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A Simple Route to Functional Highly Branched Structures: RAFT Homopolymerization of Divinylbenzene

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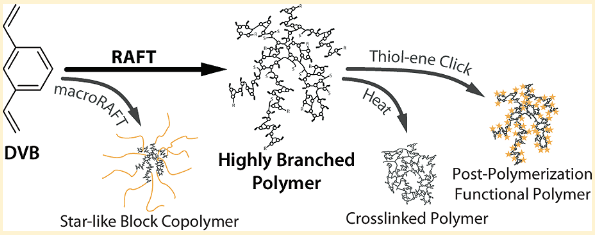
S Supporting Information

ABSTRACT: This work reports on a facile approach to the synthesis of highly branched polymers by the homopolymerization of commercially available divinyl benzene (DVB) via reversible addition−fragmentation chain transfer (RAFT) polymerization. The presence of RAFT agents allows conversions as high as 68% before cross-linking, instead of 15% for conventional free radical polymerization (FRP). The study extends this new approach by synthesizing starlike block copolymers of methyl acrylate (MA) and DVB by exploiting the living characteristic offered by RAFT polymerization. The resulting highly branched DVB polymers are used to produce *in situ* cross-linked polymeric particles following thermal stimuli. In addition, we exploit the large number of residual double bonds in the highly branched p(DVB) to further functionalize the polymer via thiol−ene click chemistry.



INTRODUCTION

Branched polymers have vastly different physical properties to their linear analogues[1] and as a result can be used for a variety of applications. An extreme example of branched polymers is dendrimers, which have very high degrees of branching. In a dendrimer, the branches are arranged into layers, or generations, and each potential branch point is fully occupied up to the final generation number. Dendrimers have small hydrodynamic volumes and an absence of chain entanglement due to their densely packed and globular structures.[1] These properties provide uncommon rheological properties that are sought after in applications such as viscosity modifiers.[2−4] Furthermore, the numerous accessible end points in dendrimers make them suitable candidates for applications in fields such as biomedicine and catalysis.[2] For example, by designing the core and shell of dendrimers, one can encapsulate drugs for delivery.[5,6] Unfortunately, dendrimer synthesis requires the addition of each generation stepwise, with purification in each iteration.[7−9] This makes large-scale synthesis and applications of dendrimers difficult.[2,3] As a result, inexpensive highly branched polymers have gained recent interest and attention as an alternative to dendrimers.[2,3,10]

Highly branched polymers have similar properties to dendrimers.[11] Unlike the regular arrangement of branches in a dendrimer, the branch points in a highly branched polymer are distributed randomly throughout the polymer. The major advantage of highly branched polymers is that the synthesis is generally very simple and can often be done in one pot. In 1952, Flory proposed the synthesis of a hyperbranched polymer by the polycondensation of AB_n type monomers, where $n \geq 2$ and A reacts with B,[12] and with advances in polymer chemistry and industrial demand, there are now many elegant syntheses for highly branched polymers.[13−16]

One popular method of synthesizing highly branched polymers is the self-condensing vinyl polymerization (SCVP) method introduced by Fréchet and co-workers.[17] This approach offers a flexible route to synthesizing highly branched polymers by combining the initiating moiety and vinyl moiety on the same monomer. These monomers, known as inimers,[18] propagate among themselves to produce the highly branched polymer.[19] SCVP by radical methods is inexpensive compared to ionic polymerization; however, in many cases the inimer must be synthesized for a specific application.

An alternative synthesis for high molecular weight highly branched polymers is the "Strathclyde synthesis", introduced by Sherrington et al.[20−25] In the Strathclyde synthesis, monovinyl monomers are copolymerized with small amounts of divinyl monomers in the presence of a large amount of chain transfer agent. An advantage of the Strathclyde synthesis is that the degree of branching can easily be varied by changing the ratio of divinyl monomer to chain transfer agent. In this method, linear copolymers with pendant vinyls are formed, and as the reaction progresses, these linear chains propagate through the pendant vinyl groups of other linear chains to form highly branched polymers.

In recent years, the development of living radical polymerization (LRP) has allowed for good control over chain lengths and has opened up a variety of polymer architectures.[26] In all LRP methods the growing polymer chain is predominantly in a dormant state, and only occasionally becomes an active radical, thus considerably minimizing termination reactions.[27] The three most common LRP techniques are nitroxide-mediated polymerization (NMP),[28] atom transfer radical polymerization (ATRP),[29,30]

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and reversible addition−fragmentation chain transfer polymerization (RAFT).[31] The use of LRP methods to synthesize polymers via SCVP[32−38] gives highly branched polymers of high molecular weights and narrower molecular weight distribution. ATRP and RAFT have also been used to mediate the copolymerization between mono- and divinyl monomers[39−52] to yield polymers with better defined structure than those obtained via conventional FRP Strathclyde synthesis.

As an extreme case of the Strathclyde synthesis, Wang and co-workers reported the homopolymerization of divinyl monomers mediated by ATRP.[53] Their system relies on manipulating the deactivation equilibrium, varying Cu(I):Cu(II) to control the rate of propagation. After optimization, their system achieved 60% polymer conversion but with a dense and highly branched structure that had not been achieved by other approaches.

The present work explores the homopolymerization of divinylbenzene mediated by RAFT agents. Our pursuit of synthesizing highly branched structures with RAFT polymerization offers two main benefits: the commercial availability of RAFT agents as well as the flexibility to control the system by varying the ratio of RAFT agent, initiator, and monomer. The RAFT polymerization of divinyl monomers leads to the synthesis *in situ* of an inimer, which then undergoes SCVP to form dense highly branched polymers. As well as studying the polymer growth, we apply a model based on kinetic random branched theory (KRBT)[54] to extend our understanding of the structures produced. To further highlight the usefulness of this approach, highly branched polymers are synthesized from both small- and macro-RAFT agents, since the latter allows the introduction of additional functionality into the polymer. This work also shows how these divinylbenzene-based polymers can be used to generate *in situ* cross-linked polymeric particles through thermal treatment and how they can be further functionalized via thiol−ene chemistry.

■ EXPERIMENTAL SECTION

Materials. Divinylbenzene (DVB, Fluka, technical grade) was received as a mixture of 80% divinylbenzene and 20% ethylstyrene (mixture 2.3:1 meta:para isomer ratio for both species). DVB was run through an inhibitor removal column before use. 2-Propanoic acid dodecyltrithiocarbonate (PADTC) was synthesized following procedures typically used in the literature.[55] 2,2′-Azoisobutyrnitrile (AIBN) was recrystallized from methanol. Methyl acrylate (MA, 99%), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), toluene (99%), methanol (99%), chloroform (99%), and tetrahydrofuran (THF, 99%) were used from Sigma-Aldrich and used as received unless specified otherwise.

