Controlled Synthesis of Amphiphilic Block Copolymers Based on Poly(Isobutylene) Macromonomers

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ABSTRACT: The synthesis of a monoacrylate functionalized poly(isobutylene) (PIB) macromonomer (PIBA) has been achieved by a two-step reaction starting from a commercially available PIB. Firstly, terminal olefins (vinylidene and trisubstituted olefin) of PIB were transformed to a phenolic residue by Friedel-Crafts alkylation followed by subsequent esterification of the phenol with acryloyl chloride, catalyzed by triethylamine. PIBA structure was confirmed by ^{1}H-NMR, ^{13}C-NMR and GPC before utilizing in the RAFT copolymerization with *N,N*-dimethylacrylamide (DMA) to obtain statistical copolymers (P[(DMA-*co*-(PIBA)]). Monomer conversions were consistently higher than 85% for both DMA and PIBA as monomer feed composition was varied. Chain extension of poly(*N,N*-dimethylacrylamide) with PIBA to synthesize block copolymers (P[(DMA-*b*-(PIBA)]) was also achieved with near quantitative monomer conversions (>97%). Block formation efficiency was not quantitative but purification of block copolymers was possible by selective precipitation. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

KEYWORDS: amphiphilic block copolymer; block copolymers; copolymerization; macromonomer; polyisobutylene; RAFT polymerization

INTRODUCTION Polyisobutylene (PIB) macromonomers have been of substantial interest, both academically and technologically, as they allow the synthesis of graft copolymers with other monomers,[1–3] polymer networks and amphiphilic polymer co-networks (APCN).[4–8] These materials have been demonstrated to be effective for a number of applications, such as polymeric surfactants and dispersants, sealants, coatings, adhesives, and drug delivery vehicles.[9–15]

Preparation of PIB graft copolymers and APCN rely on the synthesis of well-defined mono or multi functionalized PIB macromonomers. This has been previously achieved by hydroboration and oxidation of allyl terminated PIB to hydroxyl terminated PIB, which can be subsequently esterified with (meth)acryloyl chloride to PIB (meth)acrylate.[1,16,17] Moreover, allyl terminated PIB has been successfully epoxylated to the corresponding epoxy terminated PIB.[18] More recently bromoallyl terminated PIB has been converted into PIB end capped with a variety of functional groups including many monomer classes; (meth)acrylate, vinyl ether and epoxy by nucleophilic substitution facilitated by a phase transfer catalyst to quantitative conversions.[19,20] Storey and coworkers have demonstrated a one-step reaction, immediately following the living carbocationic polymerization of PIB, by capping the living polymer with phenoxyalkyl (meth)acrylates to synthesize well defined telechelic PIB (meth)acrylates.[21]

These PIB macromonomer syntheses techniques show a progression to simplified synthetic routes requiring less demanding synthetic steps. However, certain PIB end groups may be required and are achieved by terminating the living carbocationic polymerization with specific reagents. These reagents can be avoided by utilizing a source of commercial PIB, which could be modified to a PIB macromonomer with high chain end group fidelity via post-polymerization functionalization of the end group. Such a source of commercial PIB exists and is commonly known as highly reactive PIB as the material is primarily end capped by a vinylidene.[22] The vinylidene group is commonly reacted with maleic anhydride to yield polyisobutenylsuccinic anhydrides (PIBSAs), which are imidized with primary amines to the corresponding polyisobutenylsuccinimides (PIBSIs).[23] Furthermore, highly reactive PIB is used to alkylate phenol via a Friedel-Crafts alkylation to synthesize polyisobutenyl phenols (PIBPs) that are precursors for the so called "Mannich type dispersants."[24–26]

RAFT polymerization has been widely utilized since its discovery in 1998 to synthesize well defined block copolymers and statistical copolymers of predictable and controllable molecular weight as well as monomer composition.[27–33] An acrylate macromonomer was chosen as there has been impressive recent literature that controls the homopolymerization and copolymerization, with acrylamides, of acrylates to synthesize highly sequence controlled multiblock copolymers[34] as well as sequence controlled oligomers.[35] This is a strong demonstration of the high end group fidelity that can be achieved during RAFT polymerization.

Herein, this study firstly pursues the synthesis of a PIB macromonomer by transforming highly reactive PIB to PIBP followed by the esterification of the phenolic end group to an acrylate using acryloyl chloride in the presence of triethylamine. To the best of our knowledge this methodology has only been utilized before to synthesize telechelic PIB acrylates.[36] Second, we demonstrate the use of RAFT polymerization to prepare a wide range of graft, block and statistical copolymers of acrylamide monomer and said PIB acrylate macromonomer.

EXPERIMENTAL

Materials

Phenol (Fisher Scientific, >98%), sulfuric acid (BDH laboratories, 98%), magnesium sulfate (Fisher Scientific), 35% HCl solution (VWR), triethylamine (Aldrich, ≥99%), acryloyl chloride (Aldrich, 97%) were all used as received. DCM, *n*-hexane, ethanol, DMF, THF and toluene used were all HPLC grade and used as received. *N,N*-dimethylacrylamide (Aldrich, 99%) and 2-(dimethylamino)ethyl acrylate (Aldrich, 98%) were destabilized by passing through a short column of basic aluminium oxide prior to polymerization. Functional polyisobutylene was provided by Innospec LTD and used as received.

Synthetic Procedures

Synthesis of Polyisobutylene Macromonomer (PIBA)—Fridel-Crafts Alkylation of Phenol with Polyisobutylene

PIB (50.1 g, 50.1 mmol, 1 eq.) and phenol (47.0 g, 501 mmol, 10 eq.) were dissolved in DCM (300 mL) and cooled down to 0 °C. Concentrated sulfuric acid (3.2 mL, 60.1 mmol, 1.2 eq.) was added drop wise to the solution maintained at 0 °C. Mixture was allowed to reach room temperature and left stirring for 60 h. DCM removed by rotary evaporator and resulting viscous liquid was dissolved in *n*-hexane (200 mL). Organic layer washed with 90% ethanol 10% water solution (2 × 50 mL), DMF (4 × 50 mL) and again with 90% ethanol 10% water solution (2 × 50 mL). Organic layer was dried over magnesium sulfate before filtering and removing all *n*-hexane to yield the product PIBP.[24] ^{1}H-NMR (400 MHz, $CDCl_3$,303 K): δ/ppm 0.97–1.03 ((-CH_3)$_3$, PIB α-terminus), 1.05–1.16 ((-CH_3)$_2$, PIB repeat unit), 1.39–1.46 (s, -CH_2-, PIB repeat unit), 1.80 (s, -CH_2C(CH$_3$)$_2$(C$_6$H$_5$OH)), 6.75 (d, C$_6$$H_5$OH), 7.22 (d, C$_6$$H_5$OH). GPC: M_n 1200 g/mol, M_w 1900 g/mol, $Đ$ 1.60.

