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A new approach to 3-miktoarm star polymers using a combination of reversible addition–fragmentation chain transfer (RAFT) and ring opening polymerization (ROP) via "Click" chemistry

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ABSTRACT

The synthesis of AB_2-type miktoarm star polymers using a combination of reversible addition–fragmentation chain transfer (RAFT), ring opening polymerization (ROP) and "Click" chemistry was demonstrated in this work. An azide functional RAFT agent was used to polymerize butyl acrylate, polyethylene glycol acrylate and *N*-isopropylacrylamide monomers. Propargylamine was reacted with glycerine carbonate to obtain a dihydroxy functional alkyne compound which was used for the ring opening polymerization of ε-caprolactone (ε-CL) and lactide. The resulting alkyne functional polycaprolactone (PCL) and polylactide (PLA) polymers were reacted with azide functional polymers in the presence of copper bromide (CuBr) catalyst to obtain miktoarm star polymers. The polymers were characterized by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy. The star polymers had low polydispersity (~1.3) with well-defined structures. These polymers have a number of potential applications including crosslinking agents for polyurethane (PU) coatings for biodegradable and fouling release applications.

1. Introduction

The development of controlled radical polymerization (CRP) techniques has provided access to a plethora of new polymeric architectures such as star polymers [1], hyperbranched polymers [2], dendrimers [3], graft polymers [4], etc. Star polymers have gained interest in recent years due their compact structures and peculiar rheological properties [5,6]. Functionalized star polymers can be used as building blocks for polymer networks [7,8] and for crosslinking reactions [9]. Star polymers are mainly categorized by their two main synthesis techniques: core-first [10] and arm-first [11,12]. The core-first method uses living polymerization from a multifunctional core initiator [13]. This method can be used for growing multiple arms simultaneously from one core molecule. For the arm-first method, a polymer with a reactive end functional group is reacted with a multifunctional core to give a star polymer. With the arm-first method, functional polymer arms of different chemical compositions can be synthesized separately and coupled to the multifunctional core to form a star polymer with varying chemical composition. These types of star polymers having different molecular weights or chemically different arms are termed as miktoarm star polymers [14].

Since miktoarm star polymers can be tailor-made with unique chemical compositions, research in this field has been of interest in both academic and industrial fields. Miktoarm star polymers have interesting solution and solid state properties [15]. Heteroarm polymers are known to phase separate and form ordered nanoscopic phases [16,17]. Miktoarm star polymers with polydimethylsiloxane (PDMS) arms may have applications in the field of nanolithography and nanotechnology [18].

CRP techniques such as atom transfer radical polymerization (ATRP) [19], reversible addition–fragmentation chain transfer (RAFT) [20], and nitroxide mediated polymerization (NMP) [21] along with ring opening polymerization (ROP) [22,23] have been previously used for the synthesis of miktoarm star polymers. "Click" chemistry, which was first introduced by Kolb et al. [24], has also been extensively used to form block, graft and star polymers in combination with CRP techniques. "Click" chemistry uses the Cu(I) catalyzed Huisgen (2 + 3) cycloaddition reaction between an organic azide and a terminal alkyne group [25]. Miktoarm star polymers have been previously synthesized by a combination of ATRP and "Click" chemistry [26,27]. Star polymers having a combination of meth-(acrylates) and styrenic arms synthesized using the combination of

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ATRP and "Click" chemistry were obtained in high yields with polydispersity index (PDI) of less than 1.09 [27]. Similarly, ABC type heteroarm star polymers have also been synthesized using ATRP, ROP and "Click" chemistry [26].

There have been no reports yet on the synthesis of miktoarm star polymers by a combination of RAFT, ROP and "Click" chemistry. Herein, we demonstrate the first report on synthesis of AB_2-type 3-miktoarm star polymers by a combination of RAFT, ROP and "Click" chemistry. One of the main advantages of ROP of cyclic esters using hydroxyl-functional initiators is that they are facile reactions and many cyclic esters are commercially available. Similarly, CRP reactions using RAFT are often conducted under simple conditions which do not require vacuum lines, inert conditions or highly dried reagents [20]. Polymerizations of most acrylates, methacrylates and styrenic monomers can be easily controlled using a single RAFT agent, whereas in case of ATRP specific combinations of initiators and ligands have to be selected for polymerization of various monomers. Also, fewer purification steps are required when conducting polymerizations using the RAFT technique.

