Thermo-Responsive, UV-active Poly(Phenyl Acrylate)-*b*-Poly(Diethyl Acrylamide) Block Copolymers

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ABSTRACT

The homopolymerization of phenyl acrylate (PA) was investigated for the first time by nitroxide mediated polymerization (NMP) with the succinimidyl form of the SG1-based unimolecular initiator 2-[*N-tert*-butyl-2,2-(dimethylpropyl)-aminooxy]propionic acid (BlocBuilder MA). The control of PPA homopolymerization was improved by the use of 15 mol% additional free nitroxide SG1 ([tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxidanyl) and dispersities, M_w/M_n, of around 1.2 were achieved. A PPA homopolymer was then successfully chain extended with diethyl acrylamide (DEAAm) to form a block copolymer of PPA-b-PDEAAm where the PDEAAm segment is thermo-responsive, while the PPA block is potentially UV-active. The thermo-responsive behavior of the block copolymer in 0.5 wt% aqueous solution was studied by UV-Vis spectrometry and dynamic light scattering (DLS), indicating cloud point temperatures of 26-30 °C, close to reported for PDEAAm homopolymers.

1. Introduction

A great deal of interest has been focused on the inclusion of photosensitive chromophores into thermo-responsive polymers, which can change the behavior of the polymer when exposed to light.[1-5] Poly(phenyl acrylate) (PPA) homopolymers have been shown to undergo photo-Fries rearrangements which can significantly modify the polymer solubility, making it an ideal candidate for photosensitive applications such as for photolithography and for light-sensitive "smart" block copolymers when coupled to a stimuli-responsive segment (Figure 1).[6, 7] Photo-Fries rearrangements have been utilized in UV-induced micro- or nano-lithography and nano-scale patterning.[8, 9] Despite its potentially interesting properties, particularly if it was to be incorporated into block copolymers, phenyl acrylate (PA) has only been homo/copolymerized by conventional free-radical polymerization[9, 10] and ionic polymerization[11] and not in the open literature by any Reversible-Deactivation Radical Polymerization (RDRP) technique such as nitroxide mediated polymerization (NMP),[12-16] atom transfer radical polymerization (ATRP)[17-19] and reversible addition fragmentation transfer polymerization (RAFT).[20, 21] There has been some mention of polymerizing PA in the patent literature however. Multi-walled carbon nanotubes were dispersed using block copolymers, preferentially using poly(acrylic acid)-block-poly(methyl methacrylate) using NMP [22] for which PA could be used in the hydrophobic block [23] but no kinetic details were presented. Glaser described an ATRP process for which PA could be used as a possible monomer but again no specific examples of PA kinetics were provided.[24] To control the functionality of the block copolymer, it is imperative to exert a high degree of control of the molecular weight and composition of the block copolymer; therefore making an RDRP technique highly attractive, particularly since it avoids the stringent requirements for typical, traditional living polymerizations.

The goal of this manuscript is thus to examine the NMP of PA using the so-called SG1-based nitroxide, BlocBuilder-MA, as the unimolecular initiator, which was modified to a succinimidyl form (to be termed NHS-BlocBuilder herein). The succinimidyl group could be used to couple with amines,[25, 26] a reaction often used in peptide coupling.[27] Further, NHS-BlocBuilder dissociates 15 times faster compared to BlocBuilder MA, which essentially mimics the effect of adding more free nitroxide at the onset of the polymerization, which should help to control the polymerization better.[28] We then tried to attach a thermoresponsive segment by chain extension with diethyl acrylamide (DEAAm). Poly(DEAAm) (PDEAAm) exhibits a lower critical solution temperature ~33 °C in aqueous media and was shown recently to be controllable by BlocBuilder initiators.[28] After showing that potentially UV-active, thermoresponsive block copolymers can be made, testing of the solution behavior of the block copolymers in aqueous media was performed. This study will then serve as the starting point for further studies to manipulate the solubility of the copolymer, specifically the PPA block, by employing UV irradiation to incur the photo-Fries rearrangement.

Insert Figure 1.

Figure 1 Synthetic route for UV-alterable/thermo-responsive block copolymers by NMP, where (1) is the homopolymerization of phenyl acrylate (PA) using NHS-BlocBuilder, followed by (2) the chain extension of the PPA homopolymers with diethyl acrylamide (DEAAm) and the potential molecular change resulting from (3) photo-Fries rearrangement of the phenyl acrylate units due to UV exposure.