Synthesis of Polyisobutylene Macromonomer (PIBA)—Esterification of PIBP with Acryloyl Chloride

PIBP (30.13 g, 30.13 mmol, 1 eq.) was dissolved in THF (150 mL) and cooled down to 0 °C. TEA (5.3 mL, 37.03 mmol, 1.25 eq.) was added to the solution followed by drop wise addition of acryloyl chloride (3.1 mL, 38.15 mmol, 1.25 eq.) to the solution maintained at 0 °C and left to stir at 0 °C for 4 h before allowing to reach room temperature and left to stir for a further 18 h. THF removed by rotary evaporator and resulting viscous liquid was dissolved in *n*-hexane (150 mL). Organic layer was washed with 1 M HCl solution (3 × 40 mL), 90% ethanol 10% water solution (2 × 40 mL), DMF (4 × 40 mL) and again with 90% ethanol 10% water solution (2 × 40 mL). Organic layer dried over magnesium sulfate before filtering and removing all *n*-hexane to yield the product PIBA. ^{1}H-NMR (400 MHz, $CDCl_3$, 303 K): δ/ppm 0.97–1.03 ((-CH_3)$_3$, PIB α-terminus), 1.05–1.16 ((-CH_3)$_2$, PIB repeat unit), 1.39–1.46 (s, -CH_2-, PIB repeat unit), 1.84 (s, -CH_2C(CH$_3$)$_2$(C$_6$H$_5$OH)), 5.98 (d, -CH=CH$_f$$H_g$), 6.29 (q, -C$H$=CH$_fH_g$), 6.58 (d, -CH=C$H_fH_g$), 7.04 (d, C$_6$$H_5$O-), 7.37 (d, C$_6$$H_5$O-). GPC: M_n 1400 g/mol, M_w 2100 g/mol, $Đ$ 1.56.

RAFT Homopolymerization of DMA

In a typical polymerization, DMA, BDTMP, V601 and toluene were charged into a Schlenk tube and degassed by gentle bubbling of N_2 gas for 30 min. Schlenk tube was submerged into an oil bath at 70 °C. Samples taken via degassed syringe at desired time points. Schlenk tube removed after 1 h and placed into liquid N_2 to quickly reduce the temperature and terminate polymerization. Reaction mixture was diluted with acetone and P(DMA) was precipitated into a large volume of *n*-hexane, filtered and dried overnight under vacuum. Product was a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$, 303 K): δ/ppm 1.40–1.93 (m, -CH_2-), 2.14–2.74 (m, -CH-), 2.74–3.23 (m, -N(CH_3)$_2$).

RAFT Homopolymerization of PIBA

In a typical polymerization, PIBA, BDTMP, V601 and toluene were charged into a Schlenk tube and degassed by gentle bubbling of N_2 gas for 30 min. Schlenk tube was submerged into an oil bath at 70 °C. Schlenk tube removed after 18–22 h and placed into liquid N_2 to quickly reduce the temperature and terminate polymerization.

RAFT Copolymerization of DMA and PIBA

In a typical polymerization, DMA, PIBA, BDTMP, V601 and toluene were charged into a Schlenk tube and degassed by gentle bubbling of N_2 gas for 30 min. Schlenk tube was submerged into an oil bath at 70 °C. Samples taken via degassed syringe at desired time points. Schlenk tube removed after 8 h and placed into liquid N_2 to quickly reduce the temperature and terminate polymerization. The reaction mixture was diluted with THF and P[(DMA)-*co*-(PIBA)] was precipitated into a large volume of acetone. P[(DMA)-*co*-(PIBA)] was allowed to settle before carefully decanting off the excess acetone, P[(DMA)-*co*-(PIBA)] dissolved in THF and precipitated again in acetone before removing excess solvent under vacuum. Product collected was a very viscous pale yellow

liquid. ^{1}H-NMR (400 MHz, $CDCl_3$, 303 K): δ/ppm 0.98–1.02 (s, (-CH_3)$_3$, PIB α-terminus), 1.06–1.18 (-CH_3)$_2$, PIB repeat unit), 1.40–1.49 (m, -CH_2-, PIB repeat unit), 1.52–1.96 (m, -CH_2-, P(DMA) repeat unit), 2.33–2.75 (m, -CH-, P(DMA) repeat unit), 2.75–3.21 (m, -N(CH_3)$_2$, P(DMA) repeat unit).

Chain Extension of P(DMA) with PIBA

In a typical polymerization, P(DMA) (**P1**), PIBA, V601 and toluene were charged into a Schlenk tube and degassed by gentle bubbling of N_2 gas for 30 min. Schlenk tube was submerged into an oil bath at 70 °C. Schlenk tube removed after 24 h and placed into liquid N_2 to quickly reduce the temperature and terminate polymerization. Reaction mixture was diluted with THF and P[(DMA)-*b*-(PIBA)] was precipitated into a large volume of acetone. P[(DMA)-*b*-(PIBA)] was allowed to settle before carefully decanting off the excess acetone, P[(DMA)-*b*-(PIBA)] dissolved in THF and precipitated again in acetone before removing excess solvent under vacuum. Product collected was a very viscous pale yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$, 303 K): δ/ppm 0.98–1.02 (s, (-CH_3)$_3$, PIB α-terminus), 1.06–1.18 (-CH_3)$_2$, PIB repeat unit), 1.40–1.49 (m, -CH_2-, PIB repeat unit), 1.52–1.96 (m, -CH_2-, P(DMA) repeat unit), 2.33–2.75 (m, -CH-, P(DMA) repeat unit), 2.75–3.21 (m, -N(CH_3)$_2$, P(DMA) repeat unit).

Characterization Techniques

Gel Permeation Chromatography

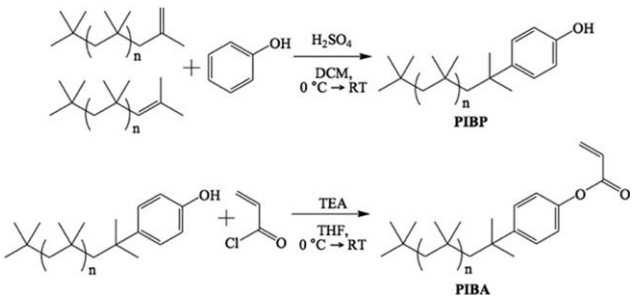
Molecular weight averages and polymer dispersity was determined by GPC. GPC measurements were performed on an Agilent 1260 infinity system equipped with 2 PLgel 5 μm mixed-D columns (300 × 7.5 mm), a PLgel 5 μm guard column (50 × 7.5 mm), a refractive index detector (RID) and variable wavelength detector (VWD). The system was eluted with THF and 2% v/v TEA at a flow rate of 1 mL/min and the RID was calibrated with linear narrow polystyrene standards.

Nuclear Magnetic Resonance Spectroscopy

^{1}H-NMR and ^{13}C-NMR spectra were measured using a Bruker AV-400. Chemical shifts are reported in parts per million (ppm) and all spectra are referenced against the residual solvent peak found in the deuterated NMR solvent. Abbreviations used for peak multiplicity are as follows; s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Gas Chromatography—Flame Ionization Detection

GC-FID was used to measure monomer conversions for homopolymerization of DMA. GC-FID analysis was performed using an Agilent Technologies 7820A. An Agilent J&W HP-5 capillary column of 30 m × 0.320 mm, film thickness 0.25 μm was used. The oven temperature was programmed as follows: 40 °C (hold for 1 min) increase at 30 °C/min to 300 °C (hold for 2.5 min). The injector was operated at 250 °C and the FID was operated at 320 °C. Nitrogen was used as carrier gas at flow rate of 6.5 mL/min and a split ratio of 1:1 was applied. Chromatographic data was processed using OpenLab CDS ChemStation Edition, version C.01.05.



