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ARTICLE

Branched Poly(phenylacetylene)

Marta Angoy,[†] M. Isabel Bartolomé,[†] Eugenio Vispe,[†] Petr Lebeda,[‡] M. Victoria Jiménez,*,[†] Jesús J. Pérez-Torrente,[†] Scott Collins,*,[†,⊥] and Stepan Podzimek[‡,§]

[†]*Departamento de Química Inorgánica, Instituto Universitario de Catálisis Homogénea, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain,* [‡]*Department of Polymer Materials, University of Chemical Technology, Pardubice, Czech Republic, and* [§]*SYNPO, S. K. Neumanna 1316, 532 07 Pardubice, Czech Republic.* [⊥]*Present address: 739 Champagne Dr. Cobble Hill, BC V0R 1L4, Canada.*

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ABSTRACT: Characterization of poly(phenylacetylene) (PPA) samples produced using Rh(I) complexes featuring hemilabile phosphine ligands by size exclusion chromatography, multiangle light scattering (SEC-MALS), or asymmetric flow field flow fractionation (A4F)-MALS has revealed that some of these PPA samples contain a mixture of linear and branched polymer. The occurrence and extent of branching is dependent on both catalyst structure and polymerization conditions. The levels of branching are consistent with either terminal branching through copolymerization of macromonomer or chain transfer to polymer, where the branched species are less reactive toward further polymerization than the linear chains. The MM dependence of B, the number of branches per molecule, or λ, the number of branches per 1000 repeat units, suggests that the latter explanation may be correct, but further work is needed.

Introduction

Branched polymers, especially hyperbranched materials, possess significantly different physical properties from their linear isomers, including lower solution or melt viscosity, solubility, etc.[1] These materials find increasing utility as additives for polymer processing, surface coatings, and materials for encapsulation and drug delivery. Hyperbranched materials are generally produced by step growth (co)polymerization of AB_n ($n \geq 2$) type monomers or controlled chain growth (co)polymerization involving di- or polyfunctional monomers at conversions below the gel point. Another distinctly different approach involves chain walking, ethylene insertion polymerization using late transition metal, particularly Pd−α-diimine, catalysts.[2] Chain transfer to polymer, as occurs in the free-radical-initiated polymerization of *inter alia* ethylene or vinyl acetate, leads to material containing linear, short-chain, and long-chain branched material,[3] with the largest macromolecules typically possessing the most long-chain branching.[4] It is also possible to prepare polymers with sparse to dense branching through copolymerization of terminally unsaturated macromonomers with monomer; this process occurs *in situ* during ethylene polymerization using e.g. constrained geometry catalysts.[5]

Poly(phenylacetylene) (PPA), prepared by transition-metal-mediated polymerization of phenylacetylene (PA), is an example of a polymer displaying electrical conducting properties.[6] PPA is soluble in common organic solvents, is stable in air, and displays semiconductor properties. The conductivity strongly depends on the *cis*/*trans* content of the polymer; the conductivity of the *all-trans* polymer is about 10^{10} greater than the *all-cis* polymer.[7] In addition to electrical conductivity, other physical properties such as photoconductivity, optical nonlinearity, liquid crystallinity, gas-selective permeability, or magnetic susceptibility could also be of special importance in such materials.[8]

Several transition-metal-based catalysts for the polymerization of substituted acetylenes have been described; examples include Ziegler catalysts,[9] classical group 5 or 6 metathesis polymerization catalysts,[10] or well-defined Schrock-type carbene complexes.[11] Although there are several initiators that induce stereospecific living polymerization of polyacetylenes,[12] in general, the reactions are not stereoselective and give mixture of *cis* and *trans* polymers.[13] The reactivity of rhodium(I) complexes toward arylacetylenes includes dimerization, cyclization, and oligomerization, depending on both the structure of the acetylene and the reaction conditions.[14] Of particular note, rhodium catalysts are also efficient for the polymerization of monosubstituted acetylenes with formation of highly stereoregular polymers, in some cases in a living manner.[15]