In this work, azide functional poly(butyl acrylate) (PBA), poly(polyethylene glycol acrylate) (PPEGA) and poly(*N*-isopropylacrylamide) (PNIPAM) were synthesized using an azide functional trithiocarbonate RAFT agent. A dihydroxy functional alkyne intermediate was synthesized by reacting propargylamine with glycerine carbonate which was used for the ring opening polymerization of ε-caprolactone and lactide to form alkyne functional polyesters. The "Click" coupling between the azide functional polyacrylates and the alkyne functional polylactones afforded the AB_2-type 3-miktoarm star polymers by a combination of RAFT and ROP. Poly(ethylene glycol) (PEG) based polymers have a wide range of solubilities both in organic and aqueous media. They also have several biomedical applications due to low toxicity [28]. PNIPAM is a water soluble polymer and undergoes a reversible phase transition at low critical solution temperature (LCST) at 32 °C [29]. PNIPAM is water-swollen and forms hydrogels below LCST, whereas above 32 °C the water is released from the gel causing the chains to collapse resulting in dramatic decrease in volume. This property of PNIPAM has found applications for drug delivery [30], substrate for cell attachment and growth [31], and other applications in the field of biomaterials [32]. Similarly poly(lactide) (PLA) and poly(ε-caprolactone) (PCL) are extensively studied as they are known to be biodegradable and biocompatible [33]. PLA and PCL based polymers have also been studied as controlled released drug carriers and delivery of model protein compounds [34]. Thus, combining these polymers into miktoarm star polymers has the potential to result in polymers with unusual and interesting properties.

2. Experimental

2.1. Materials

Chain transfer agent (CTA) *S-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate*, (TTC1) was a gift from Lubrizol. 2-azidoethanol was synthesized according to the literature procedure [35]. Hexane, ethyl acetate (EA), dichloromethane (DCM), *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopydridine (DMAP), propargylamine (PgAm), butyl acrylate (BA), styrene (STY), *N*-isopropylacrylamide (NIPAM), ε-caprolactone and lactide were purchased from Aldrich. Polyethylene glycol acrylate (PEGA) was received from Sartomer. 2,2′-azobis(2-methylbutyronitrile) (AMBN) (VAZO 67) was received from Dupont Chemicals. Glycerine carbonate was a gift from Huntsman Chemicals. All materials were used as received without further purification.

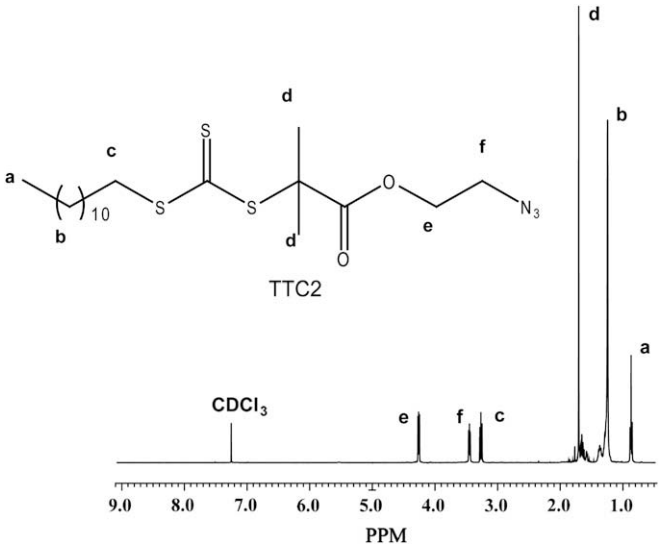


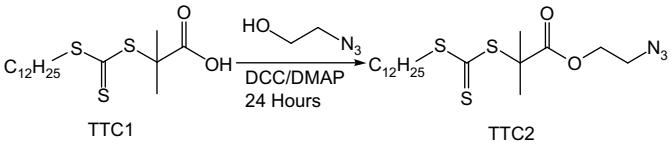
Fig. 1. ^{1}H NMR of azide functional RAFT agent TTC2.

2.2. Instrumentation and measurements

The chain transfer agent was characterized using nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared spectroscopy (FTIR). Polymers were characterized using gel permeation chromatography (GPC), differential scanning calorimetry (DSC), NMR and FTIR. ^{1}H NMR measurements were done at 23 °C using a JOEL-ECA (400 MHz) NMR spectrometer with an autosampler accessory. All measurements were made using $CDCl_3$ as solvent. The data was processed using the Delta software package. Molecular weight was determined using a Waters 2410 gel permeation chromatograph equipped with a refractive index detector. A 1% sample solution in THF using a flow rate of 1 ml/min was used. FTIR measurements were made using a Nicolet Magna-850 FTIR spectrometer. Samples were coated on a potassium bromide salt pellet and spectra acquisitions were based on 16 scans with data spacing of 1.98 cm^{-1}. The FTIR was set for auto gain to monitor spectral ranges of 4000–500 cm^{-1}. A DSC Q1000 from TA Instruments with an autosampler was used for glass transition temperature (T_g) and melting point (T_m) determinations. Samples synthesized from "Click" chemistry were subjected to a heat–cool–heat cycle from −90 to +150 °C by ramping at 10 °C/min for both heating and cooling cycles. The second heating cycle was used to characterize the samples.

2.3. Synthesis of azide functional RAFT agent (TTC2)

The azide functional RAFT agent was synthesized according to a literature procedure with a slight modification [35]. In a 250 ml round bottom flask equipped with a magnetic stir bar, 2.0 g (5.48 mmoles) of TTC1, 0.71 g (2.74 mmoles) of 4-dimethylaminopydridine (DMAP), 0.953 g (10.96 mmoles) of 2-azidoethanol and 100 ml of dichloromethane (DCM) were added. The reaction was stirred for 15 min at room temperature and 1.16 g (5.48 mmoles) of



Scheme 1. Synthesis of azide functional RAFT agent TTC2.