SCHEME 1 Synthesis of PIBP by Friedel-Crafts alkylation of phenol with vinylidene/trisubstituted olefin PIB (*top*), synthesis of PIBA by esterification of PIBP with acryloyl chloride (*bottom*).

Ultraviolet—Visible Spectroscopy

UV measurements were performed on a PerkinElmer UV/Vis Spectrometer Lambda 35.

RESULTS AND DISCUSSION

Polyisobutylene Macromonomer Synthesis

An acrylate macromonomer synthesis is very attractive as there are a wealth of methods to synthesize PIB with hydroxyl functionality; hydroboration of PIB,[16,17] Friedel-Crafts alkylation of phenol with PIB[24–26] as well as reacting PIBSA with ethanolamine.[37] These PIB hydroxyls can then be esterified to an acrylate functionality by reacting with acryloyl chloride, acrylic acid or via transesterifcation with other acrylates. All these methods have been used extensively in monomer synthesis. Of the three methods mentioned above for synthesizing PIB with a hydroxyl group, Friedel-Crafts arylation of phenol with PIB was investigated in this study (Scheme 1).[24]

This method has been shown to be highly efficient at transforming the terminal olefin end group to a phenol. The most common terminal olefins (vinylidene and trisubstituted) are converted to the same *para* functionalized phenol resulting in the highest possible end group fidelity from the PIB supplied.[24] Furthermore, reaction conditions are nonstringent and reaction achieves very high functionalization using a strong acid as catalyst at room temperature. As illustrated in Scheme 1, Friedel-Crafts alkylation of phenol was performed using concentrated sulfuric acid as a catalyst in DCM with a large excess of phenol.

Selected conditions were shown to be successful by ^{1}H-NMR. Disappearance of all peaks corresponding to the two types of olefin present was observed as expected, confirming that both varieties of olefin end groups are transformed into a phenol of which the presence is confirmed by two new doublets at 6.68 ppm and 7.16 ppm (Fig. 1).

Relative integration of the PIB α-terminus –C(CH_3)$_3$ and ω-terminus olefin functionality (both the vinylidene and trisubstituted) indicates that 80% of the PIB chains contain an olefin functionality that can modified to the desired phenol. Following Friedel-Crafts alkylation of phenol, integration of

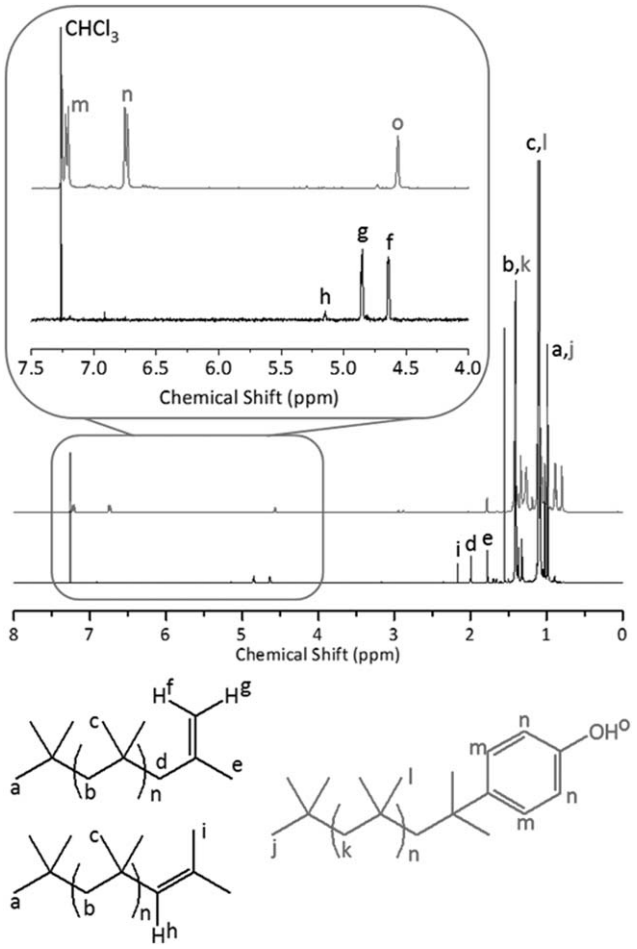


FIGURE 1 ^{1}H-NMR ($CDCl_3$, 400 MHz, 303 K) of PIB (*black*) and PIBP (*red*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the $-C(CH_3)_3$ terminus to phenolic protons indicates that 81% of polymer chains are functionalized with an ω-terminus phenol. Therefore, all end group functionality that can be modified has been. This result agrees very strongly with the literature procedure used to prepare polyisobutylene phenol (PIBP). Furthermore, addition of phenol to the PIB end group is shown by GPC equipped with a VWD measuring at 270 nm. Non-functionalized PIB does not have any UV light absorbance at 270 nm. Therefore, this polymer does not show any UV response in the GPC chromatogram. However, once PIB is functionalized with phenol it is capable of absorbing at 270 nm and is now detectable by GPC with a UV detector (See supplementary information). GPC was also used to measure the M_n of PIBP by RID. M_n was found to decrease slightly after Friedel-Crafts alkylation, from 1250 to 1200 g/mol and the dispersity remain unchanged at 1.60.

Following the synthesis of a hydroxyl functionalized PIB by synthesizing PIBP it is now desired to transform said hydroxyl into a monomer, more specifically an acrylate monomer. This could be achieved via one of two common routes for acrylate synthesis. The first one is by reacting a hydroxyl with acryloyl chloride in the presence of base and the second route is by reacting with acrylic acid in the presence of a coupling agent. However, phenols are known to react slowly with carboxylic acids so esterification of PIBP with acryloyl chloride in the presence of triethylamine (TEA) was selected (Scheme 1).

