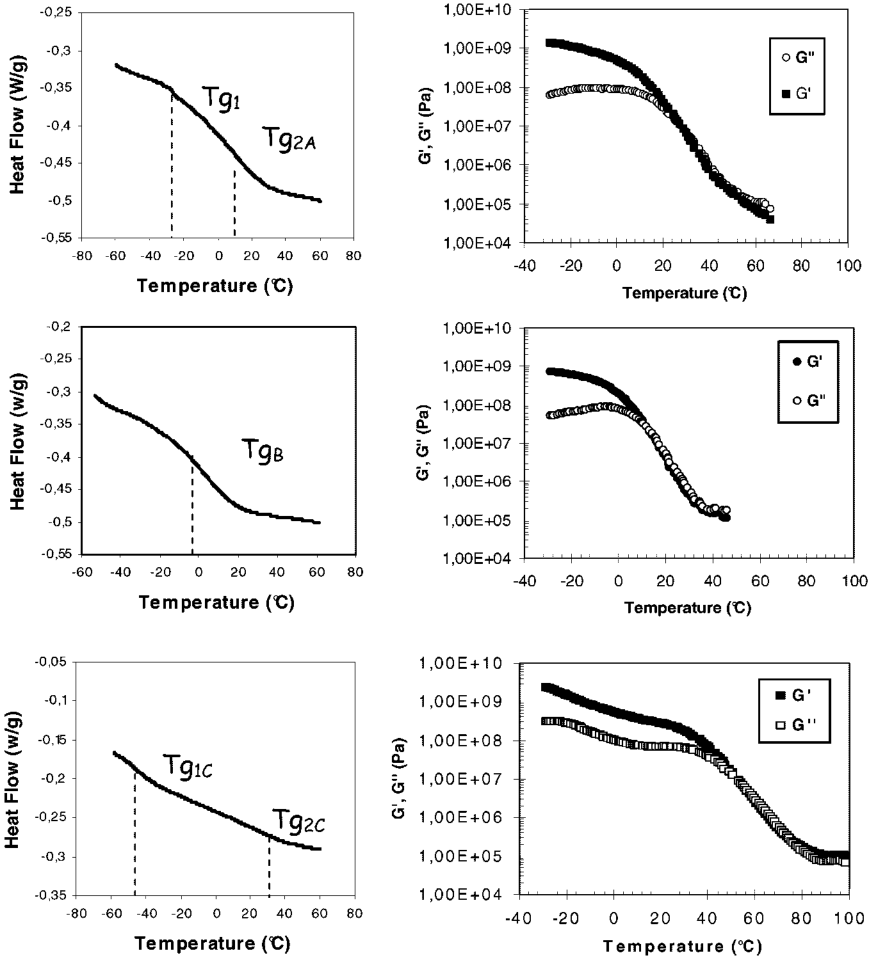

Figure 2.

DSC thermograms (left) and Temperature dependencies of the real G′ and imaginary G″ parts of the shear modulus (right) for DMA/BuA gradient copolymers (G_A, G_B and G_C, from top to buttom).

of two T_g in this gradient copolymers is related to addition rate of DMA. Indeed, by working with a low addition rate (0.8 mL/h), the concentration of BuA monomer is higher among that of DMA monomer in the initial time of the process. Consequently, we encourage first the homopolymerization of BuA at the beginning of polymerization reaction. The low T_g (−45.1 °C) corresponds to a homopolymer of PBuA,[31,32] whereas the T_g at 27.5 °C corresponds to the gradient block richer and richer in DMA up to a final composition of 40% (see Figure 1). In the case of gradient G_C, the presence of two distinct values is characteristic of a strong phase segregation in the final material with a hydrophobic phase rich in PBuA (0.25 of the apparent normalized chain length) and a second one characteristic of the gradient segment richer and richer in DMA. The same behavior is observed for the gradient G_A with the presence of two glass transition temperatures $Tg_{1A} = -27\,°C$ and $Tg_{2A} = 8.5\,°C$. Here, we can observe the presence of two values of Tg which are also characteristic of a phase segregation in the final material. These two phase transitions are associated to a difference of the composition in the main chain with a first segment rich in PBuA (≈90%)

corresponding up to 0.15 of the apparent normalized chain length (shorter than G_C) and a second one richer in DMA in the last part of the macromolecular chain, respectively for Tg_{1A} and Tg_{2A}. Moreover, it's interesting to note that these Tg_{1A} and Tg_{2A} values are relatively close and that the length of the first segment richer in PBuA is relatively short. For the gradient G_B, only one Tg is observed with a value $Tg_B = -3.2\,^{\circ}C$. The thermogram shows an extremely broad Tg domain which is correlated to a broad and strong variation of the concentration of the units monomers in the macromolecular chains as previously described in Figure 1. It means that the phase transitions are dominated by the strong "S" shape of the gradient composition with a minor influence of the two extreme blocky segments richer in PBuA in one side and DMA in the other extremity of the macromolecular chain.