Table 1
Homopolymers synthesized using azide functional RAFT agent TTC2.

Homopolymer	M_n GPC	M_w/M_n GPC
PBA-N_3	3550	1.10
PPEG-N_3	4800	1.08
PNIPAM-N_3	4600	1.10

N,*N*′-dicyclohexylcarbodiimide (DCC) dissolved in 10 ml of DCM was slowly added to the mixture. The resulting mixture was stirred at room temperature for 24 h. The solution was then filtered and DCM was removed in vacuo. The resulting crude product was eluted through a silica gel column using hexanes/ethyl acetate (95:5v/v) to yield pure chain transfer agent TTC2 as a yellow-brown oil, yield, 2.05 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$ 23 °C): δ (ppm) 0.87, 1.2–1.5, 1.7, 3.25, 3.45 and 4.26 (Fig. 1). ^{13}C NMR (100 MHz $CDCl_3$): δ (ppm) 14.2, 22.8, 25.4, 27.9, 29.0, 29.2, 29.4, 29.5, 29.6, 29.7, 32.0, 37.1, 49.7, 55.9, 64.7, 172.9, and 221.8. FTIR (KBr) (wavenumber cm^{-1}) 1735, 2104.

2.4. Representative homopolymerization of butyl acrylate using TTC2

In a 20 ml glass vial with a magnetic stir bar, 3.0 g (23.40 mmoles) of butyl acrylate, 0.505 g of TTC2, 3.0 g of toluene and 90 mg (0.4 mmoles) of AMBN were added. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 70 °C for 4 h. $M_n = 3550$, PDI = 1.10.

2.5. Representative homopolymerization of polyethylene glycol acrylate using TTC2

In a 20 ml glass vial with a magnetic stir bar, 3.0 g (23.40 mmoles) of PEGA, 0.505 g of TTC2, 3.0 g of toluene and 90 mg (0.4 mmoles) of AMBN were added. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 70 °C for 4 h. $M_n = 4800$, PDI = 1.08.

2.6. Representative homopolymerization of N-isopropylacrylamide using TTC2

In a 20 ml glass vial with a magnetic stir bar, 3.0 g (23.40 mmoles) of NIPAM, 0.505 g of TTC2, 3.0 g of toluene and 90 mg (0.4 mmoles) of AMBN were added. The vial was degassed by purging with nitrogen for 2 min. The polymerization was carried out in an oil bath at 70 °C for 4 h. $M_n = 4600$, PDI = 1.10.

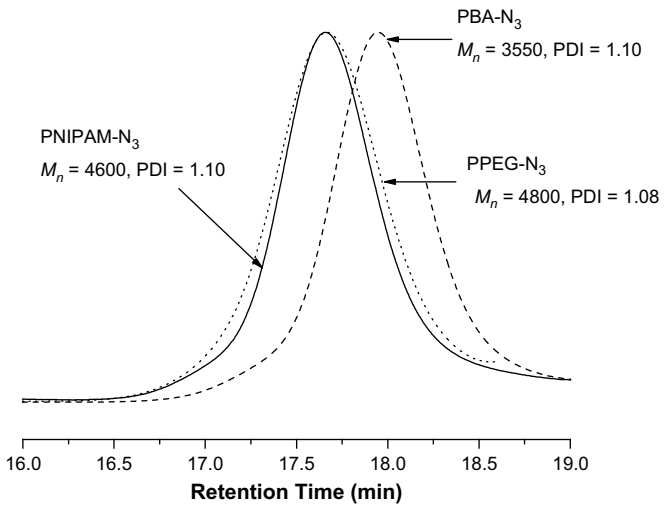


Fig. 2. GPC curves for azide terminated polymers synthesized using TTC2.

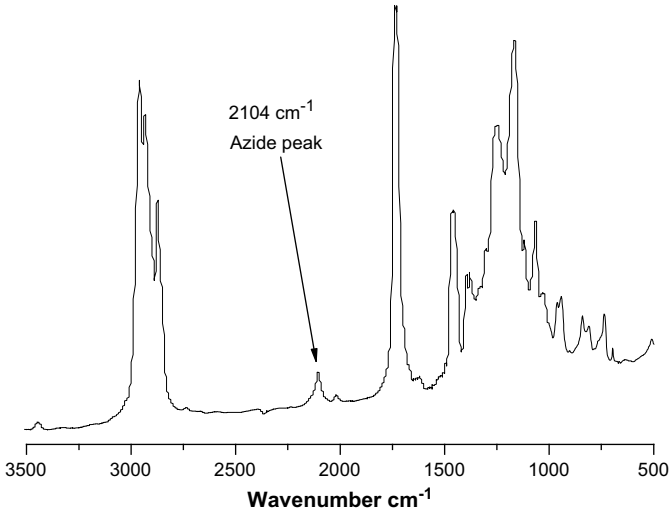


Fig. 3. FTIR spectrum of PBA synthesized using azide functional RAFT agent TTC2.