Using only a slight excess of acryloyl chloride and TEA at room temperature it was possible to esterify 98% of the PIBP to the desired macromonomer; polyisobutylene acrylate (PIBA). Esterification is confirmed by ^{1}H-NMR as shown in Figure 2. Doublets corresponding to the four phenolic protons at 6.68 and 7.16 ppm shift down field following esterification to 6.96 and 7.29 ppm respectively, furthermore the new vinyl protons are observable at 5.90, 6.21, and 6.50 ppm, which match the expected relative integrations. Furthermore, relative integration of the PIB α-terminus

$-C(CH_3)_3$ and ω-terminus acrylate functionality estimates that 77% of polymer chains bear the desired acrylate functionality. Although end group fidelity of PIBA is lower than other examples of PIB macromonomer synthesis. This synthetic methodology represents an efficient macromonomer

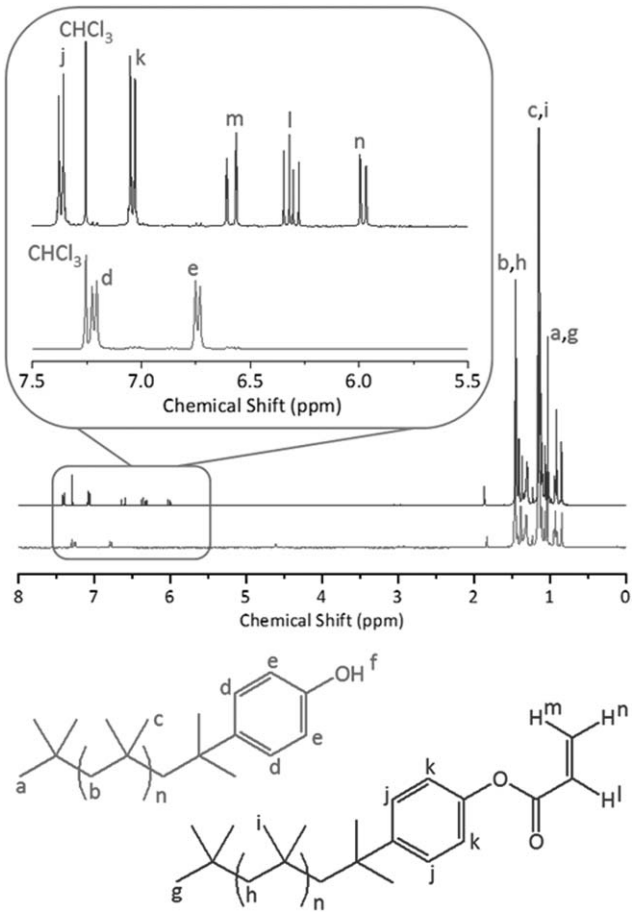


FIGURE 2 ^{1}H-NMR ($CDCl_3$, 400 MHz, 303 K) of PIBP (*red*) and PIBA (*blue*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

synthesis from readily available PIB that utilizes the vast majority of end group functionality present.

GPC measures an increase in M_n after esterification of the PIBP to PIBA. M_n increases from 1200 to 1400 g/mol and dispersity remains consistent decreasing from 1.60 to 1.57. GPC chromatograms demonstrate the increase in M_n by a slight shift to the lower elution time, but perhaps more importantly is that there is no evidence of autopolymerization occurring throughout the esterification reaction or purification that would have manifested itself as a high molecular weight shoulder.

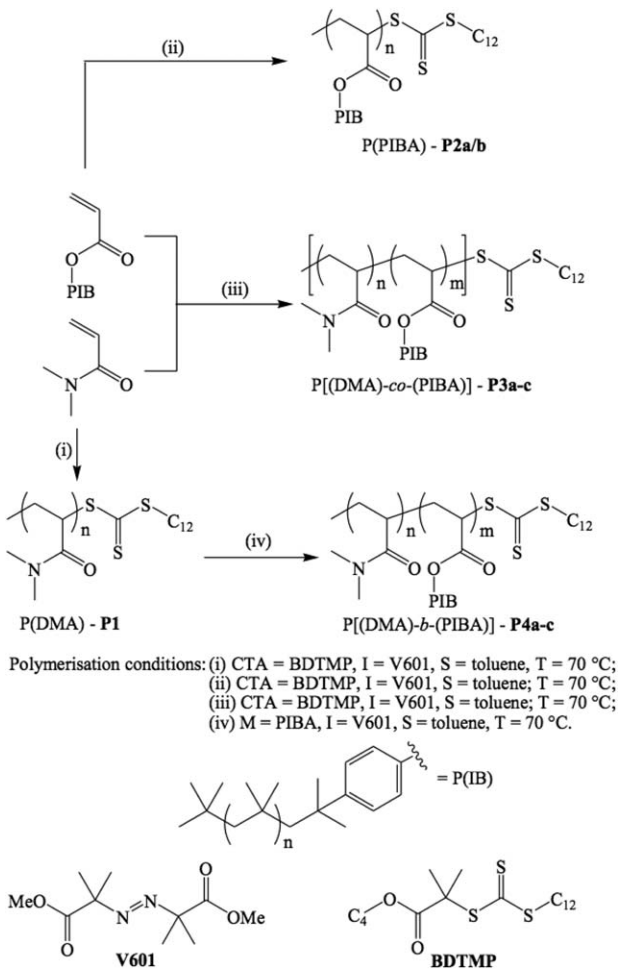
Statistical Copolymers Containing PIB Grafts by RAFT Polymerization

First, it is vital to confirm that the chosen small molecule monomer polymerises in a controllable manner before incorporation of any PIBA. Homopolymerization of *N*,*N*-dimethylacrylamide (DMA) was first attempted using BDTMP as a RAFT agent and V601 as an initiator in toluene at 70 °C (Scheme 2). These conditions were chosen as there are previous reports that utilize a trithiocarbonate RAFT agent and azo-initiator to polymerize DMA in a highly controlled manner.[38,39]

To assess if DMA could be homopolymerized under the above conditions a kinetic study has been conducted by withdrawing samples from the polymerization at regular intervals. Plotting a semi-logarithmic plot of the natural logarithm of DMA concentration against time displays a linear correlation and as such pseudo first order kinetics (Fig. 3). However, it was observed that there is an induction period for the first 15 min of the polymerization. This phenomenon has been observed in other RAFT agent/monomer pairs as well as DMA homopolymerization mediated by a dithiobenzoate.[40–42] Davis and co-workers reported that the likely origin of an induction period such as this occurs because of slow fragmentation of the initial intermediate macroRAFT radicals as the stability of the initial RAFT agent after addition of a radical is different to that of the macroRAFT radical.[42] Despite this induction period; pseudo first order kinetics are observed for the remainder of DMA homopolymerization of up to 99% monomer conversion.

Evolution of molecular weight was also measured for the RAFT homopolymerization of DMA. Very good agreement between the theoretical and measured M_n was observed, indicating that molecular weight of the P(DMA) is increasing proportionally with total monomer conversion as is expected of a controlled radical polymerization (Fig. 3).

Furthermore, P(DMA) dispersity remains consistently narrow (~1.1) throughout the entirety of the polymerization, another expectation of controlled radical polymerization. Evolution of molecular weight is also demonstrated by the shift to higher molecular weight of overlaid GPC traces (Fig. 3). RAFT homopolymerization of DMA was subsequently scaled up (~10 g) to synthesize P(DMA) (**P1**) that will be chain extended with PIBA.



SCHEME 2 Synthesis of P(DMA) (*i*), synthesis of P(PIBA) (*ii*), synthesis of P[(DMA)-*co*-(PIBA)] (*iii*), synthesis of P[(DMA)-*b*-(PIBA)] (*vi*). CTA = chain transfer agent, I = initiator, S = solvent and M = monomer.

After obtaining kinetic measurements for RAFT homopolymerization of DMA the intention was to terminate the polymerization at 60 min, (80% conversion) as here is evidence that terminating RAFT polymerizations at lower monomer conversion improves the end group fidelity of the final polymer. However, despite terminating the polymerizations after 60 min the monomer conversion was slightly higher. Measuring the GPC of **P1** with the RID and VWD set to 308 nm provided two GPC chromatograms, which overlap perfectly. This indicated that the obtained polymer does bear a trithiocarbonate functional group as the trithiocarbonate end group absorbs at 308 nm (Fig. 3).