The presence of these glass transition temperatures is confirmed by the thermomechanical measurements performed with a constant deformation pulsation (1 rad/s) within a broad temperature range. Indeed, thermomechanical characterization of the three gradient copolymers is shown in Figure 2 (right) in the form of temperature dependencies of the real (G′) and imaginary parts (G″) of the shear modulus for gradient copolymers G_A, G_B and G_C. The dependencies indicate one extremely broad segmental relaxation for the G_B sample, indicating a broad and strong variation of the incorporation of the monomers units in the macromolecular chains. The maximum of G″ modulus corresponds to the glassy temperature noted $T_{\alpha B} = -6\,^{\circ}C$. This phenomenon is well correlated with the behavior observed by DSC. Two distinct T_α are present in the G_C called $T_{\alpha 1C} \approx -25\,^{\circ}C$ and $T_{\alpha 2C} \approx 30\,^{\circ}C$. The segmental relaxation obtained at 30 °C is extremely broad, indicating a broad variation of the incorporation of the monomers units in the macromolecular chains. The presence of two separated glassy temperatures $T_{\alpha 1C}$ and $T_{\alpha 2C}$ is in agreement with the result obtained by DSC. The difference between the values of glass transition temperatures obtained by DSC and the glassy temperature T_α obtained by rheological measurement for the G_C are attributed to the different temperatures ramps ($2\,^{\circ}C \cdot min^{-1}$ in rheological experiments and $20\,^{\circ}C \cdot min^{-1}$ in DSC). For gradient G_A, we observe a broad plateau with a constant value of the imaginary G″ of 10^{+8} Pa between −20 and 10 °C and centered around –9 °C. The presence of this plateau is associated to the overlap of the two close glassy temperatures Tg_{1A} and Tg_{2A}, observed by DSC. In this experiment the two transitions are not separated but appear as a broad transition.

Moreover, we can observe a maintenance of the rheological modules for the copolymer Gc at high temperature even after the glass transition temperature of the sequence richer in PBuA. A such behavior is characteristic of the presence of a separation phase characterized by the coexistence of "soft" elastomer pure PBuA phase and "hard" amphiphilic thermoplastic PBuA-*grad*-PDMA phase. This result could be very interesting because such gradient copolymer could be plasticized under specific and controlled conditions to tune their adhesion properties. In this case, due to the value of $T_{\alpha C2}$ close to the human being temperature (≈30 °C), these properties, especially adhesion, could be controlled by the contact with skin moisture.

Effect of the Gradient Shape Composition on the Surface Organization

In the previous paragraphs, we have shown the effect of gradient shape composition on the bulk properties. One other interesting effect could be the ability of these new polymeric materials to self-organize in surface of films. As we have recently described for Styrene/ButylAcrylate system, gradient copolymers can be organized and self-assembled in bulk soft matter in order to create a new type of nanostructured polymeric materials.[28] In order to compare the influence of the gradient shape composition on the surface organization we have also used a diblock copolymer P(DMA-*b*-BuA) synthesized by NMP from a PBuA of molecular weight 22 000 g · mol^{-1} with a polydispersity index of 1.33. This block copolymer is characterized by a molecular weight of 33 000 g · mol^{-1} with a polydispersity index of 1.28 and a composition of 58/42, respectively in PDMA/PBuA (^{1}H NMR). By DSC, this block copolymer presents a phase segregation with two glass transitions at −44 °C and 115 °C, respectively for the pure sequences of PBuA and PDMA.

The study of surface morphology of the gradient copolymers is carried out by Atomic Force Microscopy (AFM) on thin films obtained by spin coating (Figure 3).

