Crosslinked Nanoparticles from Stars by Intramolecular Crosslinking: A Bottom Up Approach to Polymeric Nanoparticles


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INTRODUCTION

Polymer structure and architecture are critical features in nanoscience and nanotechnology given the potential of nanometer-sized features for a variety of applications. For this reason, there has been an explosion of interest in nanoparticles in Chemistry, Material Science and Biology.1 The formation of nanoparticles is usually characterized by two distinct processes: (1) assembly of molecules into nanostructures and (2) stabilization of these nanostructures. Micro- and miniemulsion polymerization is a useful way of producing polymer particles in varying sizes.2 Likewise self assembly of monomers and polymers followed by stabilization of the assembled structures is receiving increased attention. In this regard, amphiphilic block copolymers self assemble for form micelles which can be stabilized by crosslinking in either the core3 or the shell4 of the block copolymers self assembly for form micelles which can be used to generate multiarm stars of any termination, the number of polymer arms added in each stage which can be decorated with additional polymer chains. In the absence of crosslinking, the macroinitiator to DVB produces a crosslinked polyanionic core polymer particles in varying sizes.2 Likewise self assembly of nanoparticles from single polymer molecules by mean collapse initiated by intramolecular carbon-carbon bond forming reactions and have demonstrated the templating effect of such thermally labile nanoparticles in the formation of nanoporosity in thin films.3 Here we demonstrate the formation of small, functionalized, crosslinked, polymeric nanoparticles from reactively functionalized multifarium stars prepared by anionic polymerization. The size of the crosslinked nanoparticle is dictated by that of the polymeric precursor. In an arm-first synthetic approach, multifunctional stars can be generated by the addition of living, linear polystyrene to divinylbenzene (DVB).5 The reaction proceeds in two main stages; first the addition of the macroinitiator to DVB produces a crosslinked polyanionic core decorated with linear polystyrene arms. In the presence of a polymerizable monomer, the core provides polymer growth sites which can be decorated with additional polymer chains. In the absence of any termination, the number of polymer arms added in each stage will be the same. This procedure can be used to generate multiarm star homopolymers or miktoarm block copolymers.5,6 The morphology of these materials is best described as a star with pendant arms emanating from a small crosslinked core.

The synthetic procedure provides considerable versatility. For example, the use of a functionalized initiator results in the positioning of the functionality at the ends of the initial pendant arms; alternatively quenching the polymeric arms which grow from the polyanionic core locates the functionality at the ends of the chains added in the second step. In principle, the incorporation of latent crosslinking substituents into the growing arms provides a route to highly crosslinked nanoparticles with dimensions commensurate with the stars. The latent crosslinking functionality can be incorporated into either the initial, final or even both arms. A suitable latent crosslinking group must be inert to the anionic polymerization conditions and be activatable on demand (e.g. light, heat, chemical transformation etc.). Ideally the latent functionality should be selectively transformed into a stable linkage. Alternatively, crosslinking could be achieved by reaction of the activated intermediate with appropriate functionality on other arms or by intramolecular reaction with added polyfunctional reagents. In the case of linear polymers, intramolecular reaction leads to chain collapse accompanied by large changes in the molecular dimensions. For star polymers, smaller volume changes would be expected since the connectivity of the star largely defines the shape of the molecule.

Benzocyclobutene substitutents constitute one class of latent reactants which are generally stable to the anionic polymerization conditions. This substituent is thermally converted by ring opening to a highly reactive o-xylylene which can stabilize by bimolecular reaction or polymerization.7,8 Either route would be effective for crosslinking the polymer arms.

EXPERIMENTAL

Star Polymer Preparation: Into a dry flask was added 245 mL of dry cyclohexane, 6,74g (64.8 mmol) of styrene and 0.94 g (7.2 mmol) of vinyl benzocyclobutene (V-BCB) under Argon. To this was added 2.1 mL, (0.7M in cyclohexane) of the initiator 3-(t-butyldimethylsiloxo)-2,2-dimethyl-1-propyllithium and 8mL of THF. After 30 minutes, an aliquot was withdrawn for SEC analysis. To the solution was added 0.19g (1.47 mmol) of p-divinylbenzene (p-DVB/LLE = 1.0). The reaction was stirred 30 minutes and a aliquot of the half-star was removed and quenched in methanol. To the remainder was added a mixture of styrene (3.84g, 36.9 mmol) and V-BCB (0.53g, 4.1 mmol). After 30 minutes stirring, the reaction was quenched in ethanol to produce the star polymer in quantitative yield. The polymer was dissolved in CH2Cl2, acetone (1:3) and precipitated into isopropanol.

Crosslinked Nanoparticle: The TBDMS-protected star was dissolved (5%) in dibenzy ether (DBE) and added dropwise to an equal amount of DBE at 240 °C at a rate of 15 mL/hr. After the addition, the heating was continued for 0.5 hr and most of the solvent removed under vacuum. The solution was precipitated into methanol to yield the crosslinked particle in quantitative yield. The sample was reprecipitated two more times.

