

Synthesis, characterization and self-assembly in the solid state of block copolymers containing *N*-isopropylacrylamide

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1. Abstract

Linear A-B block copolymers where A and B are immiscible, assemble in the solid state into ordered, complex morphologies depending on their composition and molecular weight. Most of these polymers, typically with molecular weights of 20K to 200K g mol⁻¹, show domain sizes from 10 to 80 nm, representing exciting new nanomaterials. In this contribution we report the preparation of two series of diblock copolymers with pol(*N*-isopropylacrylamide) (PNIPAAm) as first block and poly(methyl methacrylate) (PMMA), an hydrophobic-glassy polymer, or poly(hexyl acrylate) (PHA) an hydrophobic-viscoelastic polymer, as second block. All block copolymers were synthesized controlling their size and composition by means of reversible addition-fragmentation chain transfer (RAFT) polymerization. Different annealing methods were tested to improve the regularity of nano-domains formed by self-assembly in the solid state, as studied by TEM micrographs.

2. Introduction

The self-assembly property of block copolymers has lead to the design of a number of highly sophisticated nanostructured soft materials which today open a new frontier in material science having implication in many fields such as: Photonic crystals , drug delivery, catalyzers and many others where ordered microphase separation at the nanoscale is a crucial factor [1]. Matsen and Schick mean-field theory [2] (MFT), showed that the phase behavior in the case of a diblock copolymer is determined by two parameters, namely, χN and f , where χ is the Flory-Huggins segment-segment interaction parameter, N is the degree of polymerization, and f is the block copolymer composition. The product χN determines the degree of segregation of the blocks. Leibler [3], using the random phase approximation (RPA), predicted that for $f = 0.5$, the limit between the order to disorder transition (ODT) corresponded to $\chi N \sim 10.5$. For $\chi N < 10.5$ the block copolymers do not show microphase separation and the entropy of mixing dominates the free energy of the blend. Close to the ODT the system is in the so called weak segregation limit where the interface between the domains is somehow diffuse. In contrast, in the strong segregation limit ($\chi N \gg 10.5$) the narrow interfaces will separate well-developed almost pure

micro domains. For diblock copolymers, a lamellar (lam) phase is observed for symmetric diblocks ($f = 0.5$), where as more asymmetric diblocks form hexagonal-packed cylinder (hex) or body-centered cubic (bcc) spherical structures. A complex bicontinuous cubic gyroid (gyr) (space group *Ia-3d*) phase has also been identified for block copolymers between the lam and hex phases near the ODT, and a hexagonal-perforated layer (HPL) phase has been found to be metastable in this region [4].

The last 15–20 years has been witness to unprecedented advances in controlled polymer synthesis. This has been due, in part, to the discovery and development of controlled free radical polymerization (CRP) techniques [5]. Among the above techniques, RAFT is a versatile method capable of inducing living behavior for various monomers via a range of initiation methods and varying reaction temperatures [6]. RAFT also enables the formation of a variety of molecular architectures such as block copolymers, star shaped molecules and comb structures [7].

3. Experimental Section

3.1 Polymerizations

All polymerizations were performed in ampoules. In all cases, 4-cyanopentanoic acid dithiobenzoate and 4,4-azobis(4-cyanopentanoic acid) were used as the CTA and initiator, respectively. The monomers, CTA and initiator were dissolved in 1,4-dioxane. Solutions were degassed by three freeze-pump-thaw cycles. After degassing, the ampoules were flame-sealed under vacuum and heated in an oil bath at 70 °C. The polymerizations were terminated by rapid cooling and freezing. The homopolymers obtained, also named macro-CTA's since they include the CTA-moiety, were purified by repeated precipitations. Products were dried in vacuum.

3.2 Block Copolymerizations

Well characterized homopolymers synthesized in the first step were used as macro-CTA's. The macro-CTA was dissolved in 1,4-dioxane (20 ml) before adding the second monomer in different amounts aiming different compositions, and the initiator. The copolymerization procedure was the same as for polymerization.

3.3. Characterization methods

The homopolymers and blockcopolymers were characterized by gel permeation chromatography (GPC) with a light scattering detector and thermogravimetry (TGA). Block copolymers were annealed at 175 °C for different times: 24 h, 96 h, 264 h and 340 h. Other method tested was

injection molding at 200 °C into small rods (3 mm diameter x 40 mm length). An ultramicrotome was used to obtain ultrathin sections (50-70 nm) for transmission electron microscopy (TEM). Sections were cut at room temperature using a glass knife. These were collected on 300 mesh uncoated copper grids and then stained in the vapor of ruthenium tetroxide.

4. Results and Discussion

The compositions and molecular weights of 10 samples of block copolymer are given in Table 1.

Table 1. Molecular Characteristics of Diblock Copolymers.

