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Well-Defined Diblock Copolymers via Termination of Living ROMP with Anionically Polymerized Macromolecular Aldehydes

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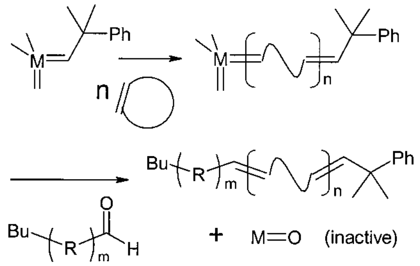
"Living" polymerizations, such as ring-opening metathesis polymerization (ROMP), atom-transfer radical polymerization (ATRP), group transfer polymerization (GTP), and anionic polymerization ("anionic"), can produce block copolymers of well-defined architecture and narrow molecular weight distribution. However, each mechanism is effective for only a limited range of monomers, greatly curtailing the diversity of accessible block copolymers. To circumvent this limitation, polymers synthesized by different mechanisms may be end-functionalized with complementary groups[1,2] and reacted together, though the resulting condensation linkages may limit the stability of the polymers. Alternatively, one may transform the polymer chain end into an initiator for a different class of polymerizations. End functionalization of ROMP polymers with a halide or an aldehyde permits the synthesis of ROMP-ATRP[3,4] or ROMP-GTP[5] block copolymers, respectively. In another approach, Li carbanion living ends can be directly converted to Ziegler−Natta[6,7] and even ROMP[8,9] active sites, but these particular ROMP centers do not yield living polymerizations, permitting little structural control over the block copolymers so obtained. Currently no method exists for the synthesis of well-defined anionic−ROMP block copolymers without introducing undesired functionality into the polymer backbone. This combination is particularly desirable, as the anionic and ROMP mechanisms operate on nonoverlapping classes of monomers, and both can produce polymers of very low polydispersity. Here, we present a method for the synthesis of such diblocks, by preparing ω-aldehyde-functionalized polymers anionically and employing these as macromolecular terminators for ROMP (Scheme 1).

Scheme 1. ROMP Block Copolymer Formation via Wittig-like Reaction with a Polymeric Aldehyde



This approach is based on the Wittig-like coupling of a living ROMP polymer and a carbonyl-bearing moiety, a reaction used previously to generate end functionalization[1,2] or to couple identical growing chains.[10] Risse and Grubbs[11] utilized a related coupling reaction to produce block copolymers from living polynorbornene and poly(oxy-2,6-dimethyl-1,4-phenylene) oligomers bearing ketone end groups, but the oxidative or halogen displacement polymerizations by which the oligomers are synthesized[12] yield inherently broad molecular weight distributions and operate on monomers different from those amenable to anionic polymerization. Here, we used Quirk and Kuang's method[13] to prepare near-monodisperse polystyrene and polyisoprene bearing a single aldehyde functionality at the chain end. Polystyrene and polyisoprene were polymerized using vacuum line techniques in cyclohexane, with *sec*- or *tert*-butyllithium, respectively. The living polymer was sealed in its reactor and transferred to a nitrogen atmosphere drybox where 2−10 equiv of dried and degassed *N*-formylmorpholine (NFM) was added and stirred at room temperature. Addition of NFM to the living end, evident

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Table 1. Characteristics of ROMP−Anionic Diblock Copolymers

ROMP block		anionic block		stoich excess	diblock	
monomer	M_n (g/mol)[a]	monomer	M_n (g/mol)[a]	CHO	yield	PDI
norbornene	20 200	styrene	15100	0.7	>0.95	1.04
ethylidene norbornene	29 200	styrene	1360	1.0	>0.95	1.07
norbornene	20 800	isoprene	16900	5.0	0.45[b]	1.03[b]
cyclopentene	11 300	styrene	1360	34.0	>0.95	1.06
cyclopentene	13 700	styrene	1360	0.4[c]	0.55[b]	1.08[b]

[a] Determined by SEC using $r_b = 2.20$ for polynorbornene, 2.11 for poly(ethylidene norbornene), 2.00 for polycyclopentene, and 1.62 for polyisoprene. [b] Value obtained by deconvoluting the reaction mixture SEC trace rather than by fractionation. [c] 92 additional equiv of PMe_3 added immediately prior to termination with PSA.