Catalysts include cationic rhodium(I) complexes $[Rh(cod)(N{-}N)]^+$ (N−N = bipy, phen), in the presence of a strong base, such as NaOH,[16] or others such as $[Rh(Tp^{R2})(cod)]^+$ (Tp^{R2}; Tp = tris(pyrazolyl)borate, R = Me, Ph, *i*-Pr),[17] and $[Rh(diene)\{(\eta^6\text{-}C_6H_5)BPh_3\}]$ (diene = cod,[18a] nbd[18b]) where a base is not required. Noyori and co-workers reported the living polymerization of PA using the complex $[Rh(C{\equiv}CPh)(nbd)(PPh_3)_2]$ or the system $[Rh(\mu\text{-OMe})(nbd)]_2/PPh_3$ in the presence of DMAP.[19] Living polymerization was also achieved using the multicomponent initiator system $[Rh(\mu\text{-Cl})(nbd)]_2/Ph_2C{=}CPhLi/PPh_3$,[20] and the vinyl complexes $[Rh\{C(Ph){=}CPh_2\}(diene)\{PR_3\}]$.[21,22] We recently reported polymerization studies of PA employing Rh(I) complexes **1**−**5** (Chart 1) with hemilabile phosphine ligands; very high molar mass (MM) PPA was produced at high conversion, and in the presence of DMAP some of these catalysts polymerize PA in a quasi-living manner.[23]

All of these rhodium(I) catalysts are thought to provide linear polymer, and though there has been the suggestion of branching in PPA, prepared using other catalysts,[24] to the best of our knowledge, the occurrence of branching in PPA has never been documented. We now report the formation of branched poly(phenylacetylene) using Rh(I) initiators bearing hemilabile phosphine ligands. The occurrence and extent of branching are dependent on both catalyst structure and polymerization conditions.

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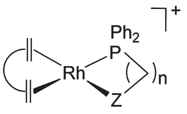
*Corresponding authors. E-mail: vjimenez@unizar.es (M.V.J.); scottcollins@shaw.ca (S.C.).

Results

The initial detection of branching in these materials resulted from some reanalyses of older samples, prepared in connection with recently published work,[23] using a SEC system equipped with a miniDAWN three angle, light-scattering, and Optilab refractive index detectors.[25] At first, it was thought that these sensitive materials[26] might have e.g. cross-linked on exposure to air for long periods of time in the bulk state, but repetition of several polymerization experiments involving different conditions and catalysts, eventually revealed that branched material was being produced during polymerization but not to the same extent by all catalysts or under all conditions.

Specifically, rhodium complex [(nbd)Rh{$PPh_2(CH_2)_3NMe_2$}]-[BF_4] (**1**), or its (tetrafluorobenzo)bicyclo[2.2.2]octadiene (tfb) analogue **2**, polymerized PA in dry THF or toluene to produce high-MM polymer which possessed a unimodal molar mass distribution (MMD) as indicated by refractive index or light-scattering detectors (M_w = 2.18 × 10^6, PDI = 2.00; Figure 1). It should be noted that these conjugated PPA materials interact strongly with the column packing, this was evident from tailing intensity on the light-scattering detectors well beyond the low-MM exclusion limit of the column set (three, PLGel Mixed B, 10 μm columns) as well as the increase in MM and r_g with elution volume evident at long elution volumes (Figure 1). This interaction can be due to simple enthalpic adsorption or to anchoring of randomly branched macromolecules in the mesopores; the two effects are difficult to separate.[27] Because of this interaction, the PDI values based on the SEC analyses are not accurate though they do correlate with the breadth of these distributions.

Chart 1



Compound	diene	n	Z
1	nbd	3	NMe_2
2	tfb	3	NMe_2
3	cod	2	OMe
4	cod	3	OMe
5	cod	3	NMe_2

As shown in Figure 1, the light-scattering detector revealed detectable increases in MM on the high-MM shoulder of the main peak (Figure 1a) and lesser increases in the radius of gyration (r_g) over the same elution volume (Figure 1b; note the logarithmic scale for MM and r_g), consistent with the presence of branched material. A log−log plot of r_g vs MM revealed significant deviations from linear behavior in the high molar mass region (Figure 2a) consistent with branching. Interaction of PPA with the column packing accounts for the curious shape of the conformation plot (Figure 2a) in the low molar mass region, since the radius (which is sensitive to the z-average MM) vs mass (which is sensitive to the w-average MM) behavior is somewhat different at longer elution volumes (Figure 1).