2.7. Synthesis of propargyl diol (Pg-Diol)

In a 20 ml glass vial equipped with a magnetic stir bar, 4.0 g (33.9 mmoles) of glycerine carbonate and 2.80 g (50.85 mmoles) of propargylamine (PgAm) were added. The reaction was carried out in an oil bath at 70 °C for 10 h. Excess PgAm was removed in vacuo to obtain a dark brown viscous liquid. FTIR (KBr) (wavenumber cm^{-1}) 1704, 2121, 2940, 3300, 3550.

2.8. Representative polymerization of ε-caprolactone (PCL) using Pg-Diol

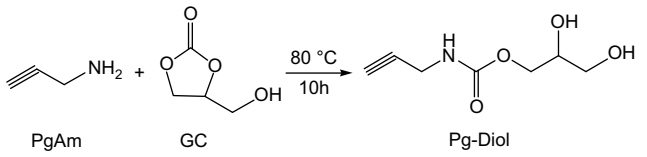
In an 8 ml glass vial equipped with a magnetic stir bar, 0.1 g of Pg-Diol, 0.66 g (5.84 mmoles) of CL and 100 μL of 10% solution of tin (II) ethylhexanoate in toluene were charged. The reaction was carried out at 110 °C for 10 h. $M_n = 2900$, PDI = 1.28.

2.9. Representative polymerization of lactide (PLA) using Pg-Diol

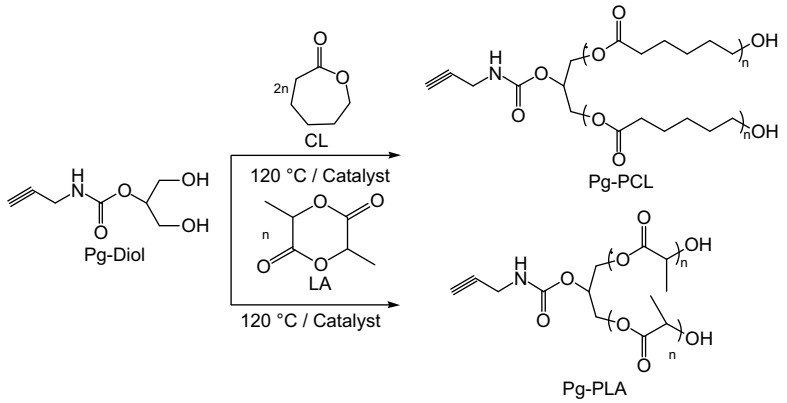
In an 8 ml glass vial equipped with a magnetic stir bar, 0.1 g of Pg-Diol, 0.84 g (5.84 mmoles) of LA and 100 μL of 10% solution of tin (II) ethylhexanoate in toluene were charged. The reaction was carried out at 110 °C for 10 h. $M_n = 2900$, PDI = 1.32.

2.10. Representative "Click" reaction of azide functional PBA with alkyne terminated PCL

In a 20 ml vial equipped with a magnetic stir bar, 0.177 g (0.005 mmoles) of azide terminated PBA, 0.15 g (0.005 mmoles) of alkyne terminated PCL, 0.0173 g (0.01 mmoles) of PMDETA and 2 ml



Scheme 2. Reaction of propargylamine with glycerine carbonate to form alkyne functional dihydroxy adduct Pg-Diol (major isomer shown).



Scheme 3. Synthesis of alkyne functional PLC and PLA blocks.

of DMF were added. The vial was purged with nitrogen for 2 min and was placed inside a nitrogen glove box. 0.0143 g (0.01 mmoles) of CuBr was added to the solution in the glove box. The reaction was carried out for 24 h at room temperature in absence of oxygen. The reaction was then exposed to air and the solution was passed through a neutral alumina column. The solvent was evaporated and the resulting polymer had $M_n = 4020$, PDI = 1.25.

3. Results and discussion

3.1. CTA synthesis and RAFT polymerization

Copper catalyzed azide–alkyne coupling in combination with CRP techniques like RAFT and ATRP has been highly successful for the synthesis of functional block copolymers [35,36]. In this work 2-azidoethanol was reacted with an acid functional trithiocarbonate RAFT agent in presence of DCC coupling agent and DMAP base to yield an azide functional trithiocarbonate RAFT agent (TTC2) (Scheme 1) in high yield. FTIR spectroscopy of TTC2 showed strong absorbance bands at 1735 cm^{-1} and 2104 cm^{-1} for the C=O stretch and the N=N=N stretch, respectively. This RAFT agent was used for controlled free radical polymerization of butyl acrylate, polyethylene glycol acrylate and *N*-isopropylacrylamide (Table 1) to obtain the corresponding azide terminated polymers (Fig. 2).