Equipment. ^{1}H NMR spectra were acquired from a Bruker 200 MHz or a Bruker 300 MHz in *d*-chloroform unless specified otherwise. Size exclusion chromatography (SEC) was used to determine molecular weight distributions on a Polymer Laboratories GPC-50 with a Polymer Laboratories PLGel 5 μm guard column and two Polymer Laboratories PLgel 5 μm mixed-C columns, using tetrahydrofuran (with 0.000 03 wt % hydroquinone) at 1.0 mL min^{-1} as the eluent, and equipped with a PL-RI differential refractive index detector, a PL-BV 400RT viscometer, and a Precision Detectors PD2020 light scattering detector. Narrow poly(styrene) standards were used to calibrate the SEC for universal calibration methods.

A UV lamp, Spectroline ENF-280C/FE (365 nm, 230 V, 0.17 A), was used for the thiol−ene click experiment. IR spectra were obtained using an Alpha-E ATR-IR with Opus software. Thermal characterization data were obtained from a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer purged with nitrogen gas using a platinum crucible and a TA Instruments DSC 2920 modulated DSC purged with nitrogen gas using aluminum pans. The heating profiles are detailed in the Supporting Information. P(MA)-*b*-p(DVB) (19.7 mg), p(MA) (13.8 mg), and p(DVB) (4.5 mg) were subject to the heating method outlined by the low-temperature cycle followed by the high-temperature cycle. An exception was p(DVB) which was raised up to 180 °C in the high-temperature cycle. An empty aluminum pan was used as a reference for all samples. Furthermore, a pinhole was introduced to the aluminum pan of p(MA)-*b*-p(DVB) and p(MA) samples to relieve pressures from solvent evaporation. The T_g values were determined as the midpoint between the onset and the end of a step transition. Degradation temperatures reported were found using the thermal analysis software.

Syntheses. *Kinetics and Molecular Weight Evolution Studies for the Free Radical Polymerization of DVB.* 0.5 mL of a stock solution of DVB (1.42 g, 0.0109 mol), AIBN (3.6 mg, 0.022 mmol), and toluene (2.97 g, 0.0321 mol) was transferred and sealed in semi-micro test tubes. Each tube was purged with nitrogen gas for 10 min while submerged in a cold water bath. The test tubes were then placed on a hot plate preheated to 60 °C. After the desired polymerization times, samples were exposed to air and brought to room temperature.

Kinetics and Molecular Weight Evolution Studies for the RAFT Polymerization of DVB. 0.5 mL of a stock solution of RAFT polymerization of DVB (2.87 g, 0.0220 mol), PADTC (0.31 g, 0.87 mmol), AIBN (7.4 mg, 0.045 mmol), and toluene (5.96 g, 0.0647 mol) was transferred and sealed in semi-micro test tubes. Each tube was purged with nitrogen gas for 10 min while submerged in a cold water bath. The test tubes were then placed on a hot plate preheated to 60 °C. After the desired polymerization times, samples were exposed to air and brought to room temperature.

Synthesis of p(MA) Macro-RAFT Agent. A mixture of MA (2.98 g, 0.0346 mol), PADTC (0.46 g, 1.3 mmol), AIBN (10.6 g, 0.0646 mmol), and toluene (6.51 g, 0.0707 mol) was transferred to a sealed round-bottom flask equipped with a magnetic stirring bar. The sample was immersed in a cold water bath and purged with nitrogen gas for 15 min. The sample was stirred and heated at 70 °C with a preheated oil bath equipped with a thermocouple. After 3 h (91% conversion) the sample was exposed to air and brought to room temperature. Toluene and MA was removed *in vacuo* for 48 h.

Kinetics and Molecular Weight Evolution Studies for the Synthesis of p(MA)-b-p(DVB) via RAFT. 0.5 mL of a stock solution of DVB (1.83 g, 0.140 mol), p(MA) macro-RAFT agent (M_n = 2410 g mol^{-1}, PDI = 1.08, 1.37 g, 0.567 mmol), AIBN (4.5 mg, 0.027 mmol), and toluene (2.62 g, 0.0284 mol) was transferred and sealed in semi-micro test tubes. Each tube was purged with nitrogen gas for 10 min while submerged in a cold water bath. The test tubes were then placed on a hot plate preheated to 60 °C. After the desired polymerization times, samples were exposed to air and brought to room temperature.

Batch Synthesis of p(DVB). p(DVB) was prepared by transferring a mixture of DVB (2.84 g, 0.0218 mol), PADTC (0.31 g, 0.87 mmol), AIBN (0.0071 g, 0.043 mmol), and toluene (5.93 g, 0.0643 mol) to a sealed round-bottom flask equipped with a magnetic stirring bar. The sample was immersed in a cold water bath and purged with nitrogen gas for 15 min. The sample was stirred and heated at 60 °C with a preheated oil bath equipped with a thermocouple. After 24 h (78% polymer conversion) the sample was exposed to air and brought to room temperature. Sample was precipitated, with solvent decanted, from ice-cold methanol three times before excess solvent was removed *in vacuo* for 48 h.

Batch Synthesis of p(MA)-b-p(DVB). P(MA)-*b*-p(DVB) was prepared by transferring a mixture of DVB (1.95 g, 0.0150 mol), p(MA) macro-RAFT (M_n = 2410 g mol^{-1}, PDI = 1.08, 1.44 g, 0.597 mmol), AIBN (0.0040 g, 0.024 mmol), and toluene (1.92 g, 0.0209 mol) to a sealed round-bottom flask equipped with a magnetic stirring bar. The sample was immersed in a cold water bath and purged with nitrogen gas for 15 min. The sample was stirred and heated at 60 °C with a preheated

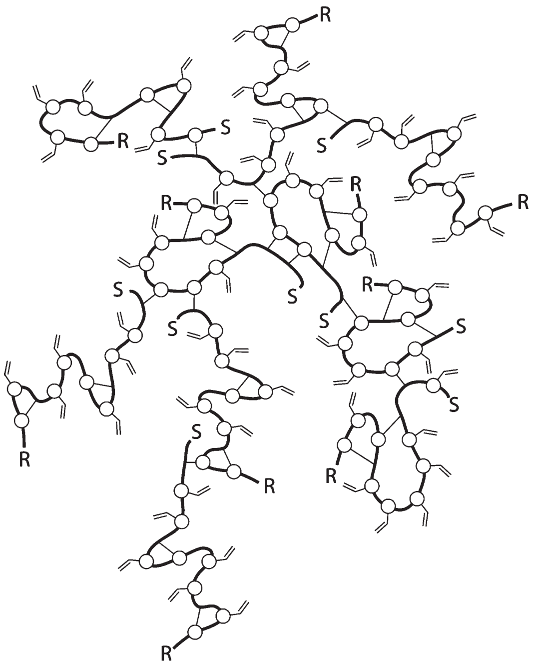


Figure 1. Schematic representation of a highly branched polymer synthesized by the RAFT polymerization of DVB. In this figure, R represents the leaving group of the RAFT agent and the S represents the thiocarbonylthio group.

oil bath equipped with a thermocouple. After 13 h (36% polymer conversion) the sample was exposed to air and brought to room temperature. DVB and toluene was removed *in vacuo* for 48 h.