Analysis of this sample by A4F-MALS confirmed the initial SEC-MALS results. Since there is no column packing for the sample to interact with, a normal conformation plot was obtained where deviation from linearity is evident at higher molar mass (Figure 2b), consistent with the presence of branching.[27] Polymerizations in the presence of radical scavengers like BHT did not hinder branch formation (nor polymerization), suggesting that free-radical-induced branching was not responsible for this behavior.

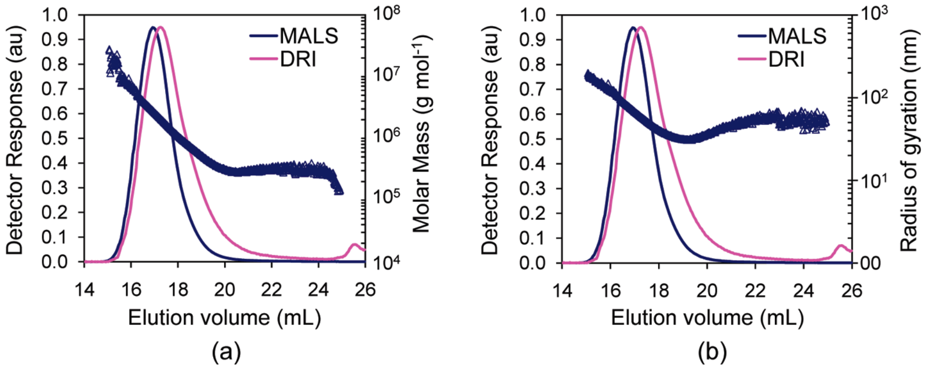


Figure 1. Light scattering (blue) and refractive index (magenta) chromatograms: (a) MM and (b) r_g vs elution volume (mL) plots for a PPA sample prepared using [(nbd)Rh{$PPh_2(CH_2)_3NMe_2$}][BF_4] (**1**) in dry THF.

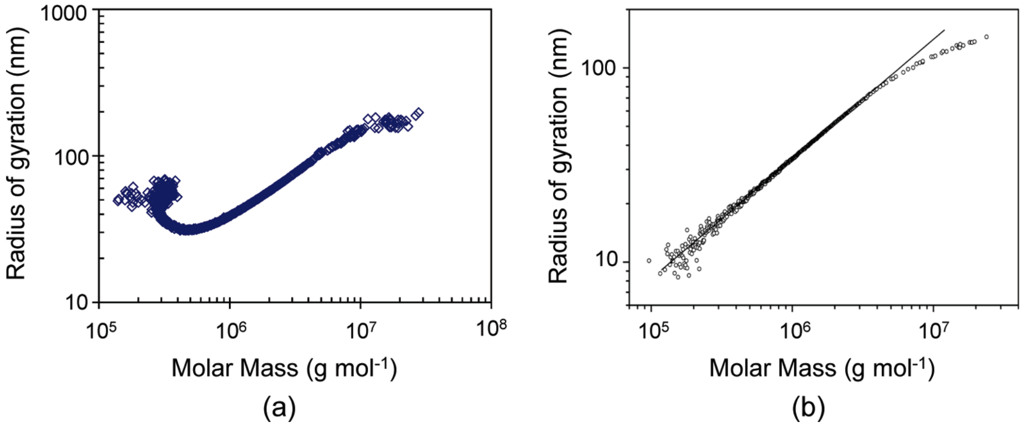


Figure 2. Log−log plots of r_g vs MM for a PPA sample prepared using complex **1** in THF analyzed by (a) SEC-MALS and (b) A4F-MALS. The slope of the linear portion of the latter plot is m = 0.60.[28]