Reaction kinetics of polymers using a similar azide functional RAFT agent has been previously studied by Gondi et al. [37]. Perrier et al. recently reported the potential loss of azide groups in the presence of electron deficient monomers like acrylates especially at high reaction temperatures and long reaction times (~20 h) [38]. In this work, all polymerizations were carried out at 70 °C and were terminated after 4 h. Hence it is expected that the resulting polymers have a high degree of end-group functionalization. Fig. 3 shows the FTIR spectrum of azide terminated PBA synthesized using TTC2. The spectrum shows a strong band at 2104 cm^{-1} which corresponds to the azide group on the PBA chain. Similarly, FTIR spectra of PPEG and also PNIPAM show the azide absorption peak at 2104 cm^{-1}.

3.2. Synthesis of Pg-Diol and alkyne functional PCL and PLA

Pg-Diol was synthesized by reacting propargylamine (PgAm) with glycerine carbonate (GC) (Scheme 2). The reaction of PgAm with GC results in two isomers depending on which ester bond is broken during the reaction. The first isomer has 1° and 2°

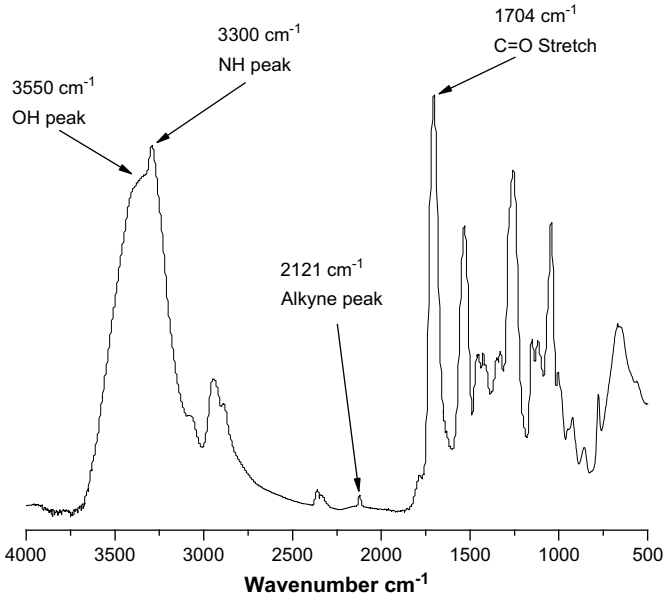


Fig. 4. FTIR spectrum of Pg-Diol.

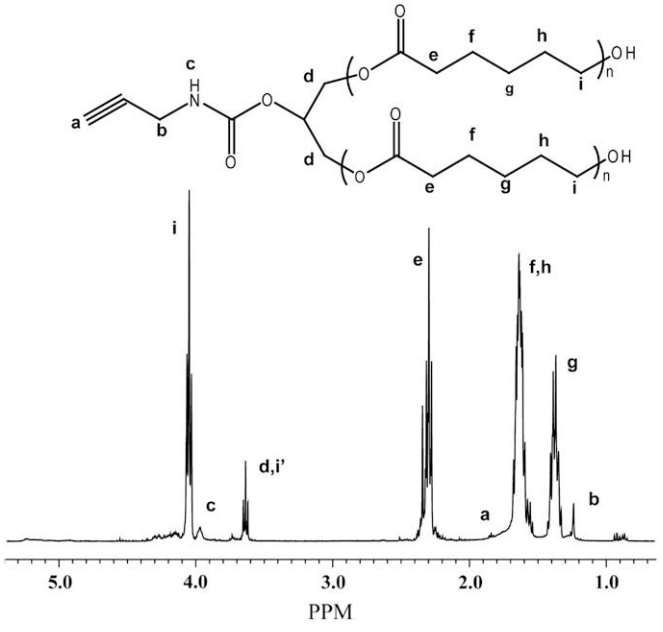


Fig. 5. ^1H NMR of Pg-PLC with 5 ε-CL groups per hydroxyl.

Table 2
Synthesis of dihydroxy functional PCL and PLA arms with alkyne group.

Entry	Monomer (mmoles)	Pg-Diol (mmoles)	No. of ε-CL or LA per hydroxyl	M_n (GPC)	M_w/M_n (GPC)
1	ε-CL (5.84)	0.584	5	2900	1.28
2	ε-CL (11.68)	0.584	10	5050	1.24
3	LA (5.84)	0.584	5	2900	1.24
4	LA (11.68)	0.584	10	4700	1.21

