

Controlled Radical Polymerization of Bicyclic Olefins: A Simple Approach to Stabilizing Polystyrene Derived from Atom Transfer Radical Polymerization Methodologies

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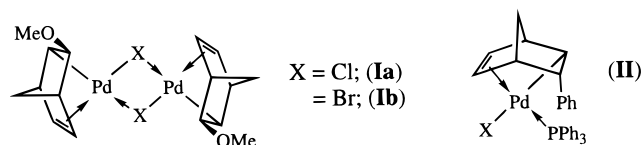
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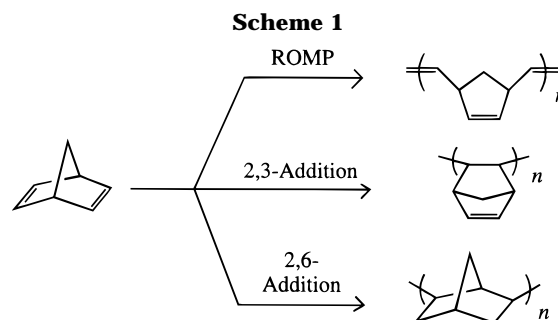
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The bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene ring systems are versatile in their polymerization behavior in that they can form polymers with very different microstructures depending upon the initiator employed. Ring-opening metathesis polymerization (ROMP) initiators yield structures with an unsaturated backbone.¹ Olefin insertion initiators yield the 2,3-addition polymer (or more correctly the 5,6-addition for the substituted monomers discussed herein),² and 2,6-addition polymerizations (via intramolecular cyclizations) are produced when cationic³ initiators are used. Radical-initiated polymerizations of norbornadiene results in a copolymer possessing both 2,3- and 2,6-addition units.⁴ However, selective 2,6-addition is observed in radical polymerizations of a monoester substituted norbornadiene, presumably due to resonance stabilization of the propagating radical.⁵ These structures are illustrated in Scheme 1 for norbornadiene.

The innate appeal of these rich structural motifs and the widely different properties observed for the isomeric polymers (vide infra) has prompted us to study both the homo- and copolymerization of 2,3-disubstituted norbornadiene derivatives. Although norbornadiene itself has been successfully homo- and copolymerized via insertion mechanisms using cationic palladium(II) complexes,^{1c,6} these initiators proved ineffective in the polymerization of electron-deficient derivatives⁷ such as diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**1**). However, by choosing initiators that compensate for this electron perturbation, living polymerizations of these monomers can be obtained.⁸ Polymerizations of **1** required the use of more electron rich neutral palladium(II) complexes such as bis(*μ*-halo)bis(*exo*-6-methoxy-2-norbornene-*endo*-*σ*,2 π)dipalladium (halo = chloride, **Ia**; bromide, **Ib**).⁹ Likewise, living copolymerizations



of **1** with carbon monoxide could also be accomplished using the monophosphine (or pyridine) adduct, bromo-(*endo*-6-phenyl-2-norbornene-*endo*-5 σ ,2 π)(triphenylphosphine)palladium (**II**).^{8b,10} Not surprisingly, the structures of both poly-**1** and poly(**1-co**-CO) are exclusively



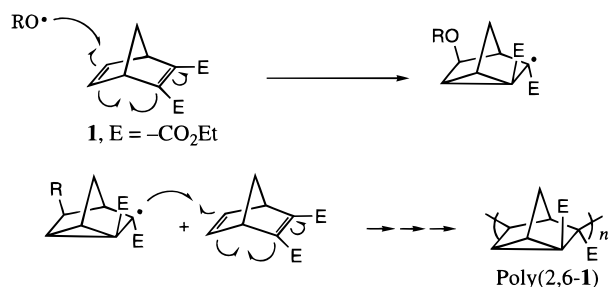
composed of 5,6-insertion units, and no 2,6-additions can be detected.

Obtaining the 2,6-addition isomer of poly-**1** proved far more elusive. Attempts to cationically polymerize **1** failed to produce any polymer, undoubtedly due to the electron deficient nature of the olefin. We recently discovered, however, that **1** will undergo radical polymerization to exclusively give the 2,6-addition structure. Furthermore, these monomers are amenable to controlled polymerizations using living radical techniques.¹¹ These findings and the use of **1** to thermally stabilize polymers derived from atom transfer radical polymerization (ATRP)^{12–14} methods are reported herein.

