

Supporting Information for:

**Single-End-Functionalized Polycyclopentene via Ring-Opening
Metathesis Polymerization with Concurrent Chain Transfer**

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Derivation and Discussion of Equation 1

Consider the case of a reversible living polymerization, with instantaneous monomer concentration $[M]$, and an active site (living end) concentration $[S^*]$ which is constant from initiation to termination. The total number of monomers enchainned by an active site between initiation and termination (kinetic chain length) is denoted by ν , and is equal to $\alpha[M]_0/[S^*]$, where α is the fractional monomer conversion at termination; $[M]_0$ is the initial monomer concentration. At low conversions, the initial rate approximation applies:

$$\begin{aligned} \text{at low } \alpha: \quad \nu &= t(R_{p,0})/[S^*] = t(-d[M]/dt)/[S^*] = t(k_p[M]_0[S^*] - k_{-p}[S^*])/[S^*] \\ &= t(k_p[M]_0 - k_{-p}) = tk_p([M]_0 - [M]_{eq}) \end{aligned} \quad (S1)$$

where t is the time between initiation and termination, $R_{p,0}$ is the initial rate of polymerization, and k_p and k_{-p} are the rate constants for propagation and depropagation; $k_{-p}/k_p = [M]_{eq}$, the equilibrium monomer concentration. In the absence of chain transfer, and with simple

termination (one active site producing one “dead” chain, no coupling), the number-average degree of polymerization $x_{n,0} = \nu$ (living polymerization).

In the presence of chain transfer, x_n is simply given by the ratio of the net propagation rate (including depropagation) to the rate of events which terminate physical chains (*i.e.*, chain transfer, plus active site termination at the end of the polymerization). In the low- α regime (initial rate approximation), the net propagation rate is $R_{p,0} = k_p([M]_0 - [M]_{eq})[S^*]$. The rate of chain transfer is given by:

$$R_{tr} = k_{tr}[CTA][S^*] = C_T k_p [CTA][S^*] \quad (S2)$$

In the low- α regime (initial rate approximation), $[CTA]$ is considered constant ($= [CTA]_0$), so R_{tr} is also constant. The “rate” of termination R_{term} is simply $[S^*]/t$, as all active sites are terminated at time t . Thus:

$$\begin{aligned} x_n &= R_{p,0} / \{R_{term} + R_{tr}\} = k_p([M]_0 - [M]_{eq})[S^*] / \{([S^*]/t) + C_T k_p [CTA][S^*]\} \\ &= k_p([M]_0 - [M]_{eq}) / \{(1/t) + C_T k_p [CTA]\} \end{aligned} \quad (S3)$$

But t is simply related to ν through equation S1, yielding:

$$x_n = k_p([M]_0 - [M]_{eq}) / \{(k_p([M]_0 - [M]_{eq})/\nu) + C_T k_p [CTA]\} \quad (S4)$$

whose reciprocal is:

$$\begin{aligned} 1/x_n &= \{(k_p([M]_0 - [M]_{eq})/\nu) + C_T k_p [CTA]\} / k_p([M]_0 - [M]_{eq}) \\ &= 1/\nu + C_T [CTA] / ([M]_0 - [M]_{eq}) \end{aligned} \quad (S5)$$

Since $x_{n,0} = \nu$, and $[M] = [M]_0$ and $[CTA] = [CTA]_0$ at low α , equation S5 is identical to the Article’s equation 1. When $[M]_{eq} \approx 0$ —as is the case for many monomers, but not CP—equation 1 reduces to the commonly-presented form,¹ where the second term is simply $C_T [CTA] / [M]$.

Thus, equation 1 is identical to the classic expression derived² for pseudo-steady-state (*e.g.*, free radical) polymerization, but for very different reasons. In the pseudo-steady-state case, the

termination rate is given by the destruction rate of the active sites (*e.g.*, bimolecular reaction of radicals), or equivalently, the rate of generation of active sites, as these are equal at pseudo-steady-state. Equation 1 is valid instantaneously for *any* conversion α , and $x_{n,0}$ can differ from v depending on the termination mechanism (*e.g.*, $x_{n,0} = 2v$ for termination by coupling two growing chains). In the living case, equation 1 is valid only for low conversions (*i.e.*, it is strictly valid instantaneously at $\alpha \approx 0$), and relies on $v = x_{n,0}$ (*i.e.*, that the termination reaction proceeds without coupling) as a way to determine v . Put differently, the proper quantity to use as the first term on the right-hand side of equation 1 is $1/x_{n,0}$ for pseudo-steady-state polymerizations (even if $x_{n,0} \neq v$), while $1/v$ is the proper quantity to use for living polymerizations taken to low conversion. Happily, the two are identical for the case considered here (termination of living CP ROMP by propionaldehyde).