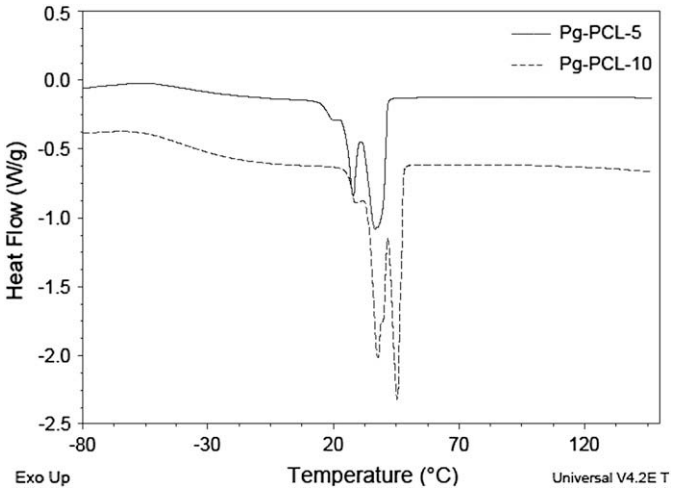


Fig. 6. DSC plots for Pg-PCL with 5 and 10 repeating units per hydroxyl.

hydroxyls, and is the major product, whereas the second isomer which contains only 1° hydroxyls is the minor product [39]. It should be noted that in Scheme 3 only the first isomer with both 1° and 2° alcohols is shown.

The reaction was monitored by FTIR spectroscopy (Fig. 4) and was carried out until the cyclic carbonate carbonyl peak of GC at 1800 cm^{-1} disappeared. The resulting product had characteristic peaks at 3550, 3300, 2121, and 1704 cm^{-1} corresponding to −OH, −NH, −C≡C, and −C═O, respectively.

Pg-Diol was used as the intitiator for ring opening polymerization of ε-CL and LA (Scheme 3). The resulting macromonomer had two PCL or PLA arms per alkyne group.

Ring opening of ε-CL using an alkyne functional hydroxyl initiator has been previously reported and it was confirmed that the alkyne group remains intact during the polymerization [40]. Macromonomers with primary and secondary diols on the polymer chain have been previously used as initiators for the ring opening polymerization of caprolactones using tin catalysts. The study indicated that both hydroxyl groups are active for the ROP of caprolactone and the amount of unreacted secondary hydroxyl group is very low [41]. Further studies have been done using monomers like propane-1,2-diol, butane-1,3-diol and hexane-1,5-diol as initiators for ring opening polymerization of caprolactone and in each case, the ratio of initiation by primary and secondary hydroxyl was found to be dependant on the reaction conditions [42]. Hence it is expected that in the present study, both primary and secondary hydroxyls would have initiated the ring opening polymerization of the cyclic monomers.

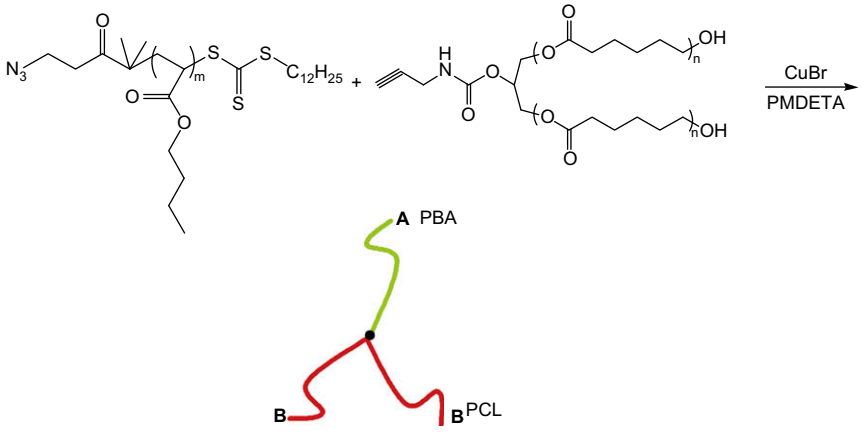
Polymers based on PCL and PLA are of particular interest in the field of controlled drug release [43]. These polymers have unique sol–gel properties, where they can be injected in the solution form and they form gels at body temperature [34]. In this work, polymers having two different lengths of PCL and PLA blocks per hydroxyl group were synthesized from Pg-Diol. Both polymers had 5 and 10 repeating units per hydroxyl groups resulting in 4 different alkyne functional polymer compositions. Fig. 5 shows the ^{1}H NMR spectrum of Pg-PCL synthesized as per Scheme 3 (Table 2).

Fig. 6 shows that the T_m for the PCL blocks increases with the number of repeating units of ε-CL per hydroxyl. Similar observations have been previously made for PDMS–PCL block copolymers where the T_m increases with increase in ε-CL repeating units on the polymer backbone [44]. Both polymers are crystalline since the T_m value of the polymers is above room temperature.

3.3. "Click" reactions

Copper catalyzed azide–alkyne coupling reactions are highly efficient and have been successfully used in novel polymer materials synthesis [45]. In this work, the three azido functionalized polymers were reacted with the alkyne functional PCL and PLA polymers resulting in dihydroxy functionalized 3-miktoarm star polymers. Although miktoarm polymers have been previously synthesized using RAFT [20] and also by a combination of ATRP and ROP using "Click" chemistry [26], there have been no references on the synthesis of miktoarm polymers by a combination of RAFT, ROP and "Click" chemistry to the best of our knowledge. Miktoarm polymers are of special interest because of their unique properties in the solid state and ability to self arrange in solution [46].