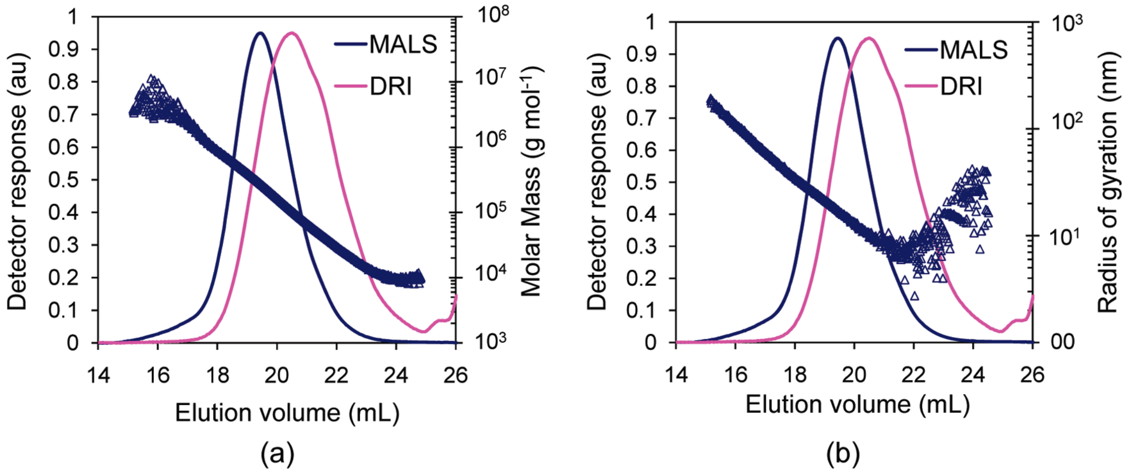


Figure 3. Light scattering (blue) and refractive index (magenta) chromatograms: (a) MM and (b) r_g vs elution volume (mL) plots for a PPA sample prepared using [(cod)Rh{PPh$_2$(CH$_2$)$_2$OMe}][BF$_4$] (**3**) in dry THF.

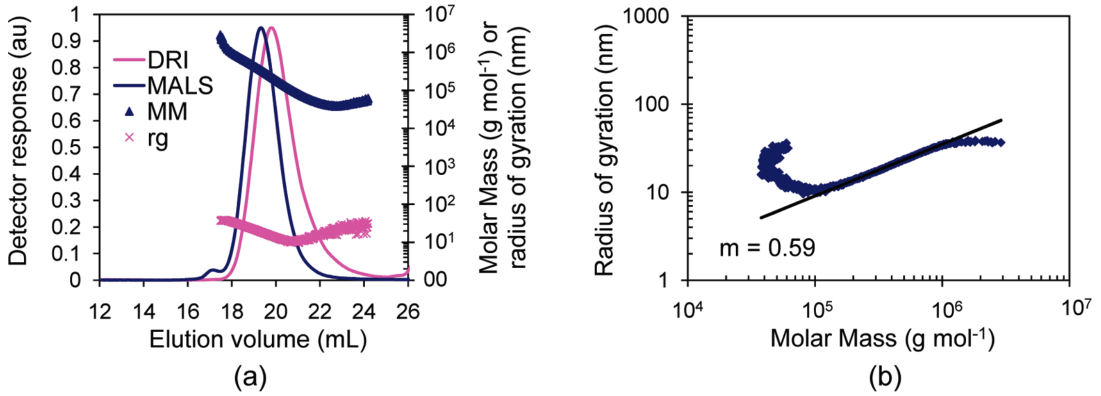


Figure 4. (a) Light scattering (blue) and refractive index (magenta) chromatograms, MM (blue ▲) and r_g (magenta ×) vs elution volume (mL) plot for a PPA sample prepared using [(cod)Rh{PPh$_2$(CH$_2$)$_3$NMe$_2$}][BF$_4$] (**5**) in dry THF. (b) Log−log plot of r_g vs MM for this sample.[28]