Also, the application of equation 1 is different between the pseudo-steady-state and living cases. In the pseudo-steady-state case, $x_{n,0}$ is held constant (corresponding to a particular set of reaction conditions) and $[CTA]$ is varied; C_T is thus extracted as the slope (divided by $[M] - [M]_{eq}$) in a plot of $1/x_n$ vs. $[CTA]$, with $1/x_{n,0}$ as the intercept. But in the living case, $x_{n,0}$ increases progressively with time and conversion; C_T is then extracted from the intercept (divided by $[CTA]/([M] - [M]_{eq})$) in a plot of $1/x_n$ vs. $1/x_{n,0}$ (with x_n and $x_{n,0}$ corresponding to identical times, hence identical conversions), and the slope is simply unity.

Note that the above discussion implicitly assumes that reinitiation is rapid, and thus that $R_{p,0}$ and v are unaffected by added CTA (as used implicitly to reach equation S3). This appears to be the case for ROMP of CP with the initiator and CTAs employed in this work, although direct measurements of α were not made. Slow reinitiation would affect R_p and R_{tr} identically, but equation S3 would still be affected because v would no longer be identical in the “no-CTA” and

“added-CTA” cases. In the case of slow reinitiation, then, equation 1 will overestimate C_T (because $1/x_{n,0}$ for the no-CTA case is less than $1/v$ for the added-CTA case).

Validity of Equation 1 with Reversibly-Binding Ligand

An additional consideration for the living ROMP of CP is that a reversibly-binding ligand, PMe_3 , is added to slow initiation relative to propagation and narrow the MWD in the no-CTA case.^{3,4} It has previously been shown⁵ that propagation and depropagation occur only from unbound sites, in which case equation S1 is unaffected: the added PMe_3 simply means that $[\text{S}^*]$ is less than $[\text{Mo}]$, as only a fraction of active sites are unbound at any instant, but $[\text{S}^*]$ is still constant throughout the polymerization so equation S1 is still valid. However, for equation S5 (equation 1) to be valid also requires that chain transfer occurs only to unbound sites, so that $[\text{S}^*]$ is the same for propagation/depropagation and transfer. To confirm this, we conducted polymerizations at two different ratios of PMe_3 :Mo (5:1 and 15:1), as increasing this ratio (at constant $[\text{Mo}]$) decreases the fraction of Mo which are unbound nearly proportionally.^{4,5} For these polymerizations, we employed 1-pentene, which is known to be a highly efficient CTA in the ROMP of CP with this initiator.⁵

Results presented in the form of equation 1 (and Figure 3) are shown for 1-pentene in Figure S1. From the intercepts, a value of $C_T = 0.65 \pm 0.01$ (one standard deviation of the fit) is obtained at 5:1 PMe_3 :Mo, and $C_T = 0.66 \pm 0.01$ at 15:1 PMe_3 :Mo. The constancy of the extracted C_T as PMe_3 :Mo is varied confirms that bound $[\text{Mo}]$ sites are inactive for chain transfer. Note that under the reaction conditions employed here, the fraction of unbound $[\text{Mo}]$ is of order 1% ($\approx 1.5\%$ at 5:1 PMe_3 :Mo, and $\approx 0.5\%$ at 15:1 PMe_3 :Mo), so any significant reactivity of the

remaining bound $\approx 99\%$ of the Mo sites would be immediately evident as a variation of the apparent C_T with $\text{PMe}_3:\text{Mo}$.