Sample	$M_{n(\text{PMMA})}^a$	$M_{n(\text{PNIPAAm})}^b$	$M_{n(\text{total})}^a$	M_w/M_n	$N_{(\text{total})}$	$f_{(\text{PNIPAAm})}$
Poly(MMA- <i>b</i> -NIPAAm)	43,930	3,870	47,800	1.152	474	0.072
Poly(MMA- <i>b</i> -NIPAAm)	50,650	7,900	58,550	1.043	576	0.121
Poly(MMA- <i>b</i> -NIPAAm)	37,020	13,670	50,690	1.147	491	0.246
Sample	$M_{n(\text{PNIPAAm})}^a$	$M_{n(\text{PMMA})}^c$	$M_{n(\text{total})}^a$	M_w/M_n		$f_{(\text{PNIPAAm})}$
Poly(NIPAAm- <i>b</i> -MMA)	30,890	44,810	75,700	1.456	721	0.379
Poly(NIPAAm- <i>b</i> -MMA)	33,670	39,590	73,260	1.446	694	0.429
Poly(NIPAAm- <i>b</i> -MMA)	45,190	38,720	83,910	1.478	787	0.508
Poly(NIPAAm- <i>b</i> -MMA)	40,710	25,400	66,110	1.490	614	0.587
Sample	$M_{n(\text{PNIPAAm})}^a$	$M_{n(\text{PHA})}^c$	$M_{n(\text{total})}^a$	M_w/M_n		$f_{(\text{PNIPAAm})}$
Poly(NIPAAm- <i>b</i> -HA)	15,300	14,360	29,660	1.994	227	0.595
Poly(NIPAAm- <i>b</i> -HA)	17,090	10,510	27,600	1.841	219	0.692
Poly(NIPAAm- <i>b</i> -HA)	24,830	6,150	30,980	1.532	259	0.848

^a From GPC. ^b Calculated as $M_{n(\text{PNIPAAm})} = M_{n(\text{total})} - M_{n(\text{PMMA})}$. ^c Calculated as $M_{n(X)} = M_{n(\text{total})} - M_{n(\text{PNIPAAm})}$. X = PMMA or PHA. Molecular weights in g mol⁻¹

Using the RAFT methodology, NIPAAm-MMA block copolymers were prepared with PNIPAAm contents from 8.6 to 63.2 vol%; therefore different morphologies at the nanoscale were anticipated. In the case of block copolymers containing HA, the polydispersities (M_w/M_n) are high indicating that the synthetic conditions needs to be improved.

Some examples of TEM images obtained after annealing are shown in Figure 1. It is clear that the time for annealing is very important since the ordering improves at longer annealing times but is still not enough for complete ordering. On the other side a similar effect is observed by injection molding, some ordering is induced but is still not enough. In the partially ordered

systems, cylinders of 50-100 nm are observed in a matrix for poly(NIPAAm_{38%}-*b*-MMA_{62%}); while for the poly(NIPAAm_{69%}-*b*-HA_{31%}) a more regular ordering is observed with cylinders of around 80 nm. Since the first polymer has a total degree of polymerization (N) more than 3 times higher than the second one, and the Tg's of PMMA and PHA are 378 K and 216 K respectively, it is expected that the energy needed for ordering (annealing) poly(NIPAAm_{38%}-*b*-MMA_{62%}) is much higher than the one required for poly(NIPAAm_{69%}-*b*-HA_{31%}).

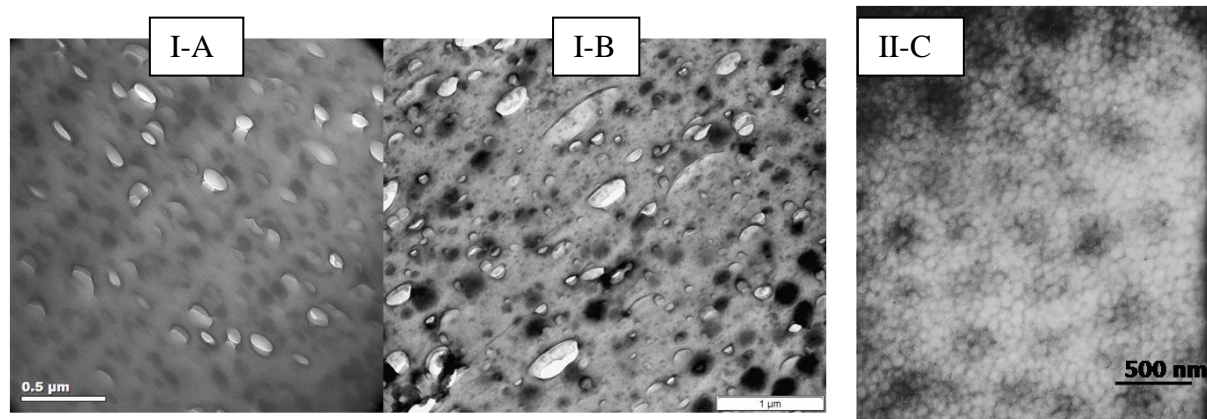


Figure 1: TEM images of (I) poly(NIPAAm-*b*-MMA) ($75,700 \text{ g mol}^{-1}$) and (II) poly(NIPAAm-*b*-HA) ($27,600 \text{ g mol}^{-1}$). A-Annealing of (I) for 96 h. B-Injection molding of (I). C-Annealing of (II) for 340 h.

5. Conclusions

Amphiphilic diblock copolymers were synthesized using RAFT polymerization. PNIPAM was used as a hydrophilic block and PMMA or PHA as the hydrophobic one. Annealing at 175°C for up to 340 h or injection molding at 200°C (one step) improved ordering in the systems, however the annealing method needs to be fine tuned for a complete ordering for the block-copolymers prepared.

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6. References

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