2. Experimental

2.1. Materials

Phenyl acrylate (PA, ≥ 98%) and diethyl acrylamide (DEAAm, 99%) were purchased from Polysciences Inc, US. while tetrahydrofuran (THF, ≥ 99%), lithium bromide (LiBr, ≥ 99%) and 1,4-dioxane (≥ 99.0%) were obtained from Fisher Scientific, Canada. Diethyl ether (≥ 99%), HPLC grade N,N-dimethylformamide (DMF, ≥ 99.8%), and toluene (99.0 %) were obtained from Sigma Aldrich, Canada. The monomers (PA, DEAAm) were purified by passage through a column containing a mixture of basic alumina and calcium hydride (40:1 weight ratio) and stored in a freezer under a head of nitrogen until required. NHS-BlocBuilder was synthesized according to the literature[29] from the commercially available unimolecular initiator 2-[*N*-*tert*-butyl-2,2-(dimethylpropyl)-aminooxy]propionic acid, which was kindly supplied from Arkema (known as BlocBuilder MA).[29] The additional [tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxidanyl (SG1, >85%) was graciously donated by Noah Macy of Arkema and used as received.

2.2. Phenyl Acrylate (PA) Homopolymerization

The PA homopolymerizations were done in a 10 mL three-neck round bottom flask with a magnetic Teflon stir bar connected to a condenser that was chilled with cooling water (5°C). A thermocouple, inserted into a thermo-well joined to the reactor, was connected to a temperature controller that used a heating mantle to heat the reactor. As an example, the synthesis of PPA-3 is shown. First, PA (1.56 g, 10.50 mmol), NHS-BlocBuilder (0.051 g, 0.11 mmol), SG1 free nitroxide (0.0048 g, 0.016 mmol) and 1,4-dioxane (1.65 g) were added to the reactor prior to being sealed with a rubber septum. Nitrogen was then used to bubble the mixture for 25 minutes, removing any dissolved oxygen in the reactor. Once sufficiently bubbled, the nitrogen flow was reduced while the needle was raised above the liquid level to allow the system to be purged throughout the reaction. The temperature controller was set to 90°C and heating at a rate of 10 $°C \cdot min^{-1}$ was commenced. After reaching the set temperature, samples were taken periodically and added to excess methanol until precipitation was observed. After 625 min, the polymerization was stopped and the reactor contents were precipitated in methanol and dried in a vacuum oven at 60 °C to evaporate any unreacted monomer or solvent that was still present. The final polymer was characterized by gel permeation chromatography (GPC) and ^{1}H NMR spectroscopy (yield = 0.50 g, final conversion = 0.31, number average molecular weight $\bar{M}_n$ = 3.8 $kg \cdot mol^{-1}$, and dispersity $\bar{M}_w / \bar{M}_n$ = 1.17, relative to poly(styrene) standards in THF at 40 °C). The kinetic plots and the evolution of the molecular weight distribution during the polymerization are shown in Figure 2. The summary of the molecular characteristics for the PPA homopolymers is shown in Table 1 below.

^{1}H NMR for PPA ($CDCl_3$, 25 °C) (δ, ppm): 1.5-2.5 (backbone, $-CH_2-CH-$); 7.0-7.4 (aromatic, $-COO-C_6\underline{H}_5$).

^{13}C NMR for PPA ($CDCl_3$, 25 °C) (δ, ppm): 36 ($-CH_2-\underline{C}H-$); 42 ($-\underline{C}H_2-CH-$); 120,123,128,140 (aromatic $-C_6H_5-$); 173 (-COO-).

2.3. Chain Extension with Poly(Phenyl Acrylate) (PPA) as Macroinitiator

The chain extension of the PPA macroinitiator was performed with the same experimental set-up as the PA homopolymerizations. PPA-5 ($\bar{M}_n$ = 10.1 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$= 1.55, 0.56 g, 3.15 mmol), DEAAm (2.04 g, 16.1 mmol) and toluene (2.60 g, 28.2 mmol) were added to the reactor, which was then sealed and bubbled with nitrogen for 25 minutes. The temperature controller was then set to 110 °C and the nitrogen flow rate reduced. The reaction was allowed to continue for 11.5 h and then the mixture was cooled, precipitated in diethyl ether and dried in a vacuum oven at 60°C overnight. The final recovered yield for the copolymer was 1.2 g ($\bar{M}_n$ = 22.6 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$= 1.91 relative to PMMA standards in DMF with 1 g L^{-1} LiBr at 50 °C; F_{PA} = by ^{1}H NMR).