Thiol–Ene Click Chemistry. 3-Mercaptopropionic acid (0.23 g, 2.3 mmol) and DMPA (0.0080 g, 0.031 mmol) were added to p(DVB) (M_n = 12 000 g mol^{-1}, M_w = 233 000 g mol^{-1}, 0.10 g) with an appropriate amount of THF (0.82 g, 0.011 mol) in a sealed glass vial. The sample was immersed in an ice bath and shielded with aluminum foil while purged with nitrogen gas for 15 min. With the aluminum foil removed, the sample was exposed to 365 nm light at room temperature (~20 °C) for 1 h before being exposed to air. The product was then precipitated, with solvent decanted, twice from methanol cooled by a dry ice–methanol bath, and then excess solvent was removed *in vacuo* for 48 h. Following the observation of residual 3-mercaptopropionic acid by ^{1}H NMR, the product was further purified *in vacuo* for 24 h at 60 °C and then for 24 h at 40 °C, but this step also resulted in some insoluble products.

■ RESULTS AND DISCUSSION

Highly Branched Polymers Based on Divinylbenzene. Divinylbenzene was polymerized via RAFT to yield highly branched polymers (Figure 1). In all syntheses the RAFT agent 2-propanoic acid dodecyltrithiocarbonate (PADTC) was used, and the ratio of divinylbenzene (DVB, used as purchased and contains 20% ethylstyrene impurity) to PADTC to AIBN was 25:1:0.05, unless otherwise stated. All polymerizations were performed at 60 °C.

Figure 2 shows the conversion of the RAFT-mediated polymerization of DVB compared to the equivalent system without the RAFT agent. As can be seen in Figure 2, the RAFT polymerization of DVB exhibits a slower rate of polymerization than conventional free radical polymerization. Although in an ideal RAFT polymerization the rates should be the same as FRP, it is well established in RAFT polymerization that some degree of retardation occurs, the cause of which is still the subject of an ongoing debate.[56−61]

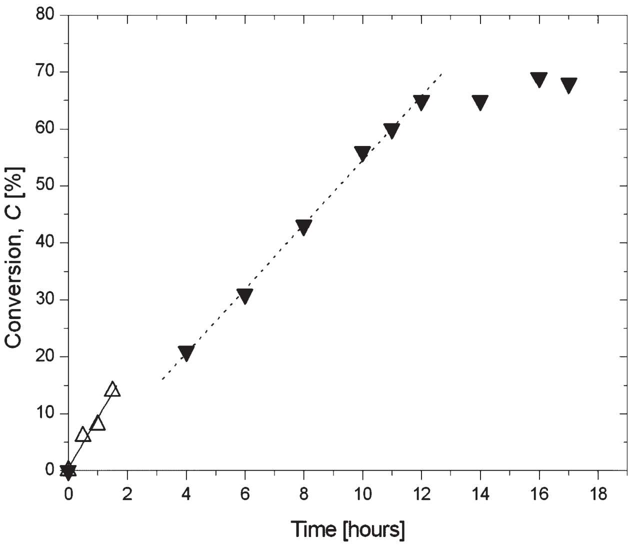


Figure 2. Kinetic plot of the FRP of DVB (△) and RAFT mediated polymerization of DVB (▼). Linear fits have been plotted for both cases as a visual aid to compare polymerization rates.

The RAFT-mediated polymerization proceeds for ~18 h and reaches 68% conversion before gelation. In contrast, the uncontrolled radical polymerization showed macrogelation after 120 min and only reached ~15% conversion before gelling. Note that conversion is expressed in this article as the amount of monomer incorporated as part of a polymer chain; this was determined by ^{1}H NMR in conjunction with a simple model to determine the contribution of the linear units to the observed vinyl signals. Details regarding the calculation of the conversion are outlined in the Supporting Information. It is likely that DVB diffuses into the polymer network to further polymerization past 68% conversion; however, an indiscriminate measurement of the polymer conversion cannot be attained by ^{1}H NMR analyses due to the heterogeneous nature of the samples, and so measurements were halted at the onset of macroscopic gelation. Nevertheless, the presence of the RAFT agent has shown to delay the onset of gelation, allowing a highly branched polymer to reach much higher conversions than conventional free radical polymerization. Figure 2 shows that the rate of the polymerization decreases after about 65% conversion. We believe this feature is due to the confinement of radicals to small regions (highly branched polymers) and as a result leads to an increase in termination and intramolecular cyclization. Also, the lower monomer concentration at high conversions will shift the dominant growth mechanism to be intramolecular cyclization and intermolecular coupling between polymers, rather than addition of new monomers.

Figure 3 shows the evolution of the SEC trace detected by DRI. These SEC traces are indicative of the molecular weight distribution and can be used to qualitatively estimate the proportion of high molecular weight polymer and the amount of low molecular weight polymers. As can be seen in Figure 3, for the first 8 h of the reaction the SEC traces are all relatively narrow and well controlled, suggesting that there is minimal branching in this regime. In contrast, after 10 h of polymerization the SEC trace develops a shoulder at short retention times. As the reaction progresses, this shoulder becomes a population of very high

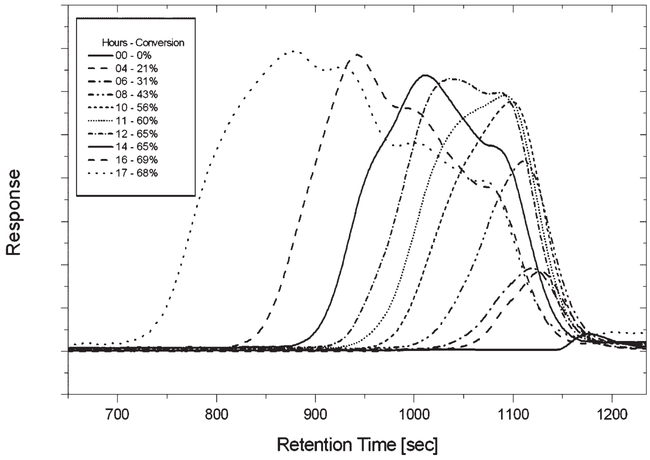


Figure 3. Molecular weight distributions of the RAFT polymerization of DVB as seen with the SEC-DRI. The response is proportional to conversion, with the exception of 0% conversion, which was modified in order to see the elution time of PADTC.