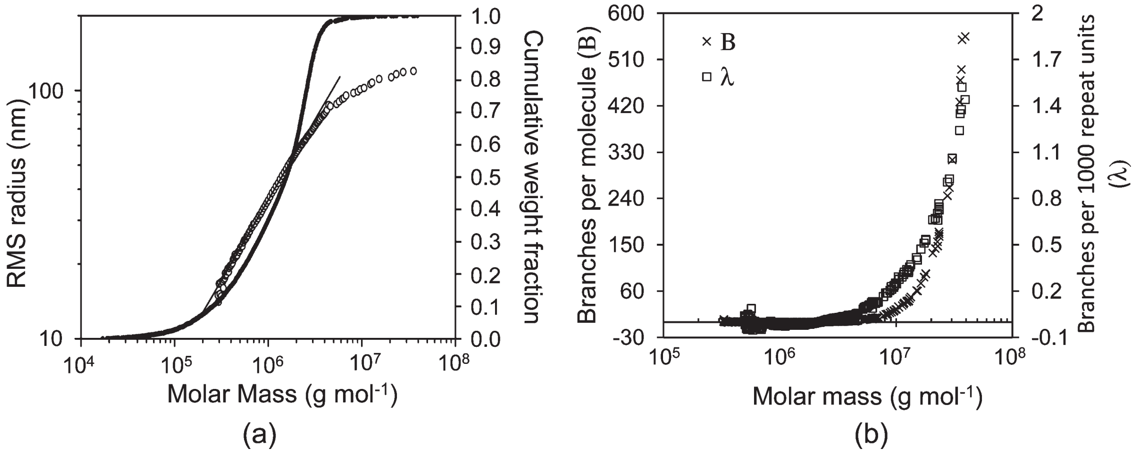
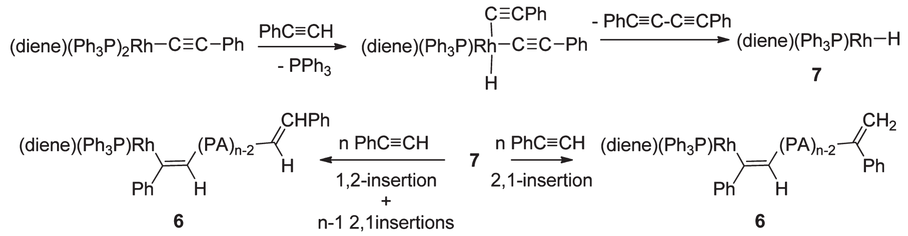


Figure 5. (a) Radius of gyration (○) and cumulative weight fraction of polymer (●) vs molar mass obtained from A4F data for a PPA sample prepared using catalyst **1** in toluene. The line represents a linear fit to the data in the range of 22−56 nm: $r_g = 0.00488 \times \mathrm{MM}^{0.645}$ (THF, 25 °C).[28] (b) Branching frequencies per macromolecule (B, ×) and per 1000 repeat units (λ, □) vs MM for this same sample.

Different behavior was observed for PPA samples prepared using [(cod)Rh{PPh$_2$(CH$_2$)$_2$OMe}][BF$_4$] (**3**) or [(cod)Rh{PPh$_2$(CH$_2$)$_3$OMe}][BF$_4$] (**4**), namely the production of linear PPA of lower MM ($M_w = 1.53 \times 10^5$, PDI = 3.09; Figure 3). Here, however, light scattering revealed the presence of a second trace component ($\ll$1 wt % based on DRI intensity) of higher MM which also appeared linear over the elution volume ranges where both MALS and DRI detectors had detectable intensity.[29]

Finally, the last catalyst investigated [(cod)Rh{PPh$_2$(CH$_2$)$_3$NMe$_2$}][BF$_4$] (**5**) also afforded PPA with a bimodal MMD by SEC-MALS ($M_w = 2.38 \times 10^5$, PDI = 1.79).[30] Both components appeared linear where both were reliably detected by DRI and MALS,[29] though as with samples prepared using catalysts

Scheme 1



1 or 2, formation of branched material could be detected at highest MM (Figure 4b).

Determination of the branching ratio $g = (r_g^{br})^2/(r_g^{lin})^2$ for these materials by SEC-MALS is complicated by interaction of these materials with the column packing. Essentially $g > 1$ for materials that interact with the column packing and elute at longer elution volumes, a spurious result. Thus, an accurate determination of either average branching frequency per macromolecule ($\bar{B}$) or branching per 1000 repeat units ($\bar{\lambda}$) or the dependency of these variables on MM is not possible.

On the other hand, analysis by A4F removes this complication. Branching frequencies of a PPA sample prepared using catalyst **1** in dry toluene ($M_w = 1.73 \times 10^6$, PDI = 3.1 by A4F; Figure 5) were calculated from the Zimm−Stockmayer equation,[31] assuming trifunctional branching and monodisperse slices. These analyses indicated that the average branching frequencies per molecule and per 1000 repeat units were $\bar{B} = 0.86$ and $\bar{\lambda} = 0.051$, respectively. This level of branching is consistent with either terminal branching (via copolymerization of unsaturated macromonomer) or chain transfer to polymer, wherein the branched, propagating species are less reactive than linear chains toward further propagation. The abrupt change in B or λ vs MM (Figure 5b) is more consistent with chain transfer to polymer in that the largest, most highly branched macromolecules are statistically more prone to grow further via this process.[4,5]