Azide terminated polymers synthesized using TTC2 were dissolved in DMF and reacted with alkyne functional PCL and PLA in the presence of CuBr and PMDETA at room temperature (Scheme 4) to synthesize twelve combinations of polymers with varying A and B



Scheme 4. Synthesis of miktoarm polymers using a combination of RAFT and "Click" chemistry.

Table 3
Conditions for "Click" reactions of azido functionalized polymers with alkyne functional PCL and PLA.

Entry	PBA (g)	PPEG (g)	PNIPAM (g)	PMDETA (g)	CuBr (g)	Pg-PCL-5 (g)	Pg-PCL-10 (g)	Pg-PLA-5 (g)	Pg-PLA-10 (g)
1	0.177			0.0173	0.0143	0.15			
2		0.24		0.0173	0.0143	0.15			
3			0.23	0.0173	0.0143	0.15			
4	0.177			0.0173	0.0143		0.25		
5		0.24		0.0173	0.0143		0.25		
6			0.23	0.0173	0.0143		0.25		
7	0.177			0.0173	0.0143			0.15	
8		0.24		0.0173	0.0143			0.15	
9			0.23	0.0173	0.0143			0.15	
10	0.177			0.0173	0.0143				0.23
11		0.24		0.0173	0.0143				0.23
12			0.23	0.0173	0.0143				0.23

Table 4
Molecular weights and PDI of the miktoarm star polymers.

Entry	RAFT polymer (M_n)	Alkyne polymer (M_n)	M_n of star polymer	PDI
1	PBA (3500)	Pg-PCL-5 (2900)	4020	1.25
2	PBA (3500)	Pg-PCL-10 (5050)	6050	1.32
3	PBA (3500)	Pg-PLA-5 (2900)	4750	1.18
4	PBA (3500)	Pg-PLA-10 (4700)	4700	1.17
5	PPEGA (4800)	Pg-PCL-5 (2900)	5250	1.13
6	PPEGA (4800)	Pg-PCL-10 (5050)	7000	1.21
7	PPEGA (4800)	Pg-PLA-5 (2900)	5660	1.10
8	PPEGA (4800)	Pg-PLA-10 (4700)	5650	1.11
9	PNIPAM (4600)	Pg-PCL-5 (2900)	6100	1.23
10	PNIPAM (4600)	Pg-PCL-10 (5050)	7780	1.25
11	PNIPAM (4600)	Pg-PLA-5 (2900)	5230	1.15
12	PNIPAM (4600)	Pg-PLA-10 (4700)	5220	1.17

blocks (Table 3). The catalyst was removed from the polymer solution by passing through a neutral alumina column and the resulting product was dried under vacuum to obtain the star polymer. The polymers were characterized by ^{1}H NMR, FTIR and GPC.

The molecular weights of the star polymers were determined by GPC using polystyrene standards and are listed in Table 4. Hence, the molecular weight values of the star polymers are relative and not absolute values. It was noted that the molecular weights of the star polymers after the "Click" reactions were always higher than that of the azido functional polymers synthesized using TTC2. Fig. 7 shows the GPC traces for PNIPAM-N_3, Pg-PCL-10 and PNIPAM-*b*-Pg-PCL-10. The resulting miktoarm polymer does show some small amount of unreacted homopolymer as a shoulder on the main GPC peak. A possible cause for this could be an error in weighing the individual homopolymers for the "Click" reaction. The "Click" reaction was also monitored by FTIR spectroscopy (Fig. 8). The azide peak for the polymers synthesized using TTC2 shows a strong absorption band at 2104 cm^{-1}, which disappears when reacted with the alkyne functional Pg-PCL and Pg-PLA polymers, indicating that the reaction has gone to completion.

^{1}H NMR of the star polymers also confirms the presence of the azido functionalized polyacrylates and PCL and PLA polymers

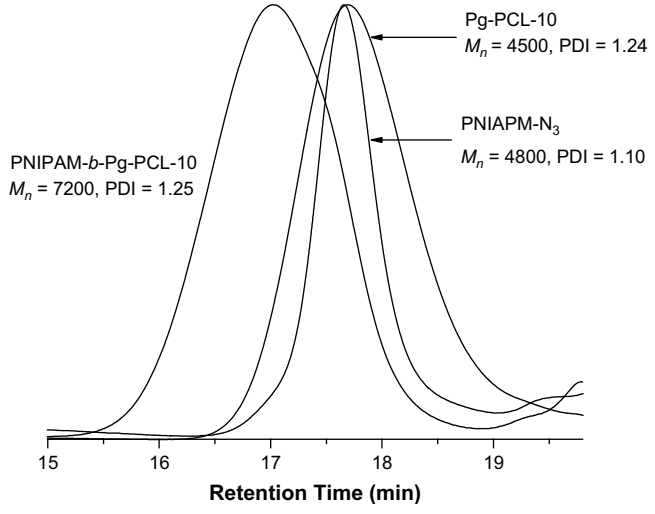


Fig. 7. GPC traces for PNIPAM-*b*-Pg-PCL-10 miktoarm star polymer after the "Click" reaction between PNIPAM-N_3 and Pg-PCL-10.