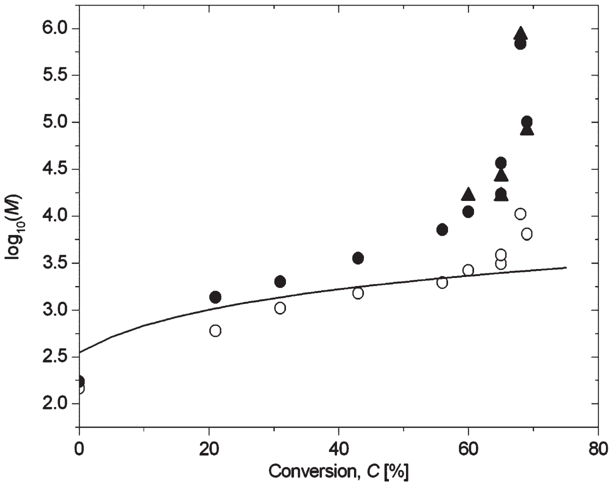


Figure 4. Molecular weight evolution of p(DVB) by RAFT polymerization: (○) M_n from SEC−universal calibration, (●) M_w from SEC−universal calibration, (▲) M_w from SEC−triple detection. (—) Theoretical molecular weight evolution for a linear growth of equivalent system.

molecular weight polymers, as seen by the large peaks at short retention time. These high molecular weight polymers are the branched polymers formed by reacting through the pendant vinyl group on the polymers. At high conversion, the distribution is very broad and multimodal, indicating a population of very highly branched polymers as well as some moderately branched and linear polymers.

Figure 4 shows the evolution of the average molecular weights with conversion and confirms the qualitative reaction mechanism drawn from the SEC traces. Figure 4 compares the experimentally determined number-averaged molecular weight (M_n) to the theoretical prediction for a linear polymer which targets 25 monomers per chain. As seen in Figure 4, M_n remains close to theory up to 40%, and the polydispersity is low. At conversions above 50%, the average molecular weight grows rapidly and deviates significantly from the equivalent linear polymer. This suggests that after approximately 40−50% conversion branching reaction become significant, and the polymers have a highly branched structure rather than a linear structure. These observations are confirmed by inspection of the corresponding SEC traces.

In the synthesis of DVB-based highly branched polymers the results suggest an initial period where linear polymers are mainly formed. This is based on the SEC analysis which shows that the molecular weight follows the theoretical evolution for a linear chain of 25 DVB units. Despite that the pendant vinyl groups were found to be 5.7 times more reactive than a vinyl group of DVB monomer, as determined during the calibration of the conversion model outlined in the Supporting Information, the linear growth observed is likely a concentration effect. Since early in the reaction there is a high concentration of unreacted DVB, which implies that the likelihood of adding a DVB unit to the growing chain is large. This leads to the formation of linear polymeric chains with pendant double bonds. As the reaction proceeds, the vinyl groups from free monomers are consumed, while the concentration in pendant vinyl groups increases, which increases the probability of a radical reacting with a polymeric pendant group.

The propagation of a growing polymeric chain radical through a pendant vinyl group on another chain results in a single polymer with molecular weight and number of pendant vinyls total the original two chains. Free monomer is not consumed during this branching reaction; therefore, polymer conversion does not increase, while molecular weight increases dramatically. Indeed, an increase in weight-average molecular weight M_w from 17 000 to 850 000 g mol^{-1} is observed when 3% of the DVB monomer is further incorporated into the polymer at 65% conversion (to 68% conversion). Since RAFT polymerization offers reasonably good control over the molecular weight of linear polymers, chains will have similar lengths at the onset of branching; hence, the overall molecular weight increases by multiples of the molecular weight of a short polymer chain. This molecular weight was determined by the ^{1}H NMR analysis of the precipitated p(DVB), which showed a vinyl to PADTC ratio of 6.3:1; i.e., a chain requires ∼6 pendant vinyl moieties before the probability of a radical to add to a free vinyl group is equal that of adding to a pendant group. By assuming the existence of linear polymers at 50% conversion (the onset of significant branching), the conversion model predicts 50% of the units contain vinyl moieties. This suggests that before intermolecular polymerization the linear polymers consist of ∼12.5 monomeric units, of which 6.25 units have partaken in intramolecular cyclization. This calculation is consistent with the six pendant vinyl moieties required to shift the growth mechanism to be predominately branching.

The propagation of a growing polymeric chain radical through a pendant vinyl group of a second polymer increases the number of pendant vinyl groups of the resulting macromolecule. This implies that a very highly branched polymer is more likely to participate in further propagation than a lightly branched polymer or a polymer chain that has yet to propagate through another polymer chain (an unbranched polymer). This behavior is evident in SEC traces (Figure 3) where high molecular weight species and remnant low molecular weight polymers coexist in the high conversion samples, thus explaining the large polydispersity at high conversions. A slight shift toward higher molecular weights of the low molecular weight species can be observed over time due to the small but finite chance for them to further polymerize. By using the SEC-DRI signal of the 68% conversion sample of p(DVB) and fitting a Gaussian curve to the peak

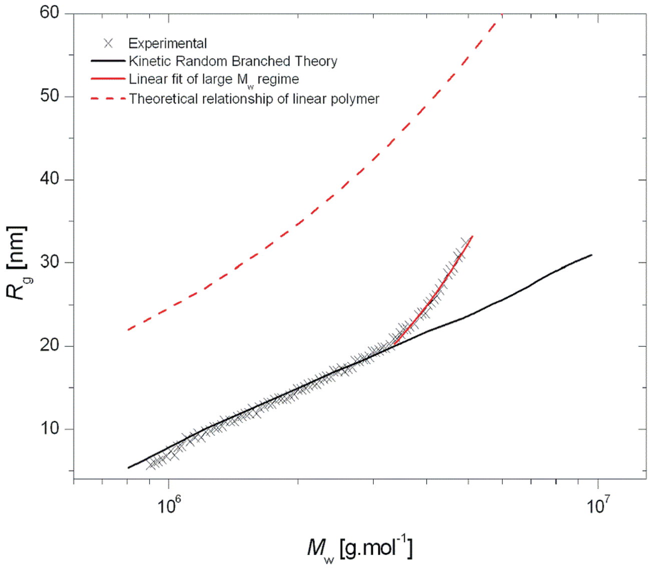


Figure 5. Data of the radii of gyration and corresponding molecular weights of the macromolecules present in the 68% conversion sample of the RAFT polymerization of DVB as obtained by multiangle laser light scattering with SEC (MALLS-SEC). The theoretical size−mass scaling for linear polymers[62] is also shown.

corresponding to the linear species (Figure S.4), comparing the integrals we estimate the sample to consist of 10% linear chains.