After selecting a suitable monomer (DMA) to copolymerize with PIBA and confirming it can be homopolymerized with good control by the selected RAFT polymerization system; initiated by V601 and mediated by BDTMP in toluene at 70 °C. This system was utilised again for the homopolymerization of PIBA (Scheme 2). This ensured that the RAFT system was suitable for each individual monomer before attempting a copolymerization between PIBA and DMA.

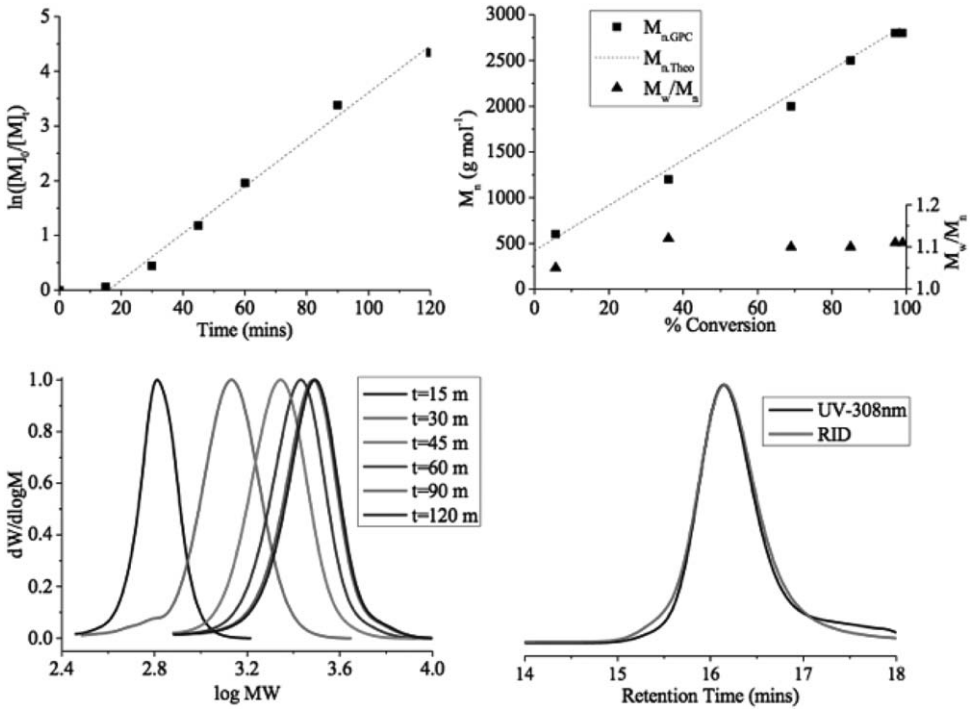


FIGURE 3 Characterization for the RAFT homopolymerization of DMA. Semi logarithmic plot (*top left*), measured and theoretical M_n of P(DMA) against total monomer conversion (*top right*), evolution of GPC traces of P(DMA) over time (*bottom left*), VWD (308 nm) and RID GPC traces of sample P1 after precipitation (*bottom right*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Initial attempts of polymerizing PIBA at a monomer to RAFT agent ratio of 25:1 were unsuccessful, resulting in very low conversions, ~10%, of PIBA to P(PIBA). This was an unexpected result but there were potential causes of this low conversion, such as phenyl acrylates being incompatible with the BDTMP/V601 system chosen, PIBA being too sterically hindered and unable to initiate/propagate fast enough, chain entanglement of the PIB chains inhibiting mobility to effective initiation/propagation or the presence of an impurity, which is inhibiting the polymerization. For instance, the residual 2% PIBP, which has a *para*-substituted phenol as an end group, would be sufficient enough to inhibit the polymerization. It is known as substituted phenols are commonly used as radical inhibitors.

A number of these potential problems could be addressed or at least minimalized by increasing the concentration of initiator. Increasing initiator concentration would increase rate of initiation and propagation as well as overpowering the PIBP, which is present and may be inhibiting the polymerization. RAFT homopolymerization of PIBA was attempted again after reducing the monomer to initiator concentration from 25:0.1 to 10:0.1 and then increasing from 10:0.1 to 10:0.25 (Table 1).

Increasing the concentration of V601 in the RAFT homopolymerization of PIBA had the desired result; PIBA conversion was increased significantly to 65% when using 0.1 equivalents of initiator to 10 equivalents of monomer and PIBA conversion further increased to 97% conversion of PIBA when increasing the equivalents of V601 to 0.25. Furthermore, GPC measures an increase in M_n for both homopolymerizations of PIBA attempted and polymer dispersity is much higher than normally expected of controlled polymerizations. However, high dispersity is expected as the initial macromonomer itself has a broad dispersity (1.57) and polymerization will only exaggerate this dispersity. Increase to higher molecular weight can be clearly seen on the GPC traces of PIBA homopolymerization and free radical polymerization after 18 and 22 h for 10% and 25% V601, respectively (Fig. 4).

RAFT homopolymerization of PIBA was only successful after increasing the V601 concentration. However, increased radical concentration could result in more termination and as

TABLE 1 Characterization for the synthesis of P(PIBA) by RAFT polymerization of PIBA

Sample	[PIBA]:[BDTMP]:[V601]	Conv. PIBA (%)	$M_{n,GPC}$ (g/mol)	$Đ$
P2a	10:1:0.10	65	3,000	2.36
P2b	10:1:0.25	97	4,600	1.93
P2c	10:0:0.10	85	4,400	12.52
P2d	10:0:0.25	95	5,800	9.84
P2e	10:0:0.50	>99	5,900	9.83
P2f	10:0:1.00	>99	6,000	9.92