^{1}H NMR for PPA-b-PDEAAm ($CDCl_3$, 25 °C) (δ, ppm): 1.0 (-CON-CH_2-C$\underline{H}_3$-); (1.5-2.0 (back-bone, -CH_2-CH-); 2.8-3.8 (-CON-C$\underline{H}_2$-CH_3-); 7.0-7.4 (aromatic, -COO-$C_6\underline{H}_5$).

^{13}C NMR for PPA-b-PDEAAm ($CDCl_3$, 25 °C) (δ, ppm): 13-15 (-N-CH_2-$\underline{C}H_3$-); 35-37 (-CH_2-$\underline{C}$H-); 35-37 (-$\underline{C}H_2$-CH-); 40 (-N-$\underline{C}H_2$-CH_3-); 120,123,128,140 (aromatic -C_6H_5-); 173 (-COO- overlapping from both monomers).

2.4. Characterization

Molecular weight characterization of the PPA homopolymers was determined using gel permeation chromatography (GPC) performed on a Water Breeze GPC. HPLC grade THF (>99.9%) was used as the eluent with a flow rate of 0.3 ml·min^{-1}, heated to 40°C while passing through three Waters Styragel® HR columns connected in series (HR1 with molecular weight measurement range of 10^2 - 5 x 10^3 g·mol^{-1}, HR2 with molecular weight measurement range of 5 x 10^2 - 2 x 10^4 g·mol^{-1}, and HR4 with molecular weight measurement range 5 x 10^3 - 6 x 10^5 g·mol^{-1}). A guard column was also used. The GPC was equipped with ultraviolet (UV 2487) and differential refractive index (RI 2410) detectors and was calibrated using linear, nearly monodisperse poly(styrene) standards with THF as eluent at 40 °C. The molecular weight characterization of the PPA-b-P(DEAAm) block copolymers was also determined using the same GPC but was equipped with 2 ResiPore (3 µm, MULTI pore type, 250 x 4.6mm) columns with a ResiPore guard column (3 µm, 50 x 4.6mm) (Polymer Laboratories) using HPLC grade DMF with 1 g·L^{-1} LiBr as the eluent and poly(methyl methacrylate) as standards. A mobile phase flow rate of 0.3 mL·min^{-1} was applied while the columns were heated to 50 °C during the analysis. The molar composition of the final samples was determined using ^{1}H NMR spectroscopy, which was performed with a 400 MHz Varian Mercury instrument. For the conversion of phenyl acrylate (X), the disappearance of the vinyl peaks at 6.0-6.4 ppm relative to the aromatic peaks at 7.0-7.3 ppm, which appear in both unreacted monomer and resulting polymer, were used to determine X by ^{1}H NMR as shown in Equation (1) below:

$$X = 1 - \frac{A_{6.0}}{\left(\frac{A_{7.0-7.3}}{5}\right)} \qquad (1)$$

where $A_{6.0}$ is the integrated area of the peak corresponding to one of the vinylic protons and $A_{7.0-7.3}$ is the integrated area of the peak corresponding to the 5 aromatic protons in the monomer and polymer.

For the copolymer, characteristic peaks for each monomer unit in the copolymer were identified: phenyl acrylate (5H, C_6H_5, 7.05 - 7.30 ppm); DEAAm (4H, -N-CH_2-, 2.85 – 3.8 ppm and 6H, -CH_3, 0.60 – 2.80 ppm). To determine the molar composition of the block copolymer with respect to PA, F_{PA}, the area of the peak corresponding to the protons from the aromatic group of the PA units were compared to the area of the peaks corresponding to the methylene protons attached to the nitrogen of the DEAAm units using the formula shown in Equation (2):

$$F_{PA} = \frac{\frac{A_{7.0-7.3}}{5}}{\frac{A_{7.0-7.3}}{5} + \frac{A_{1.0}}{6}} \qquad (2)$$

where $A_{7.0-7.3}$ is the integrated area of the peak corresponding to the 5 protons in each of the PA units and $A_{1.0}$ is the integrated area of the peak corresponding to the 6 protons from the -CH_3 groups in each of the DEAAm units. The ^{13}C NMR was also done, confirming the structure of the homopolymer and the block copolymer.