When tracking down some occasional inconsistencies in the polymerization behavior of **1** with **I**, we found that this monomer would undergo spontaneous polymerization (albeit slowly) at subambient temperatures. Tandem size exclusion chromatography–light scattering (SEC–LS) analysis¹⁵ of poly(5,6-**1**) samples prepared at room temperature using the least active initiator (**Ia**) (i.e., longest reaction times) revealed a high-molecular-weight peak in addition to the peak associated with the normal living polymerization. This high-molecular-weight fraction possessed different optical properties (e.g., differential of the refractive index as a function of concentration, dn/dc), and thus a different macromolecular structure than poly(5,6-**1**) obtained from **Ia**-initiated chains. ¹³C NMR spectroscopy analysis of the polymer mixture revealed aliphatic resonances that were inconsistent with the poly(5,6-**1**) structure but matched the resonances for the polymer obtained from spontaneous polymerization. Clearly, a competing polymerization mechanism was responsible for the presence of this high molecular weight fraction.

Upon further investigation, we found that bulk polymerizations of **1** could be radically initiated with peroxides at 65 °C (53% yield after 2 days under nitrogen). Characterization by SEC furnished a number average molecular weight of 16 200 and a PDI of 1.66 relative to polystyrene. Further analysis of the resulting polymer by NMR spectroscopy and IR spectroscopy indicated that it was identical to the autopolymerized polymer. A comparison of the IR spectra also indicates the absence of an olefinic stretch at 1628 cm^{−1}. Furthermore, the peak corresponding to the olefin carbon of poly(5,6-**1**) in the ¹³C NMR spectrum is missing, and the resonance for the ester carbonyl on the side chain shifts downfield from 163 to 171 ppm to indicate a loss of conjugation. Finally, a grouping of resonances appear between 22 and 38 ppm that are not present in the spectrum of poly(5,6-**1**). On the basis of NMR spectra and the structural precedent established from radically

Scheme 2



polymerized norbornadiene, we assigned the 2,6-addition nortricyclene structure, poly(2,6-1), to this polymer (Scheme 2).

Unlike the intermediates in the radical polymerization of norbornadiene, the propagating radical in polymerizations of **1** is structurally analogous to the propagating radical in methyl methacrylate polymerizations. Hence, within limitations, the polymerization of this monomer may be amenable to the use of controlled ATRP protocols.^{12–14} The most worrisome limitation is the slow rates of polymerization. By typical vinyl standards, **1** is slow to polymerize (*vide supra*), and this is sure to be compounded by controlled radical methodologies that rely on reduced radical concentrations to affect control. This concern was borne out: using the CuCl-bpy catalyst system with benzyl chloride as initiator, control was achieved but the rates were slow. An 11% yield of poly(2,6-1) (microstructure confirmed by NMR and IR spectroscopies) was obtained after 2 weeks at 130 °C. SEC analysis revealed that the polymerization is indeed controlled with $M_n = 2900$ and $\text{PDI} = 1.17$ vis-à-vis $M_n > 15\,000$ and $\text{PDI} > 1.6$ observed from normal radical reactions of **1**. Although **1** is not the candidate-of-choice for rapid polymer formation, it does undergo controlled cyclopolymerizations. This observation, in combination with its good thermal stability (*vide infra*), led us to investigate its use in thermally stabilizing other vinyl polymers derived from ATRP methodologies.