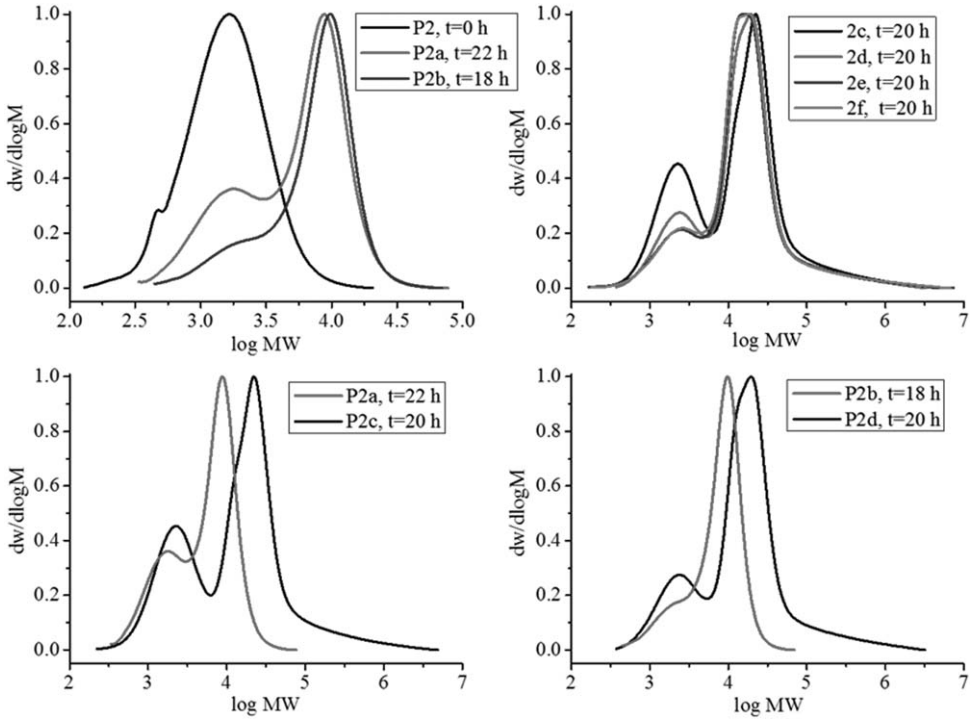


FIGURE 4 GPC traces of P(PIBA) (P2a/b) synthesized by RAFT polymerization (*top left*) GPC traces of P(PIBA) (P2c-f) synthesized by free radical polymerization (*top right*) GPC traces of P(PIBA) synthesized with 0.1 (*bottom left*) or 0.25 (*bottom right*) equivalent of V601 with and without RAFT agent present. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

such a non-living polymerization. This may cause the high polymer dispersity obtained for P2a and P2b. Therefore, a series of free radical homopolymerizations of PIBA were performed to demonstrate that the presence of the RAFT agent is essential for obtaining a lower dispersity. Table 1, samples P2c-f utilise increasing molar equivalents of V601 to PIBA. In all four free radical polymerizations of PIB extremely high dispersity is obtained ($>$9.80) and the GPC distributions are multimodal as opposed to the bimodal distributions of RAFT mediated PIBA homopolymerization (Fig. 4). Furthermore, GPC measures very high molecular weight ($>1 \times 10^6$ g/mol) polymer forming when no RAFT agent is present.

PIBA conversion was high ($\geq$85%) for all free radical polymerizations of PIBA and may indicate that RAFT polymerization of PIBA when using 0.1 molar equivalents of V601 is capable of proceeding to higher conversions given longer polymerization duration.

The RAFT polymerization system utilized was found to be suitable for both the controlled homopolymerization of DMA and PIBA to high conversion. With this knowledge the RAFT copolymerization of DMA and PIBA was then attempted to synthesize a random copolymer composed of a P(DMA) backbone with PIB grafts (P[(DMA)-*co*-(PIBA)]) (Scheme 2).

Kinetic measurements were performed for the RAFT copolymerization of DMA and PIBA. Monomer conversions could be measured independently by ^{1}H-NMR and revealed that the two monomers polymerized at a similar rate, at this given monomer ratio of DMA:PIBA = 22.5:2.5, showing pseudo first order kinetics after an induction period (Fig. 5). The induction period occurred for both DMA and PIBA and lasted the same length of time. Furthermore, the induction period lasted longer than the induction period observed throughout DMA homopolymerization, 60 min compared to 20 min. Final conversions for both DMA and PIBA were $>$99%, this is in good agreement with the conversions obtained for the RAFT homopolymerizations performed previously in this study.

Measuring the M_n of the growing P[(DMA)-*co*-(PIBA)] throughout the copolymerization reveals that the M_n increases with monomer conversion. However, the relationship between M_n and total monomer conversion is nonlinear (Fig. 5). Moreover, M_n measured by GPC at low total conversion ($<$20%) is greater than the theoretical M_n calculated but as total monomer conversion increases above 20% the measured M_n becomes significantly lower than the theoretical value. This difference in measured and theoretical M_n was also observed for the RAFT homopolymerization of PIBA is expected due to the limitation of using GPC with linear narrow molecular standards which underestimates M_n of star/graft polymers, such as this copolymer P[(DMA)-*co*-(PIBA)], as they have a lower hydrodynamic volume compared to a linear polymer of the same molecular weight.

Overlaying GPC traces of the evolution of molecular weight for P[(DMA)-*co*-(PIBA)] also demonstrates the increasing M_n

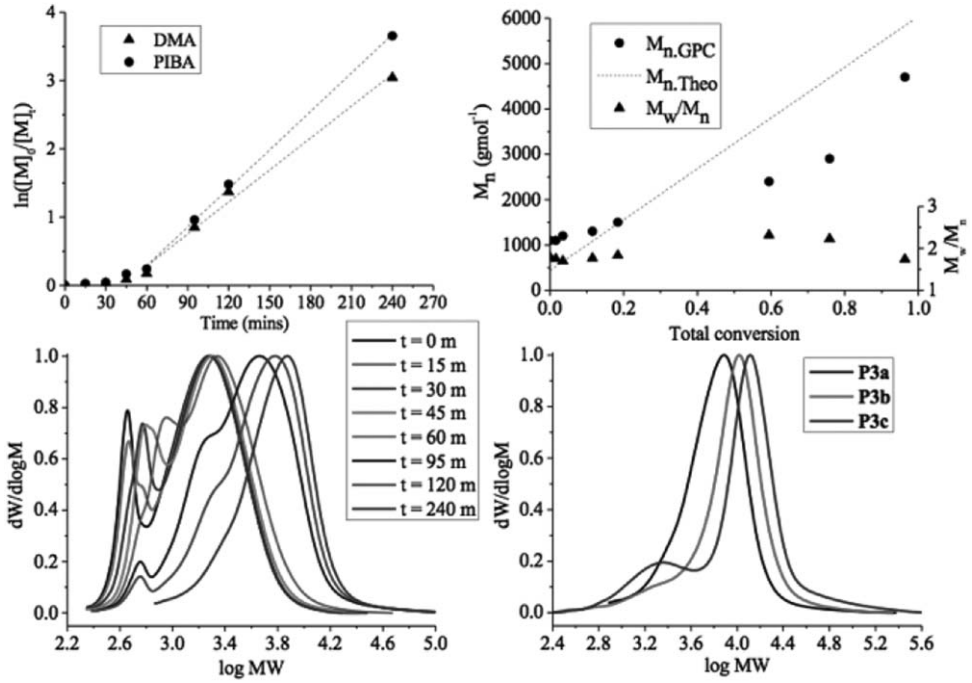


FIGURE 5 Characterization for the RAFT copolymerization of DMA and PIBA; semi logarithmic plot (*top left*), measured and theoretical M_n of P[(DMA)-*co*-(PIBA)] against total monomer conversion (*top right*), evolution of GPC traces of P[(DMA)-*co*-(PIBA)] over time (*bottom left*), GPC traces of P[(DMA)-*co*-(PIBA)] samples P3a-c (*bottom right*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

throughout the reaction (Fig. 5). RAFT copolymerization of DMA and PIBA was then attempted at different equivalents of DMA and PIBA to synthesize P[(DMA)-*co*-(PIBA)] with a greater composition of PIBA and thus contain more hydrophobic groups relative to polar monomers. Additional copolymerizations were performed at 20:5 (**P3b**) and 15:10 (**P3c**) monomer equivalents (DMA:PIBA) and were polymerized for 8 h instead of 4 given the higher proportion of PIBA (Table 2). **P3c** copolymerization yielded high conversion for both monomers. Final M_n and M_w were also higher when compared to **P3a** as the copolymer contained more of the macromonomer PIBA. However, the increase of PIBA content resulted in increased polymer dispersity as expected.