For the aqueous solution properties, the block copolymer was dissolved in de-ionized water at 0.5 wt% concentration. Light transmittance of the solution at various temperatures was measured using a Cary 5000 UV-Vis-NIR Spectrophotometer at 600 nm. The solution was equilibrated for 30 min with stirring at 5 ^{o}C and then heated at a rate of 0.5 ^{o}C·min^{-1}. The transmittance was recorded in increments at every 0.5 ^{o}C. DLS (dynamic light scattering) measurements were performed with a Malvern Zetasizer (Nano-ZS). The instrument was equipped with a He-Ne laser operating at 633 nm and an avalanche photodiode detector. The samples were heated in 1 °C increments, allowed to equilibrate for 1 min followed by 3 measurements, which were then averaged together to give one value at the temperature of interest.

3. Results and Discussion

3.1. Synthesis of PPA Homopolymers

In this study, we first demonstrate the homopolymerization of PA using a succinimidyl functional unimolecular alkoxyamine initiator (NHS-BlocBuilder[30, 31], Figure 1) followed by the synthesis of a PPA-b-P(DEAAm) block copolymer and the characterization of its thermo-responsive behavior. A series of PPA homopolymers were synthesized at either 90°C or 110°C, using NHS-BlocBuilder with 0 mol % or 15 mol % additional SG1 relative to NHS-BlocBuilder. In Figure 2A), for the polymerizations done at 90 °C, the apparent rate constant (the slope of the semi-logarithmic plot of $\ln[(1-X)^{-1}]$ versus polymerization time t indicated that the effect of additional SG1 slowed the polymerization as expected. This is due to the added SG1 pushing the equilibrium between dormant and active chains towards the dormant chains, resulting in slower polymerizations. [32,33] A similar effect of additional free SG1 nitroxide was observed for the polymerizations done at 110 °C. Note that the polymerizations done at the higher temperature of 110 °C were 2-3 times faster compared to the polymerizations done at 90 °C, under otherwise identical conditions. The PPA homopolymerizations performed using NHS-BlocBuilder with no additional SG1 (experiments PPA-1 and PPA-2) exhibited a linear increase in number average molecular weight $\bar{M}_n$ versus conversion X ($X < 0.30$, see Figure 2B) and relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \approx 1.5$, Table 1). The PPA homopolymerizations synthesized using 15 mol % additional [tert-butyl[1-(diethoxyphosphoryl)-2,2-dimethylpropyl]amino]oxidanyl (SG1) relative to NHS-BlocBuilder (experiments PPA-3 and PPA-4) had similar increases in $\bar{M}_n$ versus X to that of PPA-1 and PPA2 but the corresponding molecular weight distributions were much narrower ($\bar{M}_w/\bar{M}_n < 1.20$, Table 1). Similar reductions in $\bar{M}_w/\bar{M}_n$ have been observed when homopolymerizing other acrylates with additional

SG1.[32, 34-37] The monomodal gel permeation chromatograms (GPC) confirmed this narrowing of the molecular weight distribution with the addition of SG1 (Figure 2C-D). While the homopolymerization of PA by NMP has not been previously documented, the results are similar to those obtained for the homopolymerization of other acrylates by NMP.[35] Note that *X* of the PPA homopolymers was intentionally kept low to maximize the homopolymer's ability to cleanly re-initiate the second batch of monomer for the thermoresponsive block.

Insert Figure 2.

Figure 2 Homopolymerization of phenyl acrylate (PA) at 90°C using NHS-BlocBuilder with and without additional SG1 (15 mol% relative to NHS-BlocBuilder) where A) is the scaled conversion ($\ln[(1-X)^{-1}$ where X = conversion) versus polymerization time, B) is the number average molecular weight (M_n, filled symbols, circles = sample PPA-1, polymerization at 90 °C, squares = sample PPA-3, polymerization at 90 °C) and dispersity (M_w/M_n, empty symbols) versus X. The GPC chromatograms and the GPC chromatograms of samples taken during the PA homopolymerization at 110 °C using C) no free SG1 added (sample PPA-2) and D) 15 mol% SG1 relative to NHS-BlocBuilder (sample PPA-4).