An additional feature of the RAFT polymerization of DVB is that for conversions greater than 65% there is a decline in radical concentration. This can be best observed in the pseudo-first-order plot shown in the Supporting Information. Since at relatively high conversion it is statistically more likely for a radical to propagate through a highly branched polymer due to its large number of pendant vinyls, this could confine radicals to a small region of space and increase the likelihood for termination, causing the decrease in radical concentration observed between the 12 and 17 h samples.

The 68% conversion sample of the RAFT polymerization of DVB was fractionated by SEC before observed by a multiangle laser light scattering (MALLS) detector.[63,64] Figure 5 shows the scaling of the radius of gyration R_g with molecular weights M_w for the SEC fractions as directly measured by MALLS.[65] This experimental size−mass scaling is compared to both the theoretical predictions of kinetic random branching theory and the predicted size−mass scaling for a linear polymer. Kinetic random branching theory (KRBT)[54] is a model for the solution structure of randomly branched polymers, and it is based on random branching theory.[66−68] Random branching theory is a general model for the solution structure of highly branched polymers, and KRBT extends the ideas in random branching theory to the kinds of polymers studied in this work. In earlier work, KRBT was shown to agree well with highly branched polymers synthesized using a RAFT-mediated "Strathclyde approach" polymerization.[54]

Figure 5 shows that the DVB polymers are significantly smaller than the linear predictions, which is consistent with the assumption that they are highly branched polymers. Furthermore, Figure 5 shows that for most of the experimental data range KRBT agrees very well with the experimental data. Fitting this data series, the parameter that describes relative rigidity or flexibility of the units in the polymer (κ) suggests the formation of rigid structures. The details regarding the fitting parameters can be found in the Supporting Information. An interesting feature in Figure 5 is that the radii of gyration at molecular weights greater than 3.5 × 10^6 g mol^{-1} grow faster than an equivalent linear polymer. Although this could be due to partial gelation of these highly branched polymers,[54] this feature could also be due to the size exclusion limit[69,70] of the GPC system. One observation that supports the anomaly resulting from cross-linked structures is the calculation of the overlap concentration c^*. A concentration below c^* implies the dominant interactions are intramolecular and above c^* implies more intermolecular interactions.[71,72] The c^* was calculated for our system using eq 1, where N_A is Avogadro's number, M is the molecular weight, and r_g is the radius of gyration of the polymer. Interestingly, the c^* for polymers at the point where the high M_w trend begins (i.e., deviation from the KRBT fit) was found to be similar to the concentration of polymer in the system determined. This result suggests the size of the polymer increases until intermolecular interactions dominate ("overlap") when polymers with a large number of reactive sites cross-link rather than branch with molecules of similar or larger size. However, since the majority of the data are well described by the model for highly branched structures, we argue that the DVB polymers studied are well described as highly branched polymers rather than nanogels or other structures.

$$c^* = \frac{M}{N_A \frac{4\pi}{3} r_g^{\ 3}} \qquad (1)$$

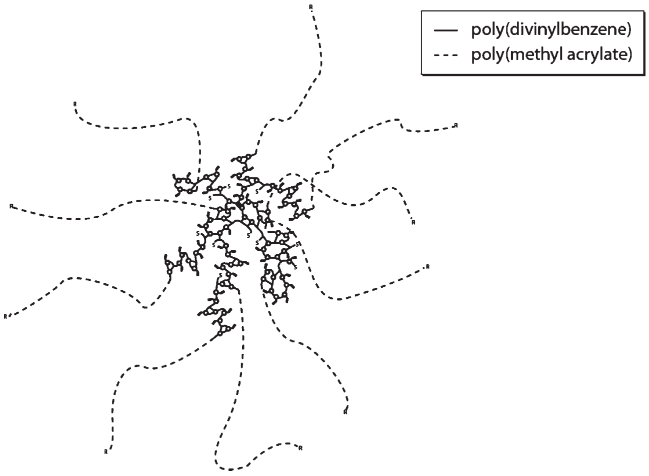


Figure 6. Schematic representation of the starlike block copolymer based on extending a linear chain of methyl acrylate with divinylbenzene.

Linear Highly Branched Block Copolymer of p(MA)-*b*-p(DVB). The earlier section established a facile new method of synthesizing highly branched polymers by the homopolymerization of divinylbenzene under RAFT conditions. This section uses the synthesis outlined earlier to create materials with distinct functionality and unique architectures. Well-defined structures showing linear polymeric chains attached to a cross-linked core (starlike polymers) were reported by Rempp et al. and Burchard et al. using anionic polymerization.[73−75] Patrickios and co-workers also synthesized starlike architectures by cross-linking star polymers produced by group transfer polymerization.[76−78] More recently, Dong et al. have accessed starlike polymers by tethering linear polymers to a hyperbranched core.[79] Here we report a facile and versatile route to similar structures.

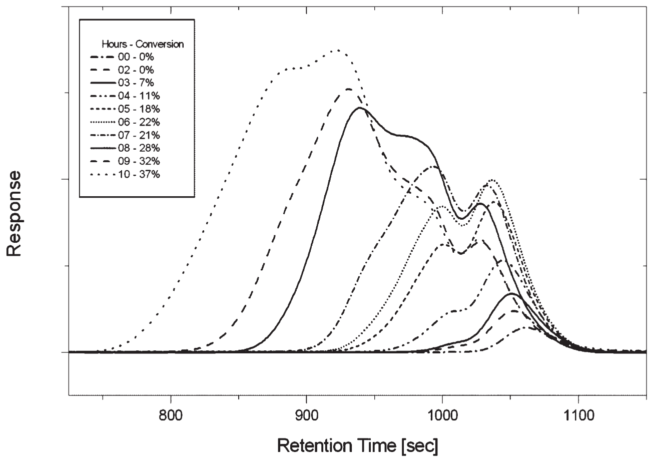


Figure 7. Molecular weight distributions of the polymerization of DVB in the p(MA)-*b*-p(DVB) system as seen with the SEC-DRI. The response is proportional to conversion, with the exception of 0% conversion, which was modified in order to see the elution time of p(MA) macro-RAFT.