Copolymerization with the highest equivalents of PIBA (**P3c**) also achieved high conversion of DMA and PIBA, 95 and 85% respectively; however, this was a deviation from the very high conversions obtained previously. Lower conversion of PIBA is also responsible for lowering the M_n of the final copolymer and is clearly visible on the GPC as the lower molecular weight distribution of a bimodal distribution (Fig. 5). Overlaying the GPC traces of the three synthesized P[(DMA)-*co*-(PIBA)] samples also demonstrates the shift towards higher molecular weight. These copolymerizations were performed with 0.1 equivalents of V601 relative to BDTMP. It was demonstrated earlier that increasing initiator equivalents from 0.1 to 0.25 increased PIBA conversion from 65 to 97%. This may be required as well as longer reaction times if higher proportions of PIBA are to be incorporated into a P[(DMA)-*co*-(PIBA)] copolymer.

Block Copolymers of P(DMA) and P(PIBA) by RAFT Polymerization

Chain extension of P(DMA) (**P1**) with PIBA was performed at increasingly higher equivalents of PIBA to P(DMA) whilst maintaining 0.25 equivalents of V601 relative to P(DMA), a ratio found earlier to be adequate at homopolymerizing PIBA to very high conversion (97%), (Scheme 2). This resulted in

TABLE 2 Characterization for the synthesis of P[(DMA)-*co*-(PIBA)] copolymers by RAFT copolymerization of DMA and PIBA

Sample	[DMA]:[PIBA]:[BDTMP]	Conv. DMA (%)	Conv. PIBA (%)	$M_{n,GPC}$ (g/mol)	$Đ$
P3a	22.5:2.5:1	100	100	5,000	1.70
P3b	20:5:1	99	100	5,300	2.21
P3c	15:10:1	95	85	4,800	3.50

TABLE 3 Characterization for the synthesis of P[(DMA)-*b*-(PIBA)] copolymers by chain extension of P(DMA) (P1) with PIBA

Sample	[PDMA]:[PIBA]	Conv. PIBA (%)	$M_{n,GPC}$ (g/mol)	$Đ$
P4a	1:4	100	6,600	1.96
P4b	1:7	100	8,500	2.02
P4c	1:10	97	8,800	3.44

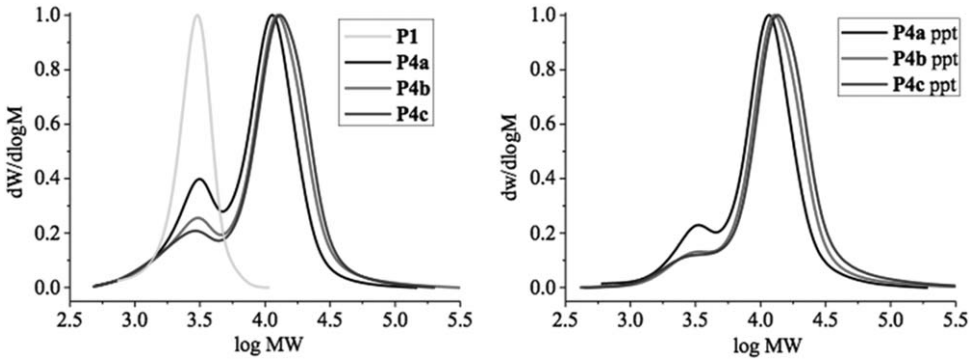


FIGURE 6 GPC traces of P(DMA) and crude P[(DMA)-*b*-(PIBA)]s (*left*) and GPC traces of precipitated P[(DMA)-*b*-(PIBA)]s (P4a-c) (*right*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a range of P[(DMA)-*b*-(PIBA)] block copolymers with a fixed chain length of the P(DMA) block whilst increasing length of the P(PIBA) block.

Chain extension of P(DMA) with PIBA was performed at three different ratios of P(DMA) to PIBA; 1:4, 1:7 and 1:10. Conversion of PIBA was very high ($\geq$97%) for all three chain extension reactions (Table 3). Furthermore, a notable increase of M_n and M_w, 2600 and 3000 g/mol, respectively, of the original P(DMA) was measured by GPC after 24 h of polymerization at 70 °C (Table 3). M_n and especially M_w increased to a greater extent as the equivalents of PIBA increased from 4 to 7 to 10. This is expected as each P(DMA) is on average chain extended with more PIBA repeat units. Inspection of the crude GPC traces of the chain extension reactions demonstrates that all three chain extensions are bimodal and the lower molecular weight distribution corresponds to the P(DMA) that was utilized as the macroRAFT agent (Fig. 6). This indicates that some of the P(DMA) failed to reinitiate and was not chain extended with PIBA. Fortunately, the solubility of the initial P(DMA) and newly synthesized P[(DMA)-*b*-(PIBA)] are sufficiently different that the P(DMA) can be removed by precipitation into *n*-hexane as the P[(DMA)-*b*-(PIBA)] is fully soluble. Purification of the P[(DMA)-*b*-(PIBA)] samples is confirmed by GPC of and the disappearance of the distribution, which corresponded to the P(DMA) (Fig. 6). However, there is still a low molecular weight shoulder on the P[(DMA)-*b*-(PIBA)] distributions, which is caused by the presence of unfunctionalized PIB which contains no terminal olefin and therefore cannot be converted to PIBA. Precipitated molecular weight averages and dispersity are reported in (Table 3).

Despite the nonquantitative chain extension of P(DMA) to P[(DMA)-*b*-(PIBA)] these chain extensions are very promising and demonstrate that such a block copolymer can be synthesized and has many potential tuneable properties; P(DMA) block length, P(PIBA) block length, length of PIB graft and potentially the use of a different acrylamide to form the initial block can provide an alternative functionality.

CONCLUSIONS

PIB terminal olefins have been successfully converted to a phenol end group by Friedel-Crafts alkylation of phenol to synthesize PIBP. It was than possible to esterify PIBP with acryloyl chloride to synthesize a PIB acrylate macromonomer, PIBA.

RAFT polymerization, mediated by BDTMP and initiated by V601 in toluene at 70 °C, was utilised to homopolymerize DMA in a controlled process to synthesize homopolymers of controlled molecular weight with low dispersities at high monomer conversion. These same conditions for RAFT polymerization were optimized slightly to successfully polymerize the newly synthesized PIBA to very high conversion (97%).

RAFT was than utilized to synthesize copolymers of PIBA; firstly PIBA was copolymerized with DMA to synthesize P[(DMA)-*co*-(PIBA)]. DMA copolymerizations were highly effective; conversion of both monomers were all above 85% even at increasing molar equivalents of PIBA and M_w increased predictably as more PIBA was incorporated into the copolymer.