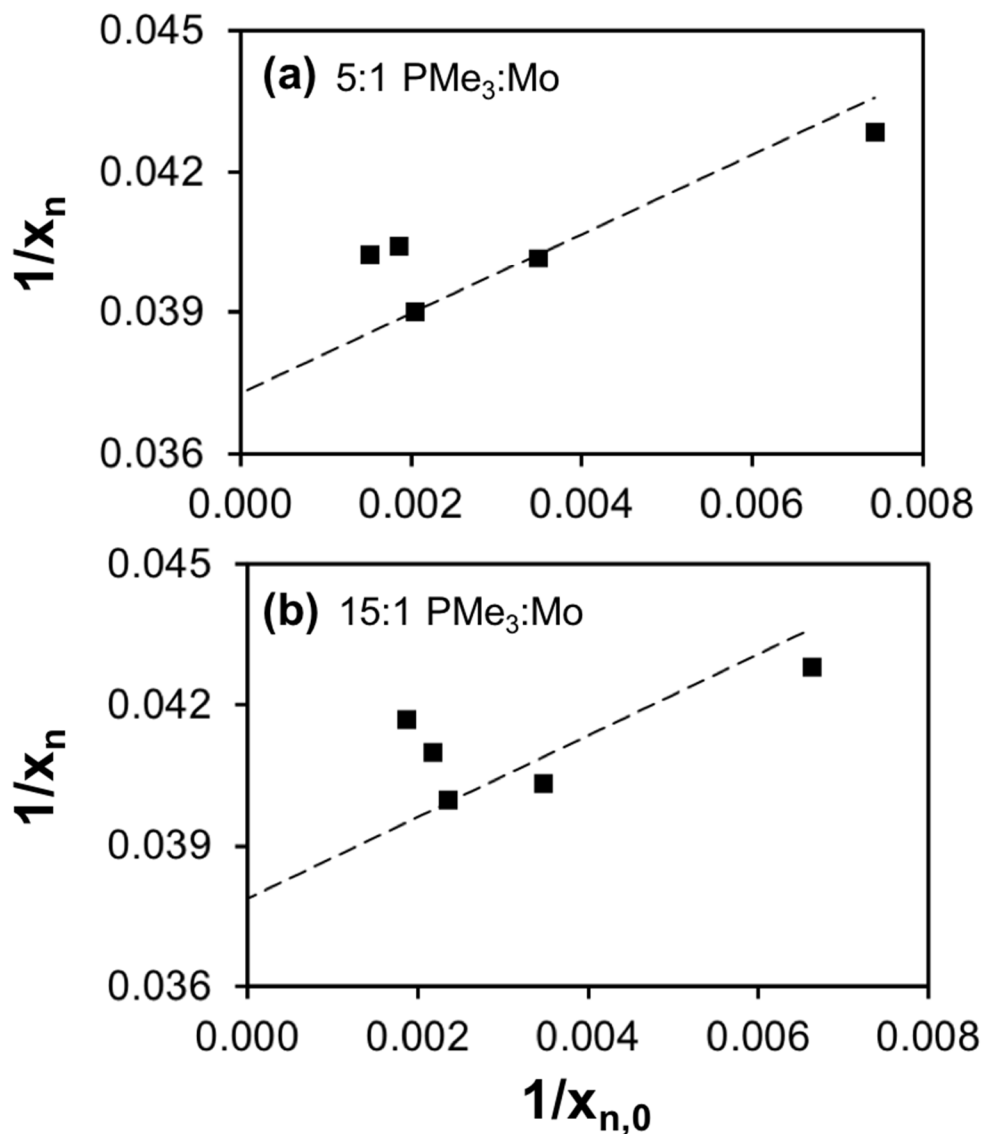


Figure S1. Demonstration of the independence of the apparent C_T , extracted according to equation 1, on $\text{PMe}_3:\text{Mo}$. CTA is 1-pentene, added at $[\text{CTA}]/[\text{M}] = 0.05$. (a) 5:1 $\text{PMe}_3:\text{Mo}$, and (b) 15:1 $\text{PMe}_3:\text{Mo}$. Intercepts are essentially identical for the two cases.

Influence of Variations in $[M]_0$

Though it was desired to conduct all polymerizations at the near-bulk concentration of 10 mol/l CP, it is physically impossible to achieve this concentration of CP when a high concentration of CTA is added. Thus, polymerizations with CTA present have $[M]_0$ slightly less than 10 mol/l, as low as 7.75 mol/l for the case of DVB at $[CTA]/[M] = 0.20$. Hence, the actual value of $[M]_0$ for the “added CTA” polymerization was used in extracting C_T from the value of the intercept according to equation 1, along with $[M]_{eq} = 1.17$ mol/l.⁶