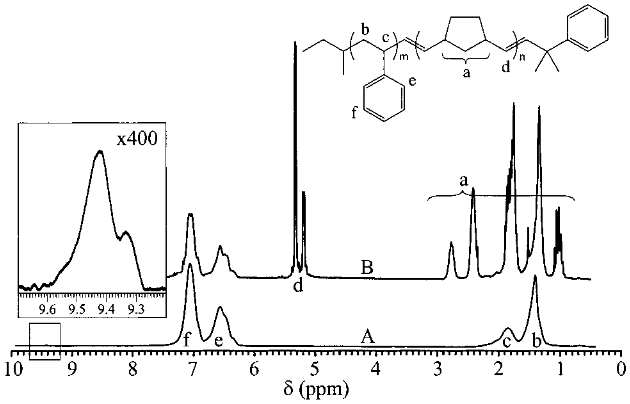

Figure 1. ^{1}H NMR of polystyrene−aldehyde (A) and polynorbornene-*block*-polystyrene (B), indicating 38 wt % polystyrene in (B). Inset shows signal from single aldehyde proton in (A).

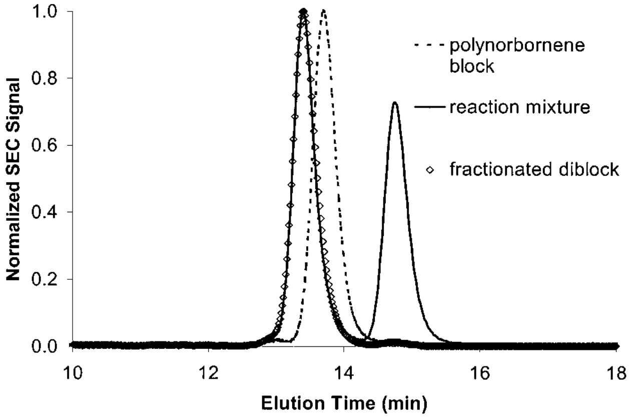

Figure 2. SEC traces for polynorbornene-*block*-polystyrene (38 wt % polystyrene by ^{1}H NMR). Diblock is well-resolved from the polynorbornene block, indicating essentially complete conversion of ROMP block to diblock.

through the attendant color loss, was complete within minutes. Several milliliters of degassed methanol was added with vigorous stirring to liberate the polymeric aldehyde. Reprecipitation and vacuum-drying yielded a white, glassy polystyrene−aldehyde (PSA) or a clear, viscous polyisoprene−aldehyde (PIA). All PSA and PIA possessed polydispersity indices (PDI) ≤ 1.12. True number-average molecular weights (M_n) were determined by size-exclusion chromatography (SEC) in toluene with refractive index detection, using hydrodynamic volume correction factors r_b (vs polystyrene) determined as described previously[14] and given in Table 1. ^{1}H NMR indicated >80% aldehyde functionalization in all cases. The ^{1}H NMR spectrum of a representative PSA is shown in Figure 1A. The PSA aldehyde protons appeared as two rotational isomers at 9.42 and 9.33 ppm, while the PSA carbonyl stretch was evident by FTIR at 1724 cm^{-1}. The spectra of PIA bore several signals in the regions of interest due to the complex chemistry of the chain end, as discussed below. PSA and PIA were stored at 0 °C for up to 2 months with no degradation apparent by SEC.

PSA and PIA were then used as macroterminators to form near-monodisperse diblocks with polynorbornene, poly(ethylidene norbornene),[15] and polycyclopentene. All metathesis polymerizations were run under drybox conditions using 2,6-diisopropylphenylimidoneophylidenemolybdenum(VI) bis(*tert*-butoxide) ([Mo]) as the catalyst. A 5:1 molar ratio of trimethylphosphine (PMe_3) to [Mo], needed to slow propagation in the cyclopentene polymerization,[16] was added in all cases for consistency. After 1 h reaction, an aliquot was removed and terminated with 100 equiv of benzaldehyde or propionaldehyde to permit determination of the ROMP block's M_n and PDI. The desired polymeric aldehyde was degassed and added to the remaining ROMP reaction mixture to form the diblock, as per Scheme 1. After 24 h, the reaction mixture was exposed to the atmosphere, thereby coupling any unterminated ROMP chains.[17] For cases where block copolymer and coupled ROMP polymer were expected to elute at similar times in the SEC trace, 100 equiv of benzaldehyde was instead added after 24 h. The resulting polymer was isolated by precipitation and in some cases fractionated in toluene/methanol to remove excess polymeric aldehyde and yield essentially pure diblock. Table 1 lists results for five ROMP−anionic diblock syntheses, where "diblock yield" is the fraction of ROMP block (present in stoichiometric deficiency) converted to diblock. The ^{1}H NMR spectrum of a representative polystyrene−polynorbornene diblock is shown in Figure 1B; the aldehyde resonances present in the spectrum for PSA were entirely absent.