The rudimentary mechanism of ATRP involves the reversible transfer of a chloride (halogen) atom between propagating radical chain ends and the copper catalyst.¹² This equilibrium controls the instantaneous concentration of active radicals and thus suppresses termination reactions. Once polymerization is complete, the chain end is capped with the chlorine atom. Unfortunately, this has a negative effect on the thermal stabilities of ATRP-derived polymers relative to the same polymers synthesized by standard radical initiators. Rationale for this observation in polystyrene can come from an examination of bond dissociation energies of model compounds. The benzyl carbon–hydrogen bond strength is 88 kcal/mol, and the carbon–chloride bond strength in benzyl chloride is 72 kcal/mol.¹⁶ On the basis of these numbers, it is expected that polystyrene chains end capped with chlorine will be less stable than their hydrogen end group counterparts. This prediction is borne out when one compares the thermal stability of polystyrene samples prepared by AIBN (AIBN-PS) and by ATRP (ATRP-PS) at similar molecular weights (ca. 10 000). Samples of AIBN-PS and ATRP-PS were synthesized using standard protocols.^{12a} The results from thermal gravimetric analysis (TGA) show that the onset decomposition temperatures (at 10% mass loss) occur at 399 and 343 °C for AIBN-PS and ATRP-PS, respectively (Figure 1).

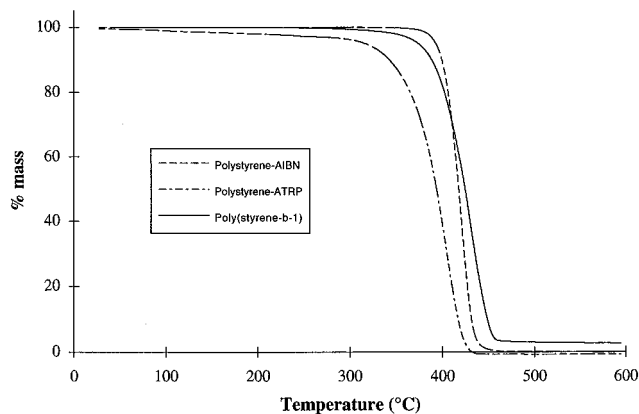
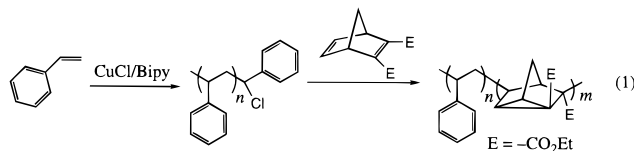


Figure 1. TGA curves for three samples: AIBN-PS, ATRP-PS, and poly(styrene-*b*-1).

To test our hypothesis, we prepared di- and triblock copolymers of **1** and styrene using the CuCl-bpy catalyst¹² with 1-chloro-1-phenylethane and 1,4-bis(1-chloroethyl)benzene, respectively, and compared their thermal stabilities to those of polystyrene alone. The procedure for the preparation of poly(styrene-*b*-1) was as follows. Polystyrene homopolymer was prepared using the CuCl-bpy-(1-chloro-1-phenylethane) initiator package. SEC-LS analysis of this sample showed it to have an $M_n = 10\,300$ and a $\text{PDI} = 1.36$. A portion of this chlorine-capped polystyrene was allowed to react with neat **1** in the presence of CuCl-bpy at 130 °C (eq 1).



Integration of the proton NMR spectrum of the resulting polymer indicated the incorporation of 5 mol % of **1** onto the polystyrene chains, and SEC-LS indicated an increase in M_n to 14 400 (relative now, not absolute) and a decrease in PDI to 1.24. As predicted, TGA analysis of poly(styrene-*b*-1) shows the increase in thermal stability of **1**-end-capped polystyrene relative to ATRP polystyrene (Figure 1). The onset temperature at 10% mass loss for poly(styrene-*b*-1) determined to be 389 °C represents a significant increase from the 343 °C onset for ATRP polystyrene and is comparable to the 399 °C onset temperature recorded for standard polystyrene. The poly(1-*b*-styrene-*b*-1) triblock shows similar behavior. We believe that changing the end group of the polystyrene to a short block of **1** is responsible for this increase in stability. The polystyrene is no longer capped with a benzylic chloride but instead with a tricyclic unit that can undergo different (and yet to be identified) nonchain breaking reactions if a radical is produced by the terminal chloride group.

In conclusion, we have shown that **1** will undergo radical cyclopolymerization to yield a fully saturated polymer consisting of 2,6-enriched repeat units. In the presence of the CuCl-bpy ATRP catalyst system, this monomer will also undergo a controlled polymerization. Finally, this monomer can be block copolymerized with styrene or used as an end-capping agent to yield a polymer with a thermal stability comparable to the stability observed for polystyrene obtained from an AIBN-initiated process.

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