In Figure 3 (left), we can observed the top surface organization of the diblock copolymer with the formation of PBuA nodules in PDMA continuous matrix. Due to the monomer composition, the DMA is the majority monomer which forms the continuous phase of this materials. The radius nodule size is around 250 nm and few coagulation of elastomer nodules can be observed with the formation of "peanuts" nodules on the extreme surface. When the proportion of DMA decreases in the macromolecular chain composition the nodular organization shift to the lamellar phase as observed in Figure 3 middle with the gradient copolymer G_A (PDMA/PBuA = 46/54). In this case the radius of the lamella increase strongly to 750 nm. Moreover, from this type of gradient, we can also observed a gradient structure from the center (richer in BuA: black zone) through the middle (strong gradient: grey zone) and finally to the outer shell (richer in DMA: white zone) of each lamella. This behavior could be associated to the presence of two distinct phase transitions observed for gradient G_A by DSC and Rheology. If the proportion of DMA always decreases along the main chain as for gradient G_C, we observe a phase inversion with nodules richer in PDMA in a matrix richer in PBuA (Figure 3 right). In this case the nodules size increases to 400 nm due the gradient sequence of the macromolecular chain, increasing the miscibility between the two chains ends rich in PBuA and PDMA. No gradient can be observed between the nodule centers and the matrix because the strong composition variation in the macromolecular chains close to block copolymer segregation (see Figure 1 and Figure 3 left). Moreover, these nodules are characteristic to the presence of a strong phase separation as previously observed with thermal/rheological properties, with two well-distinct glass transitions lower and upper than room temperature. For the gradient G_B, due to the presence of only one glass temperature lower than room temperature and to the sticky behavior of such copolymers, no images have been performed.

This study presents here for the first time, a sub-micron phase separation in gradient copolymers observed by AFM technique. These gradient copolymers behave as block copolymers when the total

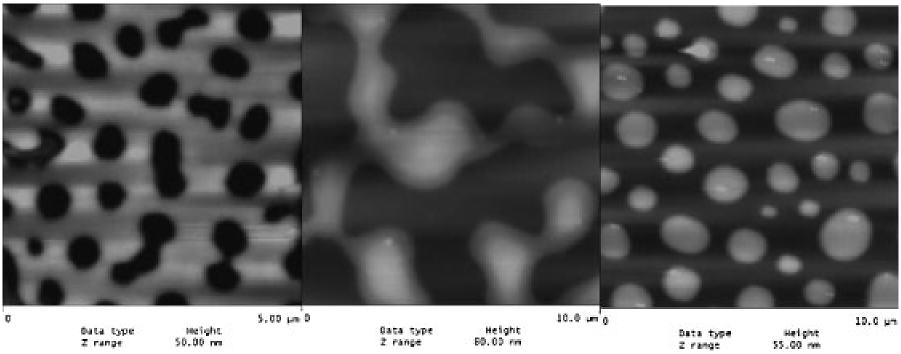

Figure 3.
AFM images of block copolymers, gradients G_A and G_C, respectively from left to right.

composition varies around 50%. Nevertheless, it seems that it could be possible to visualize the gradient composition when the composition variation gradually changes along the main chain. This surface characterization by AFM represents a preliminary study which opens a new class of amphiphilic copolymers. Indeed, the moisture influence study on these types of copolymers are underway to check the variation of the water-sensitive structures.

Conclusion

In this paper, we report the synthesis of well defined PDMA by Nitroxide Mediated Radical Polymerization using for the first time an alkoxyamine. We also demonstrate the synthesis of gradient copolymers of poly(DMA-*grad*-BuA) with different gradient shapes depending on the addition rate of DMA. The SG1 used as control agent combined with an alkoxyamine (MAMA) as initiator provides a well controlled copolymerization. The influence of addition rate on the shapes and the structures of gradient copolymers is demonstrated. The semi-batch polymerization with a low addition rate (0.8 mL/h) leads to the synthesis of gradient copolymer from macroinitiator of PBuA. These gradient copolymers demonstrate interesting rheological properties. Moreover, thanks to the combination of DMA (hydrophilic monomer) /BuA (monomer having a low T_g) and to the formation of phase segregation as observed by AFM, these systems can be used in the treatment of surfaces, for example adsorption of moisture, thanks to the hydrophilic properties of DMA. Using this methodology, the tuning of the surface/bulk properties can be achieved by the control of the amphiphilic profile in gradient copolymer.

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