Table 1 Summary of Phenyl Acrylate (PA) Homopolymerizations in dioxane solution using NHS-BlocBuilder (NHS-BB) as initiator.

Sample ID	*$[NHS\text{-}BB]_0$ (M)*	*$[PA]_0$ (M)*	*[dioxane] (M)*	*$T_{polym.}$ (°C)*	*r^a*	$\bar{M}_n{}^b$ *(kg mol^{-1})*	$\bar{M}_w/\bar{M}_n$	$\bar{M}_{n,theoretical}{}^b$ *(kg mol^{-1})*	*X^c*

PPA-1	0.034	3.6	5.8	90	0	4.0	1.52	15.5	0.36
PPA-2	0.036	3.5	5.9	110	0	7.5	1.53	14.5	0.41
PPA-3	0.034	3.4	6.0	90	0.15	3.8	1.17	14.8	0.31
PPA-4	0.036	3.5	5.8	110	0.16	11.5	1.18	14.6	0.49
PPA-5	0.033	3.5	5.9	110	0	10.1	1.55	15.8	0.50

[a] r = molar ratio of free SG1 nitroxide initially added relative to NHS-BlocBuilder unimolecular initiator.

[b] $\bar{M}_n$ is the number average molecular weight and $\bar{M}_w/\bar{M}_n$ is the dispersity as measured by gel permeation chromatography (GPC) relative to linear poly(styrene) standards in tetrahydrofuran (PPA-1 to 4) at 40 °C or poly(methyl methacrylate) standards in DMF with 1 g·L^{-1} LiBr (PPA-5) at 50 °C. $\bar{M}_{n,theoretical}$ is the theoretical molecular weight at full conversion (mass of monomer added initially relative to moles of BlocBuilder-MA initiator added initially).

[c] X is the final conversion of PPA monomer.

3.2. Chain Extension of Poly(PA) with DEAAm

A characteristic PPA homopolymer (PPA-5, $\bar{M}_n$ = 10.1 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$= 1.55) was used as a macroinitiator for the polymerization of DEAAm. We chose to test a PPA homopolymer with a broader molecular weight distribution initially to see if it was still capable of re-initiating cleanly a second batch monomer despite its relatively high dispersity. The chain extension of the PPA macroinitiator was monitored by GPC and the composition was estimated from ^{1}H NMR (Figure 3A shows the ^{1}H NMR spectrum of the PPA macroinitiator and Figure 3B is the spectrum for the PPA-*b*-PDEAAm block copolymer). The final block copolymer had a broader molecular weight distribution compared to the macroinitiator ($\bar{M}_n$= 22.6 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$=1.91, relative to poly(methyl methacrylate) standards in DMF with 1 g·L^{-1} LiBr as eluent) but still retained a monomodal molecular weight distribution. It should be noted that the molar composition of the final block copolymer measured by ^{1}H NMR does not match well based on the molecular weights estimated for the macroinitiator and the block copolymer by GPC. This is likely not surprising based on using poly(methyl methacrylate) standards in DMF for the GPC analysis as the PDEAAm segment is quite chemically different compared to that of the standards.

Table 2 Molecular characterizations for poly(PA) macroinitiator and chain extended PPA-*b*-PDEAAm.

Sample ID	PPA Macroinitiator		Chain-Extended Polymer		
	$\bar{M}_n$ (kg·mol^{-1})	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$ (kg·mol^{-1})	$\bar{M}_w/\bar{M}_n$	F_{PPA}[a]
PPA-b-PDEAAm	10.1	1.55	22.6	1.91	0.21

[a] F_{PPA} is the molar fraction of PPA in the final block copolymer PPA-*b*-PDEAAm and was determined by ^{1}H NMR. The PPA macroinitiator was PPA-5 (see Table 1) and its molecular weight was measured against poly(styrene) standards in THF at 40 ^{o}C. The PPA-*b*-PDEAAm molecular weight was measured relative to poly(methyl methacrylate) standards in DMF with 1 g·L^{-1} LiBr at 50 ^{o}C.

insert Figure 3.