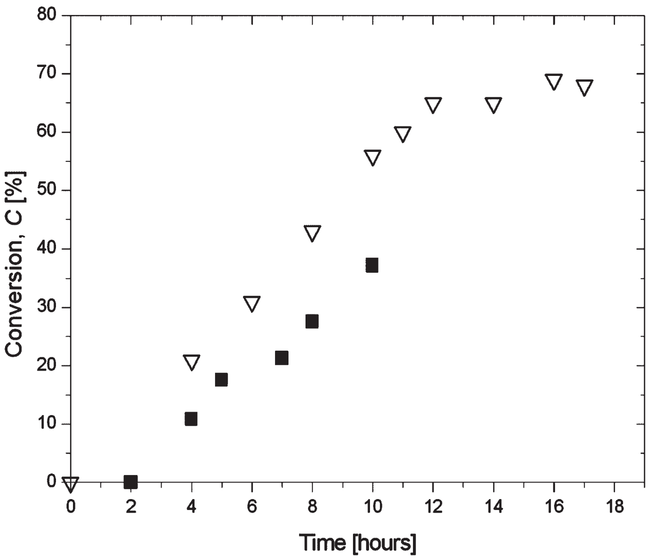


Figure 8. Kinetic plot of the p(MA) macro-RAFT-mediated polymerization of DVB (■) and PADTC-mediated polymerization of DVB (▽).

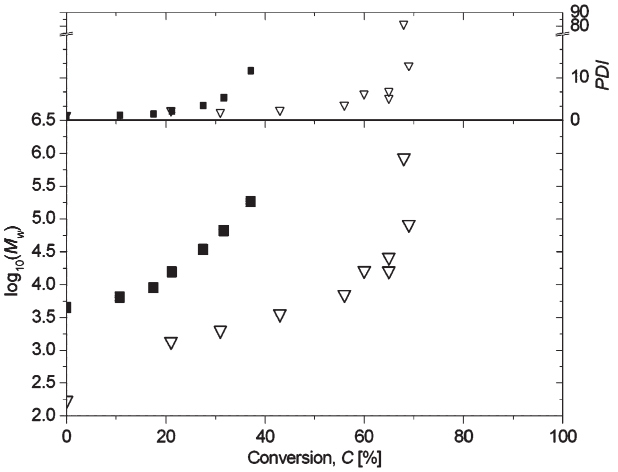


Figure 9. Molecular weight evolution of p(DVB) (▽) and p(MA)-*b*-p(DVB) (■). Points were determined by SEC−triple detection and SEC−universal calibration.

Sequentially polymerizing methyl acrylate (MA) and divinylbenzene (DVB) (see Figure 6) leads to a starlike structure with p(MA) arms attached to a core rich in vinyl moieties, which may be further modified. The polymerization of MA was mediated by PADTC at 70 °C to give living linear chains containing 23 units of MA (M_n = 2410 g mol^{-1}). The resulting p(MA) was then chain extended by polymerizing DVB.

The polymerization of DVB with the p(MA) macro-RAFT resulted in an earlier gelation (37% DVB conversion) than the polymerization of DVB mediated by PADTC (68%). A possible explanation for this phenomenon is the difference in reactivity between the p(MA) macro-RAFT agent and PADTC. Interestingly both systems cross-link with species that have reached similar hydrodynamic volumes (ca. 750 s on SEC traces). Although the p(MA) macro-RAFT-mediated synthesis of DVB polymers gelled at lower conversions, the fact that a macro-RAFT can be used to mediate the polymerization of DVB is important for materials applications, since the macro-RAFT can be used to introduce additional functionality to the material.

Figure 7 shows the time evolution of the SEC trace, detected using DRI. In Figure 7, the SEC traces of the p(MA)-*b*-p(DVB) copolymer show a highly polydispersed sample with multimodal molecular weight distributions at high conversions. This is very similar to the polymers based only on PADTC and DVB, suggesting the growth mechanism is the same for both polymers. Note that the use of anionic and group transfer polymerization has led to narrower molecular weight distributions, but both techniques require much more stringent reaction conditions. As seen in Figure 7, the low molecular weight species of p(MA)-*b*-p(DVB) samples elute at ca. 1000 s, which is earlier than the low molecular weight species of p(DVB) samples (ca. 1125 s). This is expected since the p(MA) macro-RAFT agent has a larger hydrodynamic volume than the PADTC RAFT agent.

Branching occurs past the seventh hour of the reaction as indicated by the formation of a shoulder in the SEC trace. Unlike the polymerization with PADTC, the kinetics of polymerization with the p(MA) macro-RAFT agent shows the polymer conversion increasing steadily past the onset of branching as can be seen in Figure 8. This behavior can be attributed to the branching beginning at 20% polymer conversion as opposed to the polymerization with PADTC (55%). However, at 20% polymer conversion the DVB monomer concentration is still significant enough to further linear chain growth.

Figure 9 plots the evolution of weight-averaged molecular weight for the p(MA)-*b*-p(DVB) and compares it to the p(DVB) system. The precise data used in Figure 9 have been tabulated in the Supporting Information. The similarity in the shape of the M_w vs conversion curve for both the p(MA)-*b*-p(DVB) and p(DVB) systems further suggests that the reaction of the macro-RAFT system follows a similar mechanism to the PADTC system. In Figure 9 both the p(MA)-*b*-p(DVB) and p(DVB) systems show an initial phase where the molecular weight grows relatively slowly with conversion. In contrast, at higher conversions there is a regime where the molecular weight grows very rapidly, although this rapidly growing regime occurs at >20% conversion for the p(MA)-*b*-p(DVB) system, whereas it occurs at approximately >55% conversion for the p(DVB) system.