However, differences in $[M]_0$ between the “no-CTA” and “added-CTA” polymerizations mean that the values of v (at any t) were not precisely the same in the two cases, and therefore the slopes of the data in the plots used for the extraction of C_T (such as Figure 3 and Figure S1) should not be precisely unity. Fortunately, this has no substantial impact on the values of C_T determined in this work. First, for active CTAs such as DVB and 1-pentene, where $C_T[CTA] > 0.3$, the extrapolations to the intercept are modest (*i.e.*, the individual values of $1/x_n$ are already quite close to the intercept’s value), so changing the slope has little impact on the value of the intercept. But more fundamentally, in polymerizations with PMe_3 as a reversibly-binding ligand, overall dilution of the system (at fixed CP:Mo and PMe_3 :Mo) has little impact on the rate at which molecular weight builds. This is clear from the kinetic model,^{4,5} and has also been demonstrated experimentally;⁵ physically, dilution of the system raises the fraction of unbound Mo sites, essentially compensating for the reduction in $[M]$. Consequently, the slopes of the fit lines should in fact be quite close to unity, so we have retained this value to preserve the simplicity of analysis via equation 1.

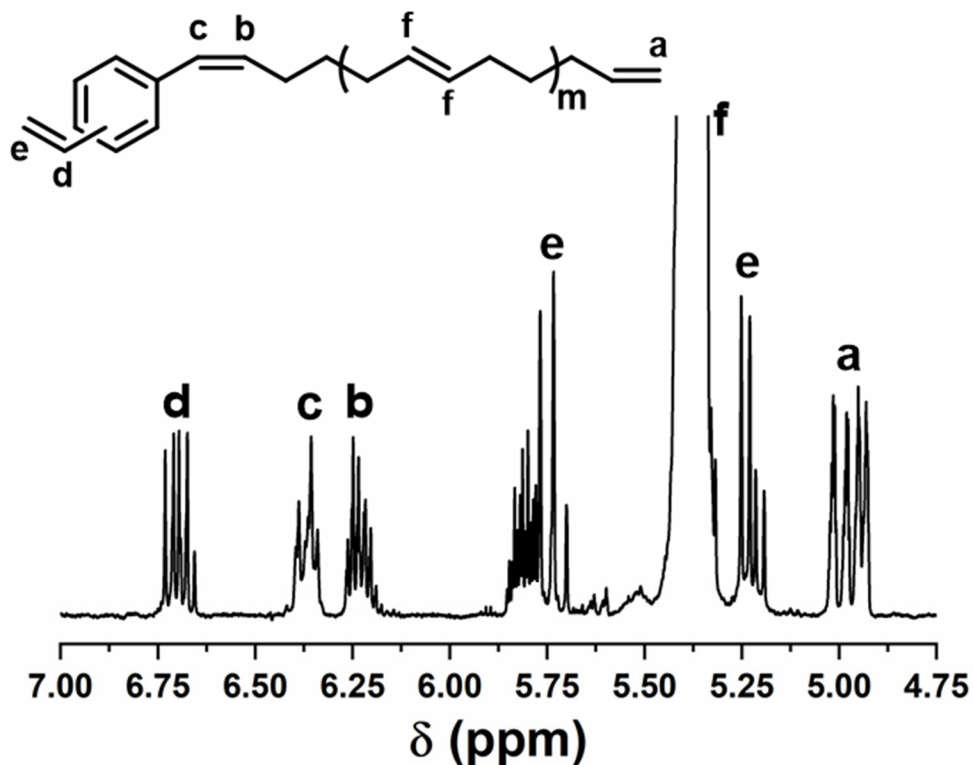


Figure S2. ^1H NMR spectrum (in CDCl_3) of styryl-functionalized PCP macromonomer used in comb copolymer synthesis, after two precipitations into methanol ($M_n = 1520$ g/mol by GPC). Peaks corresponding to styryl-functionalized PCP are labelled. All double bonds are a mixture of *cis/trans*.⁶

M_n of Macromonomer

In Figure S2, the intensity ratio of peaks **a:f** is 0.0455, suggesting an average m (as defined in the structure in the inset of Figure S2) of 21.98. However, as discussed in the text, approximately 1 in 30 chains (3.3%) does not bear a methylidene group (but instead has one styryl or ethylbenzylidene end, and one propylidene end from the terminating agent). This indicates that the true average $m = 21.98(0.967) = 21.25$, so $M_n = 68.12(21.25) + 198 = 1650$ g/mol, where 198 g/mol is the contribution from the endgroups shown in the Figure S2 inset.