Figure 3 ^{1}H NMR ($CDCl_3$) of A) poly(phenyl acrylate) homopolymer (PPA-5) and B) poly(phenyl acrylate)-block-poly(diethyl acrylamide) (PPA-b-PDEAAm).

Insert Figure 4.

Figure 4 GPC chromatograms of the PPA macroinitiator (PPA-5, solid line) and the chain extended species (PPA-b-PDEAAm, dotted line) in the chain extension experiments.

3.3. Thermo-Responsive Behavior Illustrated by UV-Visible Spectrometry and Dynamic Light Scattering

The thermo-responsive behavior of a 0.5 wt% solution of PPA-b-PDEAAm block copolymer ($\bar{M}_n$ = 22.6 kg·mol^{-1}, $\bar{M}_w/\bar{M}_n$=1.91) in water was examined by UV-Vis spectroscopy (Figure 5a) and dynamic light scattering (DLS) (Figure 5b). Due to the relatively hydrophobic PPA segment (F_{PPA} = 0.21), the block copolymers were not completely soluble in pure H_2O and the solution was slightly opaque at room temperature. This was reduced upon slight heating below the cloud point temperature. The light transmittance profile showed typical behavior of LCST-type phase separation, where the solution was nearly 100% transparent at low temperature and became cloudy (~ 10% transmittance) quickly above the critical solution temperature, reflecting the sudden solubility decrease of polymer in water. The cloud point temperature T_{cp} determined here is below the 33 ^{o}C reported by Idziak et al. for the homopolymer PDEAAm.[37] This can be ascribed to the presence of the hydrophobic PPA segment, which tends to suppress the LCST of the copolymer.[38-40] Also, the block copolymer exhibited a slight hysteresis in cloud point temperature between the heating and the cooling cycles (T_{cp} = 30 ^{o}C for heating and T_{cp} = 26 ^{o}C for cooling), which has also been observed for thermo-responsive polymers bearing tertiary amines.[40-42] It is generally attributed to the inter-polymer hydrogen bonding of the tertiary amine groups.[42, 43] In DLS measurements, the hydrodynamic diameter D_h was below 100 nm at low temperature for all cases and sharply increased to above 130 nm when the critical temperature was reached, illustrating the transformation from small micelles to large aggregated particles upon heating. The critical transition temperature observed in DLS corresponds well to that observed by UV-Vis, being about 30 ^{o}C. The relatively large particle sizes at low temperature (5-20 ^{o}C) may be attributable to the relatively high molar fraction of the water insoluble PPA segment in the block copolymer but it was still dispersible in water. As the temperature however increased, the particle size slowly decreased to approximately 70 nm as the temperature increased from 5 ^{o}C to 20 ^{o}C, as the PDEAAm corona was getting more insoluble and compressing, resulting in a smaller D_h. We observed similar behaviour in poly(oligo(ethylene glycol))-based block copolymers. [39] As the CPT was approached, the particle size sharply increased, indicating aggregation to larger particles plateauing at about 140 nm. Larger particles may have precipitated out after T_{cp} was attained. The relatively low hysterisis shown in Figure 5 suggested the copolymer could re-dissolve rather easily upon cooling.

Insert Figure 5.

Figure 5 (a) Light transmittance as a function of temperature of PPA-*b*-PDEAAm block copolymer at 0.5 wt% in de-ionized water measured by UV-Vis spectrometry; (b) hydrodynamic diameter of block copolymer (D_h) as a function of temperature for PPA-*b*-PDEAAm block copolymer in a 0.5 wt% solution in de-ionized water measured by dynamic light scattering.

4. Conclusions

In summary, we showed that that the UV-active monomer PA could be easily homopolymerized by NMP in the temperature range between 90-110 °C and the narrowest molecular weight distributions ($\bar{M}_w/\bar{M}_n$< 1.20) were attained by adding a small fraction of additional free nitroxide (about 15 mol% relative to that of BlocBuilder MA). A PPA homopolymer was used as a macroinitiator for the incorporation of a thermoresponsive DEAAm block. The resulting PPA-b-PDEAAm block copolymer exhibited cloud points in the range 26-30°C, close to that of pure PDEAAm (cloud points of 33 °C). The block copolymers will be examined next for irreversible changes in the PA solubility caused by the Photo-Fries rearangement of the PA segments, which would have a permanent effect on the thermo-responsive behavior of the block copolymers.

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