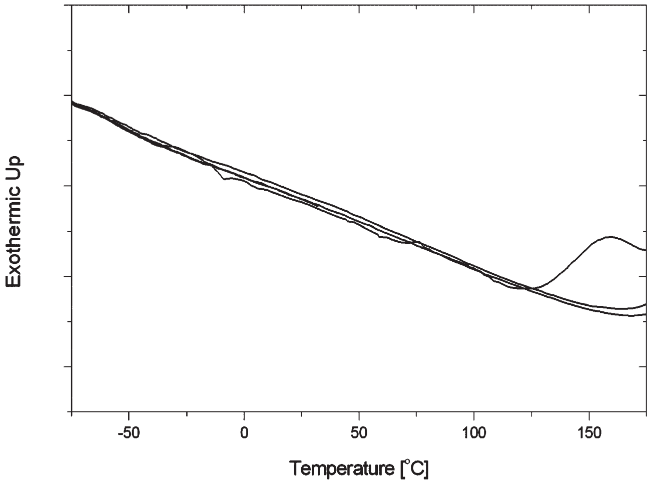


Figure 10. Differential scanning calorimetry plot of p(DVB).

The use of a macro-RAFT agent results in a multimodal molecular weight distribution observed in the SEC traces of high conversion p(MA)-*b*-p(DVB) copolymers. This is similar to the DVB homopolymer and suggests the formation of controlled mostly linear chains, which subsequently branch. The main difference between the homopolymer and the block copolymer is that the block copolymer cross-linked at a lower conversion.

Thermal Characterization of p(DVB) and p(MA)-*b*-p(DVB). Figure 10 shows the DSC plots of highly branched p(DVB). An interesting feature in this DSC curve is the one-time exothermic peak at 160 °C, which is thought to arise from the thermal self-initiation of p(DVB) followed by radical propagation through pendant vinyls groups of p(DVB). This behavior was also observed at 150−160 °C by Li et al., who proposed the self-initiation of the pendant vinyl group from p(DVB).[80] Furthermore, no T_g could be observed after the self-polymerization of p(DVB), supporting the conclusion of a cross-linked structure, with very restricted chain movement. The lack of a T_g for p(DVB) in the range of 25−200 °C was also noted by Hirano et al., who suggested the absent observation was due to the compact and rigid structure of the polymer.[81]

When the p(MA)-*b*-p(DVB) material was heated above 100 °C, the DSC curve of p(MA)-*b*-p(DVB) (Figure 11) shows an exothermic peak for the first heating run at 110 °C. This exothermic peak at 110 °C is likely to be due to the self-initiation of the pendant vinyl groups in the DVB block. Although this exothermic peak is seen in both the p(MA)-*b*-p(DVB) and p(DVB) materials, the peak is much larger for the p(MA)-*b*-p(DVB) and occurs at 110 °C for p(MA)-*b*-p(DVB) rather than 160 °C for p(DVB). The inconsistency in the temperatures required for self-polymerization in p(MA)-*b*-p(DVB) can be attributed to the plasticizing effect from the residual toluene and potentially the short p(MA) chains in the sample which can act as a plasticizer.[70] After the cross-linking of p(DVB) in the p(MA)-*b*-p(DVB) sample the T_g of p(MA) increases to 30 °C, which is 20 °C higher than the T_g of p(MA) (lit. 9−10 °C).[82,83] The increase in the T_g is associated with the entanglement of p(MA) chains within the p(DVB) matrix. After the first heating above 100 °C, no T_g could be associated with p(DVB) in the p(MA)-*b*-p(DVB) sample despite the attachment of short linear chains to highly branched structures, which could produce a plasticizing effect.

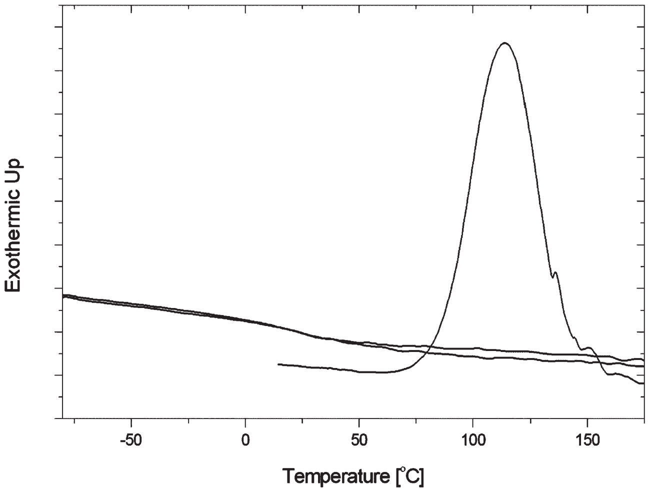


Figure 11. Differential scanning calorimetry plot of p(MA)-*b*-p(DVB).

Table 1. Samples and the Observed Decomposition Temperature(s)

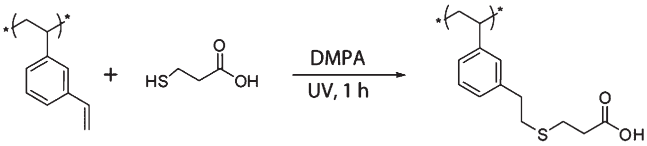
sample	decomposition temperature (°C)
PADTC	136
P(MA)	RAFT: 259, polymer: 362
P(DVB)	RAFT: 240, polymer: 469
P(MA)-*b*-p(DVB)	386[a]

[a] Single degradation curve.

The TGA analysis of PADTC shows the onset of degradation at 136 °C. While this temperature is higher in comparison to the degradation temperature of 2-ethyl propionate ethyltrithiocarbonate (EPETC) studied by Legge et al. (97 °C),[84] it is possible that the long alkyl chain and carboxylic acid group of PADTC causes the higher decomposition temperature. Furthermore, EPETC was reported as a liquid, where as PADTC was studied as a solid.

The TGA data are summarized in Table 1. Our sample of p(MA) had two distinct degradation temperatures. Degradation at 259 and 362 °C was attributed to the decomposition of the RAFT end groups (which have been thermally stabilized by the polymer)[84] and MA chain, respectively. Thermal analysis of p(MA) made by free radical polymerization and using a heating rate of 15 °C/min from Ali et al. showed a single degradation stage at 300−360 °C.[85] In the thermal analysis of p(MA) synthesized with EPETC, Legge et al. reported on two degradation temperatures, 272 and 350 °C, agreeing well with our results.[84] Our sample of p(DVB) was found to decompose at 240 and 469 °C. In agreement, Postma et al. report the use of thermal degradation at 210−250 °C to remove the trithiocarbonate group in polystyrene made by RAFT polymerization.[75] Furthermore, Li et al. published degradation temperatures of ∼460 °C for p(DVB) (by FRP).[80] The TGA also shows that 8−10 wt % of char remains after heating to 800 °C, a result that Li et al. attributed to the incomplete combustion of p(DVB) when analyzed under an inert atmosphere.[80] The TGA of p(MA)-*b*-p(DVB) showed only one point of decomposition at 386 °C although a shallow, steady weight loss was observed between 150 and 300 °C, which could be assigned to the degradation of the trithiocarbonate group. The weight begins to steeply decline at around 425 °C in the sample, suggesting the

Scheme 1. Thiol−Ene Click Reaction Using the Pendant Vinyl Groups and 3-Mercaptopropionic Acid To Functionalize p(DVB)



stabilization of p(MA) chains (49 wt % of the p(MA)-*b*-p(DVB) sample) by being incorporated as a copolymer.