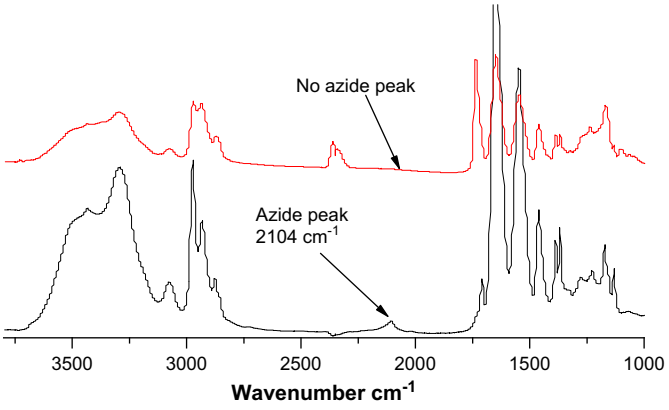


Fig. 8. FTIR spectrum of PNIPAM-N_3 (bottom) and PNIPAM-*b*-Pg-PCL-5 (top). The azide peak disappears after the "Click" reaction, which confirms the formation of the product.

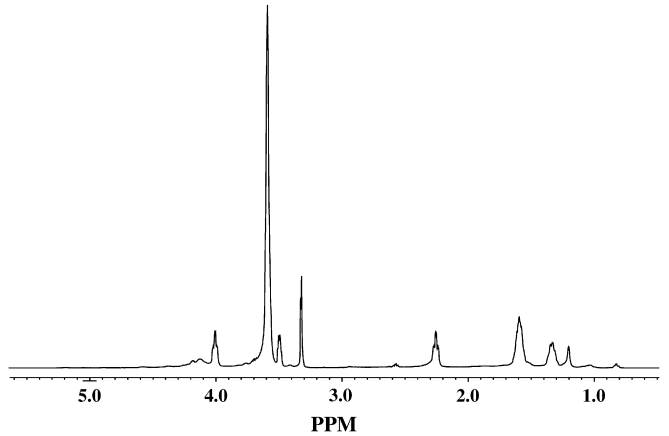


Fig. 9. ^{1}H NMR of PPEGA-*b*-PCL-5 synthesized by combination of RAFT and ROP via "Click" chemistry (entry 2 in Table 3).

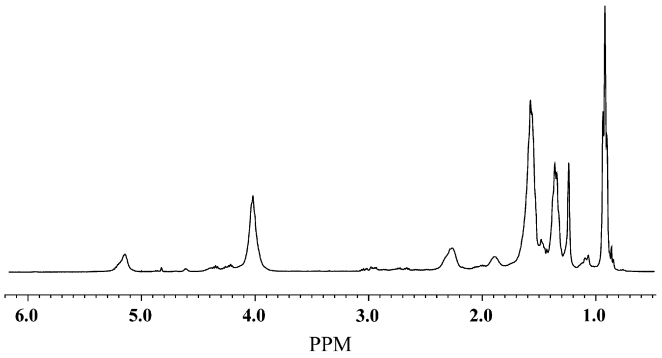


Fig. 10. ^{1}H NMR of PBA-*b*-PLA-5 synthesized by combination of RAFT and ROP via "Click" chemistry (entry 7 in Table 3).

synthesized by ROP. Fig. 9 shows the ^{1}H NMR spectrum of PPEGA-*b*-PCL-5 AB_2-type star polymer. The peaks for PEG can be seen between 3.3 and 3.7 ppm, whereas the peaks for PCL can be seen between 1.1 and 2.3 ppm and at 4.0 ppm (Fig. 10).

Similarly, the ^{1}H NMR of the star polymer with poly(butyl acrylate) and poly(lactide) arms shows characteristic peaks of PBA at 0.9, 1.24, 1.36, 1.57, 1.88, 2.25, and 4.02 ppm and PLA peaks at 5.15 and 1.24 ppm. We are currently exploring the use of these types of dihydroxy functional polymers as modifiers for high performance polyurethanes (PUs). It is expected that by tuning the composition and molecular weight of the arms of the star polymers, PU coatings with different bulk and surface properties can be achieved. These miktoarm star polymers may also have application in the areas of drug delivery and biodegradable polymers.

4. Conclusions

The synthesis of AB_2-type miktoarm star polymers using a combination of RAFT, ROP and "Click" chemistry was demonstrated for the first time in this work. An azide functional RAFT agent was used to polymerize several acrylate monomers. The resulting azido functionalized polymers were reacted with alkyne functional PCL and PLA to obtain the star polymers. The reaction products were confirmed by GPC, FTIR and NMR spectroscopy. These polymers can have potential for use as novel diols for polyurethane coatings where the bulk and surface properties can be tailor-made to suit the applications by using various monomers. The coatings have potential applications for biomaterials, drug delivery, protective coatings and fouling release coatings.

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