Finally, chain extensions of the previously synthesized P(DMA) with PIBA to synthesize P[(DMA)-*b*-(PIBA)] was achieved. P(DMA) chain extensions were very successful and >97% conversion of PIBA was obtained at increasing molar equivalents of PIBA and M_w increased predictably as more PIBA was polymerized. There was evidence of P(DMA) that was not chain extended but it was possible to remove this P(DMA) by precipitation.

Therefore, this methodology of copolymerizing and homopolymerizing a PIB macromonomer by RAFT polymerization with a chosen acrylamide can be utilized to synthesize new structures, which have multiple properties that could be tuned for a number of end uses. Firstly, copolymer architecture can be either a statistical copolymer, block copolymer or potentially a star if a multifunctional RAFT agent is utilized. Second, the chosen acrylamide could vary beyond DMA, which was used for this work. Statistical copolymers could vary in composition of PIB macromonomer to acrylamide. Block copolymers could vary in block length of acrylamide as well as the PIB macromonomer block length. Finally, the chain length of the PIB macromonomer could be tuned by functionalizing a different molecular weight PIB.

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REFERENCES AND NOTES

1 J. P. Kennedy, M. Hiza, *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 1033–1044.

2 A. Takacs, R. Faust, *J. Macromol. Sci. Chem.* **1996**, *A33*, 177–131.

3 W. Ma, Y. Wu, L. Feng, R. Xu, *Polymer* **2012**, *53*, 3185–3193.

4 J. P. Kennedy, S. Midha, A. Gadkari, *J. Macromol. Sci. Chem.* **1991**, *A28*, 209–224.

5 T. K. Georgiou, C. S. Patrickios, P. W. Groh, B. Iván, *Macromolecules* **2007**, *40*, 2335–2343.

6 G. Kali, S. Vavra, K. László, B. Iván, *Macromolecules* **2013**, *46*, 5337–5344.

7 S. K. Jewrajka, J. P. Kennedy, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2612–2623.

8 J. Scherble, R. Thomann, B. Iván, R. Mulhaupt, *J. Polym. Sci. Part B: Polym. Phys.* **2001**, *39*, 1429–1436.

9 J. E. Puskas, Y. Chen, Y. Dahman, D. Padavan, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 3091–3109.

10 R. Tripathy, J. V. Crivello, R. Faust, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 305–317.

11 N. A. Meinhardt, R. Widmer, *U.S. Patent* 3,697,428, **1972**.

12 M. Heddadj, W. R. Ruhe, G. P. Sinquin, *U.S. Patent* 7,091,306, **2006**.

13 J. P. Kennedy, S. C. Guhaniyogi, V. Percec. *Polym. Bull.* **1982**, *8*, 571–578.

14 L. Toman, M. Janata, J. Spěváček, B. Dvořánková, P. Látalová, P. Vlček, A. Sikora, J. Michálek, M. Pekárek, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2891–2900.

15 S. Shamlou, J. P. Kennedy, R. P. Levy, *J. Biomed. Mater. Res.* **1997**, *35*, 157–163.

16 T. P. Liao, J. P. Kennedy, *Polym. Bull.* **1981**, *6*, 135–141.

17 M. Haraszti, E. Toth, B. Ivan, *Chem. Mater.* **2006**, *18*, 4952–4958.

18 B. Ivan, J. P. Kennedy, *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 89–104.

19 U. Ojha, R. Rajkhowa, S. R. Agnihotra, R. Faust, *Macromolecules* **2008**, *41*, 3832–3841.

20 R. Tripathy, U. Ojha, R. Faust, *Macromolecules* **2009**, *42*, 3958–3964.

21 C. P. Roche, M. R. Brei, B. Yang, R. F. Storey, *ACS Macro Lett.* **2014**, *3*, 1230–1234.

22 A. Guerrero, K. Kulbaba, M. Bochmann, *Macromolecules* **2007**, *40*, 4124–4126.

23 S. P. Srivastava, J. Hancsók, Fuels and Fuel-Additives, 1st ed.; Wiley: Hoboken, **2014**, Chapter 5, pp. 177–208.

24 C. Hongfa, J. Tian, H. S. Bazzi, D. E. Bergbreiter, *Org. Lett.* **2007**, *9*, 3259–3261.

25 D. E. Bergbreiter, C. Hobbs, J. Tian, H. Koizumi, H. L. Su, C. Hongfa, *Pure Appl. Chem.* **2009**, *11*, 1981–1990.

26 L. R. Rudnick, Lubricant Additives: Chemistry and Applications, 2nd ed.; CRC Press: Boca Raton Florida, **2009**, Chapter 5, pp. 143–166.

27 J. Chiefari, Y. K. Chong, F. Ercole, J. Kristina, J. Jeffery, T. P. T. Le, T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1998**, *31*, 5559–5562.

28 Y. K. Chong, P. T. Tam, G. Moad, E. Rizzardo, S. H. Thang, *Macromolecules* **1999**, *32*, 2071–2074.

29 P. Lebreton, B. Ameduri, B. Boutevin, J. M. Corpart, *Macromol. Chem. Phys.* **2002**, *203*, 522–537.

30 C. M. Schilli, M. Zhang, E. Rizzardo, S. H. Thang, Y. K. Chong, K. Edwards, G. Karlsson, A. H. E. Müller, *Macromolecules* **2004**, *37*, 7861–7866.

31 X. Yin, A. S. Hoffman, P. S. Stayton, *Biomacromolecules* **2006**, *7*, 1381–1385.

32 D. Fournier, R. Hoogenboom, H. M. L. Thijs, R. M. Paulus, U. S. Schubert, *Macromolecules* **2007**, *40*, 915–920.

33 D. Quémener, T. P. Davis, C. Barner-Kowollik, M. H. Stenzel, *Chem. Commun.* **2006**, 5051–5053.

34 G. Gody, T. Maschmeyer, P. B. Zetterlund, S. Perrier, *Nat. Commun.* **2013**, *4*, 2505

35 J. Vandenbergh, G. Reekmans., P. Adriaensens, T. Junkers, *Chem. Commun.* **2013**, *49*, 10358–10360.

36 A. Lange, S. Csihony, M. Kleiner, *Pat. Application.* **2014**, WO2014090672A1.

37 R. E. Cherpeck, K. D. Nelson, *U.S. Patent* 5,993,497, **1999**.

38 A. J. Convertine, B. S. Lokitz, Y. Vasileva, L. J. Myrick, C. W. Scales, A. B. Lowe, C. L. McCormick, *Macromolecules* **2006**, *39*, 1724–1730.

39 G. Gody, T. Maschmeyer, P. B. Zetterlund, S. Perrier, *Macromolecules* **2014**, *47*, 3451–3460.

40 C. Schilli, M. G. Lanzendörfer, A. H. E. Müller, *Macromolecules* **2002**, *35*, 6819–6827.

41 P. Relógio, M. T. Charreyre, J. P. S. Farinha, J. M. G. Martinho, C. Pichot, *Polymer* **2004**, *45*, 8639–8649.

42 S. Perrier, C. Barner-Kowollik, J. F. Quinn, P. Vana, T. P. Davis, *Macromolecules* **2002**, *35*, 8300–8306.