These thermal analyses of the new materials show that highly branched p(DVB) is capable of self-cross-linking upon applying heat and can even incorporate linear polymers in the matrix. Furthermore, the lack of an observable glass transition temperature of p(DVB) supports the modeled polymer of a rigid branched structure.

Adding Functionality to p(DVB) by Thiol−Ene Click Chemistry. Click chemistry can be used to add functionality to these highly branched DVB polymers, as an alternative to using a macro-RAFT agent. The concept of click chemistry was introduced by Sharpless to describe highly efficient, versatile, and inexpensive chemistry.[86] The thiol−ene click reaction is a well-established chemical reaction involving the addition of a molecule with a thiol functional group to a double bond and has recently gained popularity in polymer chemistry.[87−89] Following a similar procedure by Lowe et al.,[89] the pendant double bonds of p(DVB) were used in the thiol−ene click reaction to transform the hydrophobic DVB polymer to a polar macromolecule. 3-Mercaptopropionic acid was bonded to the highly branched polymers by reacting with the pendant vinyl groups, as shown in Scheme 1. An excess of 3-mercaptopropionic acid was used to limit cross-linking of p(DVB).

A ^{1}H NMR spectrum of the polymer was taken before the reaction where the polymer was fully soluble in *d*-chloroform ($CDCl_3$). After exposure to UV radiation for 1 h, the resulting polymer was insoluble in $CDCl_3$ and ^{1}H NMR analysis was carried out in d_6-dimethyl sulfoxide (d_6-DMSO) where it was fully soluble. This change in solubility suggests a significantly more polar polymer after treatment. The ^{1}H NMR spectra showed the disappearance of vinyl peaks after the exposure to UV light, as shown in the Supporting Information.

Figure 12 shows the ATR-IR spectrum of the purified click product. As seen in Figure 12, the product after the click reaction has an increased absorption at the vibrational modes of the C═O stretch (1650−1750 cm^{-1}) and C−O stretch (1150−1300 cm^{-1}) relative to the C−H stretch (2800−2950 cm^{-1}). This result confirms the addition of the carboxylic acid functional group to the polymer. The stretch corresponding to C═O and C−O absorption in the initial reactants is due to the carboxylic acid group in the PADTC RAFT agent. These increases in the C═O and C−O stretches, and the disappearance in the vinyl groups as shown by ^{1}H NMR analysis, confirm that the thiol−ene reaction modified the nonpolar highly branched p(DVB) to a polar material, with many pendant acid groups.

■ CONCLUSION

This work has demonstrated the facile synthesis of highly branched polymers via the RAFT-mediated polymerization of DVB. The use of RAFT agent delayed the point of gelation in the polymerization of DVB, where gelation was observed after 68% polymer conversion in RAFT polymerization as opposed to 15% conversion for FRP. It was shown that the vinyl structure of the polymer is based on the initial formation of linear chains bearing pendant vinyl bonds, followed by their reaction with the active radical chain at higher conversion to afford the highly branched polymer.

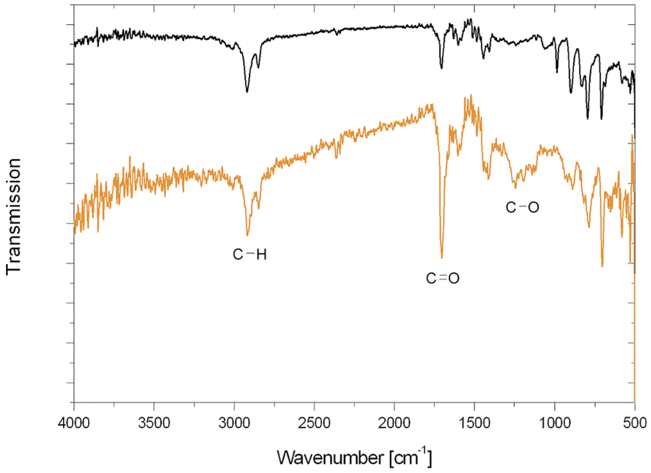


Figure 12. ATR-IR spectra of the highly branched polymer: (black) before the click reaction and (orange) after the click reaction and purification step.

This new approach to highly branched polymers was exploited to generate starlike polymer structures. By taking advantage of the living characteristic of RAFT polymerization, linear p(MA) chains were synthesized and chain extended by subsequent addition of DVB to produce a highly branched p(DVB) core with p(MA) “arms”. The polymerization was found to follow a similar mechanism as that of the homopolymerization of DVB with PADTC, although the copolymer was observed to gel at lower conversions (37%) than its homopolymer counterpart. From an application point of view, using a hydrophilic linear polymer and hydrophobic highly branched core could lead to the formation of structures that behave as unimolecular micelles in solution. These structures have received growing interest since there do not depend on a critical micelle concentration.

An interesting feature of the DVB based highly branched polymers is that at 160 °C the pendant vinyl groups of p(DVB) can be thermally initiated to trigger self-cross-linking of the macromolecules. In the case of the starlike copolymer, this resulted in the stabilization of p(MA) chains against thermal degradation possibly due to their entanglement in the p(DVB) matrix. The self-cross-linking reaction provides a means to form polymeric nanoparticles by simply heating the highly branched structures. The ability of the highly branched polymer to self-cross-link at high temperatures can be explored to generate insoluble polymeric nanoparticles (potentially functionalized) of size below 10 nm in diameter. An additional benefit of these highly branched polymers is that more functional groups can be added through the pendant vinyl groups in the polymer. In this work, thiol−ene click chemistry was used to react the vinyl groups in the polymer with 3-mercaptopropionic acid to introduce a polar functional group to the polymer. This study has shown a new route to producing functional highly branched structures by first synthesizing a vinyl-rich scaffold that can be further functionalized by thiol−ene click chemistry to introduce the desired chemical functionality. We envisage that this synthesis of highly branched polymer will be used in the future to tailor starlike block copolymers with functionality introduced to the core and shell of the polymer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Free radical polymerization of DVB, RAFT polymerization of DVB, KRBT fit, p(MA) macro-RAFT-mediated polymerization of DVB, thermal characterization, thiol−ene click chemistry, conversion model, and conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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