RESULTS AND DISCUSSION

Our synthetic route is shown in Scheme 1. The t-butyldimethyilsiloxy substituted initiator produces a living polymer with styrene and 4-vinyl benzocyclobutene (VBCB) can be randomly incorporated over a large concentration range. This functionalized macroinitiator may be appended to a crosslinked DVB core in an arm-first approach as discussed earlier. Product quenched and isolated at this point in the reaction is designated as the half-star. Knowing the molecular weight of the macroinitiator (SEC) and the absolute molecular weight of the half-star (light scattering or calibrated viscometry), the number of pendant arms can be estimated (the mass fraction of the DVB is usually long, typically 2-4%). Alternatively, the living, anionic half-star can be used to initiate subsequent polymerization of another reactive monomer (in this case styrene) to generate the full star. When VBCB is included in either or both stages, it is randomly incorporated into the polymer arms. In addition to the polydispersity (PS) resonances, the 1H NMR spectra show resonances for benzocyclobutene and methylene protons of the 4-membered ring at δ = 3.1, and the silyldimethyl end groups from the initiator at δ = 0-1.0. The 1H-NMR spectrum of the full star containing 10 mole% of VBCB in the arms is shown in Figure 1a. For this particular polymerization, a 90/10 mixture of styrene/vinylcyclobutene is used in each stage.

For this molecule, the weight percentage of the macroinitiator (defined by the ratio of monomer/initiator) was 5,200 g/mol by SEC analysis using linear PS standards. Absolute molecular weight measurements (calibrated SEC-viscometry, static light scattering etc.) gave a molecular weight of 87,000 g/mol (light scattering, Table 1) for the quenched half-star. Analysis of the data suggest the formation of a half-star with ~ 13 arms. Assuming that the second stage of the polymerization (half-star- full-star) generates an equal number of new polymer arms (no dead arms), absolute molecular weight measurements indicate that the final PS arms had a molecular weight of 4,600 g/mol. In this case, the target DP for the second polymerization was deliberately reduced to increase the chemical accessibility of the protected initiator provided by the macroinitiator. Control of reagent stoichiometries dictates the individual arm lengths, the size of the core and the number of arms added or grown in the two polymerization steps. The benzocyclobutene functionality can subsequently be activated by heating the polymer to 220-250°C. Intramolecular reactions are eliminated by either the use of ultradilute solutions or more practically by psuedo high dilution techniques (solution of polymer is slowly added to solvent heated to the reaction temperature with efficient stirring). After crosslinking, the
protons assigned to the 4-membered ring disappear from the $^1$H-NMR spectrum (Figure 1b). The evolution of molecular weight during the reaction sequence (macroinitiator-half-star-full-star) as monitored by SEC is shown in Figure 2. As expected, the SEC molecular weights of the stars (see Table 1) are underestimated reflecting the smaller hydrodynamic volume of the crosslinked particles relative to linear polystyrenes of comparable molecular weight. It is interesting that the hydrodynamic volume of the stars relative to linear polystyrenes of comparable molecular weight is little changed relative to the stars. This result is very different from the controlled collapse of functionalized linear polymers where hydrodynamic volume changes of 40-60% are often observed.9

The solution properties of the star and crosslinked nanoparticle are shown in Table 1. $R_g$ and $R_h$ measured by static and dynamic light scattering respectively are similar for both the star and the nanoparticle. This observation is consistent with the similarity in hydrodynamic radii reflected by SEC analysis. The SEC molecular weights of both the star and the crosslinked nanoparticle are both substantially lower than the values measured by light scattering or calibrated SEC-Viscometry. The 10% increase in $M_w$ measured by static light scattering upon conversion of the star to the nanoparticle may be due to a slight increase in polydispersity upon crosslinking where a small contribution from higher molecular weight species is magnified in the distribution. Finally small angle x-ray scattering (SANS) studies yielded the respective $R_g$ values. These values are similar to those measured by light scattering. In the table, we report the hard sphere radii ($R^*$) calculated from $R_g$.

CONCLUSIONS

In summary, we have described a route to crosslinked polymeric nanoparticles by the controlled collapse of functionalized stars prepared by anionic techniques. The technique involves the activation of latent thermal crosslinking functionality under conditions of pseudo-high dilution. As expected, the dimensions of the nanoparticles are defined by the precursor stars. Pendant functionality may be introduced either via the macromolecular initiator or by quenching of the arms of the growing star. The dimensions of such particles are small and provide access to a range of sizes not accessible by microemulsion polymerization techniques. This functionality, in principle, also provides a scaffolding for subsequent functionalization and polymerization. The latter provides a new route to core-shell materials where the inner core is highly crosslinked.

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REFERENCES


9. Hawker, C. J. et al. submitted for publication

Table 1: Polymer Characterization: (a) Size Exclusion Chromatography, linear polystyrene standards, THF solvent; (b) polydispersity index; (c) light scattering in THF solution; (d) Hard sphere radius based on measured $R_g$ x $(5/3)^{1/2}$; (e) quasielastic light scattering in THF; (f) Small Angle X-ray Scattering in THF; (g) radius based on fitting model.

![Figure 1: $^1$H-NMR of full-star and crosslinked nanoparticle](image1)

![Figure 2: SEC traces of living polystyrene, half-stars, full stars and crosslinked nanoparticles. THF solvent, see Table 1 for molecular weights relative to linear polystyrene standards.](image2)