Figure 2 illustrates typical SEC traces obtained for the polystyrene-containing block copolymers. The shift of the major peak to shorter elution time relative to the first block indicated successful block copolymer formation. In many cases, no detectable uncoupled ROMP block (<5%) remained after reaction with the polymeric aldehyde. Table 1 illustrates the ability to form either near-symmetric (40 wt % polystyrene) or very asymmetric (3 wt % polystyrene) diblocks from styrene and norbornene derivatives, all with low polydispersities, using modest excesses of macroterminator. After fractionation, ^{1}H NMR yielded a composition within 5% of the value predicted from the block M_n determined independently.

Polyisoprenes exhibited less efficient diblock formation (Table 1) and were far more prone to undergo side reactions during the aldehyde functionalization. These differences reflect the chemistry of the chain end; after functionalization, polyisoprene contains a β,γ unsaturation and a labile α proton that can rearrange to an α,β

unsaturation conjugated with the carbonyl. PIA aldehyde protons appeared at 10.12 ppm with secondary signals at 10.02 and 9.83 ppm, suggesting the conjugated 4,1, conjugated 4,3, and unconjugated 4,1 regioisomers, respectively. Similarly, the FTIR spectra of low-M_n PIA showed an unconjugated carbonyl stretch at 1723 cm^{-1} and a conjugated carbonyl stretch at 1669 cm^{-1} superimposed on the trans-4,1 olefinic stretch. Aldehyde functionalization of polyisoprene was inhibited by oxygen; drybox conditions and freshly degassed methanol were required to prevent chain coupling. All coupled products were brightly colored and had UV absorbances near 300 nm, suggesting an aldol condensation and subsequent dehydration to produce extended conjugation, though this undesired side reaction was not explored in detail. The lower conversion to block copolymer exhibited by PIA vs PSA was likely due to the relative stability of the conjugated PIA aldehyde as compared with the unconjugated PSA aldehyde. This problem could be circumvented by adding sufficient styrene to cap each isoprene chain with at least one unit prior to the addition of NFM. Capping the ends with 1,l-diphenylethylene produced an anion only poorly reactive toward NFM and a polymeric aldehyde that did not couple successfully with the ROMP chains.

Unlike the bicyclic olefins, cyclopentene exhibits a substantial monomer−polymer equilibrium, so polymerization was terminated well before equilibrium was approached to maintain low polydispersity.[16] For polycyclopentene, the above procedure was modified to encourage diblock formation over continued polymerization. The addition of large excesses (34 equiv) of low-M_n PSA (see Table 1) allowed for complete conversion of the ROMP precursor without broadening of the molecular weight distribution due to continued cyclopentene polymerization. Alternatively, adding 92 equiv of PMe_3 relative to [Mo] after the polycyclopentene reached the desired M_n greatly slowed polymerization[16] but still permitted reaction of the [Mo] active sites with the aldehyde. This timed addition of PMe_3 thus provides a viable route to cyclopentene-containing diblocks with high polystyrene weight fractions, which would otherwise require impracticably large PSA excesses.

This procedure represents a viable and facile method for the synthesis of ROMP−anionic diblock copolymers and should be extendable to other monomers not considered here. In this preliminary study, we used substantial excesses of polymeric aldehyde to promote prompt and complete ROMP termination, requiring subsequent fractionation to isolate pure diblock. Aldehyde excess could be reduced or eliminated through optimization of reaction conditions or by using ROMP catalysts based on tungsten or titanium,[11] which are known to react more rapidly with aldehydes[18] than does the Mo-based catalyst employed here. Because no labile linkages are introduced in coupling the two blocks together, ROMP−anionic diblocks synthesized by this method could be hydrogenated without chain scission. At room temperature, hydrogenated polycyclopentene (structurally identical to linear polyethylene[16]) and hydrogenated polynorbornene[19] are crystalline, hydrogenated polyisoprene[20] and hydrogenated poly(ethylidene norbornene)[16] are saturated rubbers, and polystyrene and hydrogenated polystyrene[21] are glasses. Thus, a substantial diversity of properties is obtainable even from the small monomer set we have explored here.

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