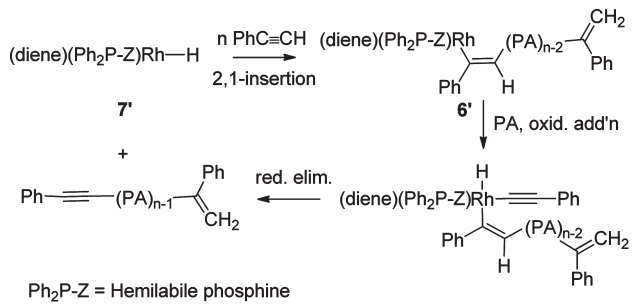
Discussion

There is little doubt as to the nature of the resting state in Rh(I)-mediated PA polymerizations using [(diene)Rh(L)$_n$X] complexes (n = 1, 2; X = halide, C≡CPh, CPh=CPh$_2$, L = PR$_3$, etc.), thanks to the pioneering work of Noyori and co-workers, where an intermediate analogous to **6** was isolated and shown to be competent for polymerization (Scheme 1).[19] In the case of Noyori's catalyst, complex **6** was envisaged to form via insertion of PA into Rh−H complex **7**, formed via reductive elimination of PhC≡C−C≡CPh, where 1 equiv of this diyne is formed per equiv of living chain.

As shown in Scheme 1, this would result in the formation of a living chain **6** with either a *cis*/*trans*-vinylene or vinylidene end group, depending on the initial regiochemistry of PA insertion into Rh−H. In the absence of DMAP which renders this process living, there is much less known about the *chain transfer* processes with these catalysts due to the high MW of the polymers typically formed; specifically, the identity of the end groups in the polymer chains, formed via chain transfer, is not known.

Synthesis of sufficiently low-MW polymer to conclusively identify end groups in our materials (using e.g. MALDI-TOF mass spectrometry) was precluded by the low initiator efficiency characteristic of these catalysts;[23] even at low monomer to catalyst ratios of 5:1 $X_n > 500$ for these materials. In the ^{1}H NMR spectrum of some PPA samples prepared using complex **4** ($X_n \sim 620$), we were able to detect olefinic signals at δ 6.08 and 5.74 ppm, both doublets with J = 1.1 Hz, which are assigned to 1,3,5-triphenyl-1,3-cyclohexadienyl groups present at levels of ca. 1.5 mol %.[26] No other (end) groups could be reliably detected.

Scheme 2



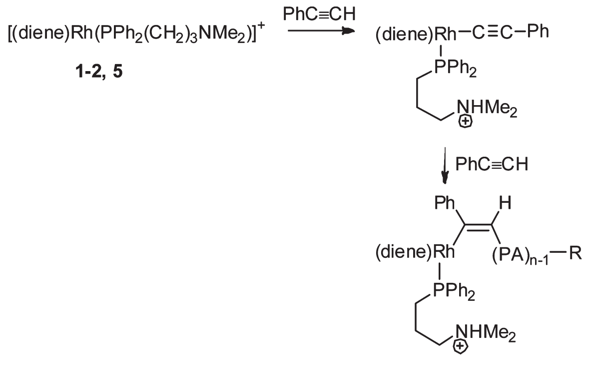
In the case of [(nbd)(Ph$_3$P)$_2$RhC≡CPh] or [(cod)RhCl]$_2$/NEt$_3$, it would appear that Rh(I)-mediated dimerization or trimerization of PA to provide rhodacyclopentadienyl[19] or hydropentalenylrhodium complexes[32] are examples of catalyst deactivation reactions that are inhibited in the presence of DMAP or sufficient quantities of PA. It is unclear that these reactions are relevant to chain transfer.

Synthesis of PA oligomers ($X_n < 15$) using TiO$_2$ supported on silica[33] or using Ni−acetylide complexes[34] has indicated that these materials have vinylidene (CH$_2$=CPh−) and acetylene (−C≡CPh) end groups. Depending on the mechanism of initiation (e.g., insertion of PA into Ni−C≡CR[34] vs insertion of PA into Ti−H[33]) and chain transfer (e.g., protonolysis of the chain end by PA to produce CH$_2$=CPh−PPA[34] or β-H elimination in the case of Ti to produce PPA−C≡CPh[33]), these *same* groups are envisaged to form in different ways. Electrocyclization of the chain-end (Cope rearrangement)[26] so as to generate either 1,3,5- or 1,2,4-triphenylbenzene byproduct[33,34] has also been suggested as a process involved in chain transfer.

