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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.

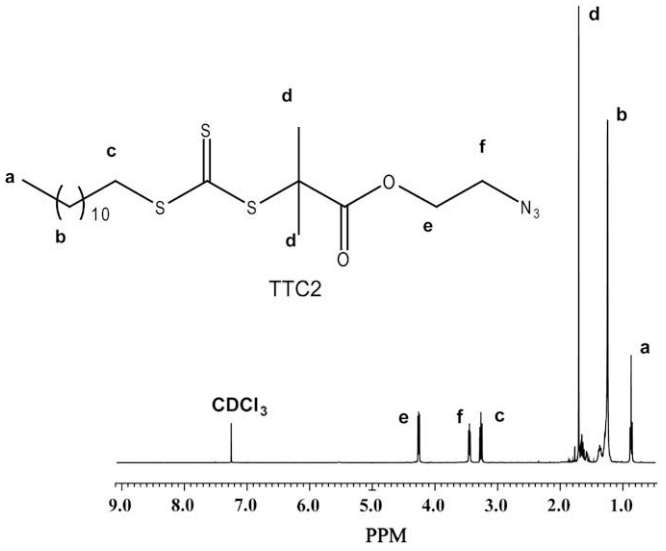


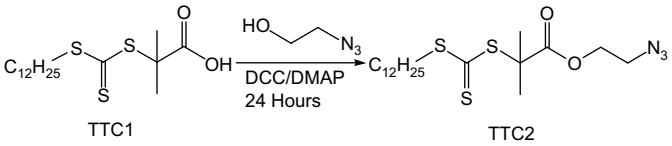

**Fig. 1.** $^1$H NMR of azide functional RAFT agent TTC2.

### 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.