On the basis of Noyori's mechanistic work, chain transfer to PA (via protonolysis of the chain end[34] or formal oxidative addition, reductive elimination) could involve formation of either vinylene or vinylidene end groups depending on the regiochemistry of PA insertion prior to chain transfer. The problem with this scenario is that it presumes that subsequent PA insertion into Rh−C≡CPh is efficient, a process known to be difficult and/or inefficient in the initiators investigated by Noyori and co-workers.[19] A more appealing alternative involves formation of Rh−H complex **7**′, accompanied by reductive elimination of ene−yne functionality (Scheme 2).

The macromonomer formed as a result of this process has terminal R$_2$C=CH$_2$ or R−C≡C−R′ functionality, which might be susceptible to copolymerization leading to terminal branching. Alternately, the Rh−H complex **7**′ could react at *any* interior C=C bond of *any* macromolecule to form a π-allyl complex. This might propagate further (via the σ-allyl), leading to branch formation. Consistent with either possible process, lower MM PPA prepared using catalyst **5** was partially consumed in a subsequent reaction involving catalyst **1** and additional monomer; the PPA isolated was composed of higher MW polymer than a blend of similar composition, with increases in the extent of branching (see Supporting Information).

Scheme 3



The susceptibility toward branch formation is obviously catalyst dependent. Complexes such as **1** and **5** are known to react with PA to afford complexes in which the hemilabile ligand is protonated at N (Scheme 3)[23] and thus monodentate, whereas those such as **3** can equilibrate between chelated bi- and monodentate forms. We do note that catalysts systems devoid of phosphine donor ligands (e.g., [(nbd)Rh-η^6-C_6H_5-BPh_3] or $[(nbd)Rh(NCCH_3)_2][BF_4]$) produce linear polymer in THF while branched (and linear) material was slowly formed using $[(cod)Rh(PPh_3)_2][BF_4]$ under the same conditions. Further work will focus on studying those factors which influence the formation of linear vs branched material and elucidating the mechanism of branch formation in these materials.

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Supporting Information Available: Experimental details and tables of MM averages for PPA samples prepared, SEC and A4F chromatograms, plots of MM and r_g vs elution volume for all PPA samples analyzed; details for separation and analyses of these materials by A4F; NMR spectra of PPA. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) For degradation of PPA in solution and the bulk state see: Percec, V.; Rudick, J. G. *Macromolecules* **2005**, *38*, 7241–7250.

(27) See: Podzimek, S.; Vlcek, T.; Johann, C. *J. Appl. Polym. Sci.* **2001**, *81*, 1588–1594 and references therein .

(28) It should be noted that the slope of the linear portions of these conformation plots varied between 0.55 and 0.65 in THF solution. Normally, one would expect a slope of ca. 0.58 for a linear polymer in a good solvent. We suspect the variation reflects the complexity of PPA behavior seen in dilute solution where both mass and size can be time and solvent dependent, reflecting *s-trans* to *s-cis* isomerization accompanied by changes to solvent−polymer and polymer−polymer interactions. See: Cametti, C.; Codastefano, P.; D'Amato, R.; Furlani, A.; Russo, M. V. *Synth. Met.* **2000**, *114*, 173–179.

(29) Since the MALS detector signal is divided by the signal from the DRI detector to produce a signal proportional to molar mass, large and systematic errors can be expected whenever the former signal is

nonzero and the latter signal very close to zero and/or dominated by noise.

(30) The origins of these bimodal MMD are not known. Evidently, there are two species that independently propagate, but since the relative amounts did not obviously correlate with the experimental conditions (solvent, *T*, or presence of water), it is a matter of speculation as to what the two species may be.

(31) See Supporting Information for details: Zimm, B. H.; Stockmayer, W. H. *J. Chem. Phys.* **1949**, *17*, 1301–1314.

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(33) Kumar, V. G.; Shoba, T. S.; Bao, K. V. C. *Tetrahedron Lett.* **1985**, *26*, 6245–6248.

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