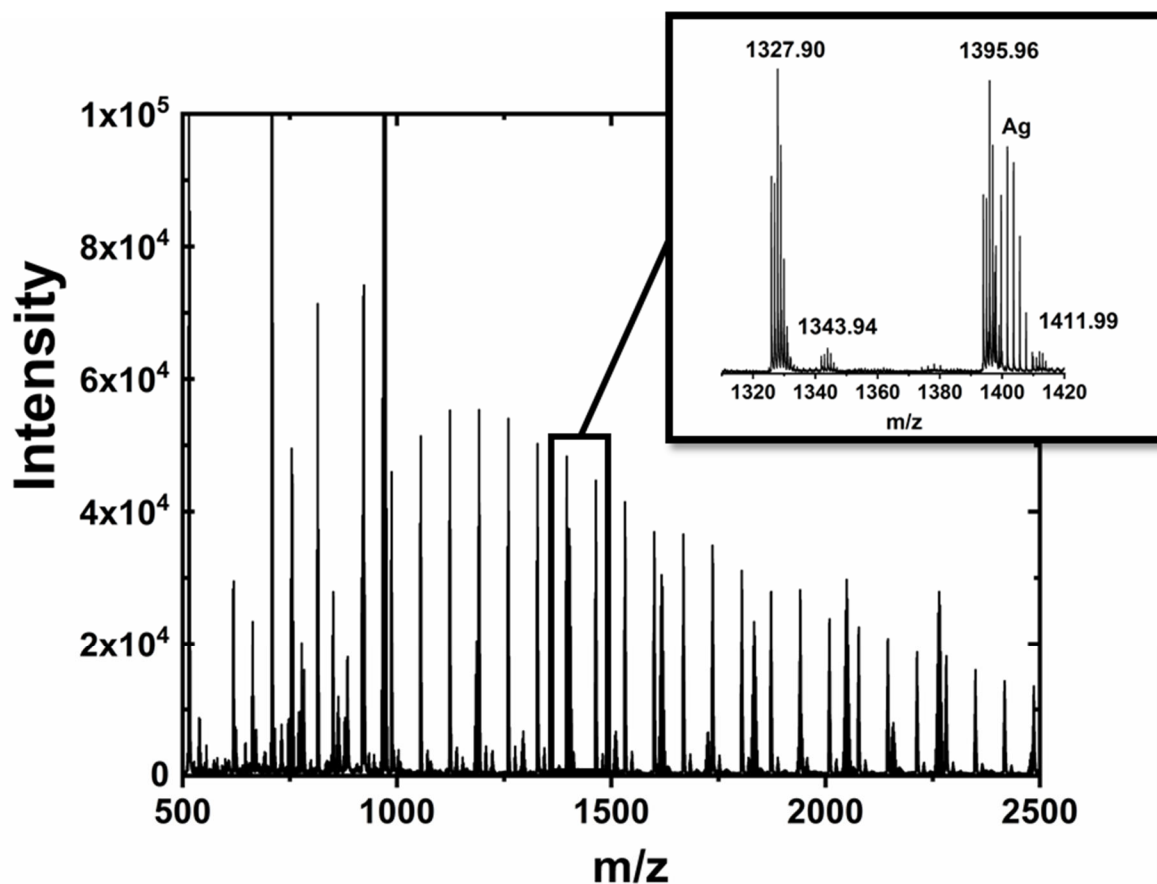


Figure S3. MALDI-ToF survey spectrum of styryl-functionalized PCP macromonomer used in comb copolymer synthesis, after two precipitations into methanol. Inset shows that the spectrum consists of one set of major peaks ($m/z = 1327.90$ and 1395.96 fall within the inset window) and one set of minor peaks (1343.94 and 1411.99 in inset), both separated by 68 g/mol (molar mass of CP repeat). Inset also shows interference from a cluster of reduced Ag near $m/z = 1405 \text{ g/mol}$, easily distinguishable from the polymer signal by the fact that its peaks are spaced by $m/z = 2 \text{ g/mol}$ (vs. the $m/z = 1 \text{ g/mol}$ spacing characteristic of $^{13}\text{C}/^{12}\text{C}$). For the Article's Figures 4 and 5, peak groups (n values) were selected for which there was no interference by Ag clusters.

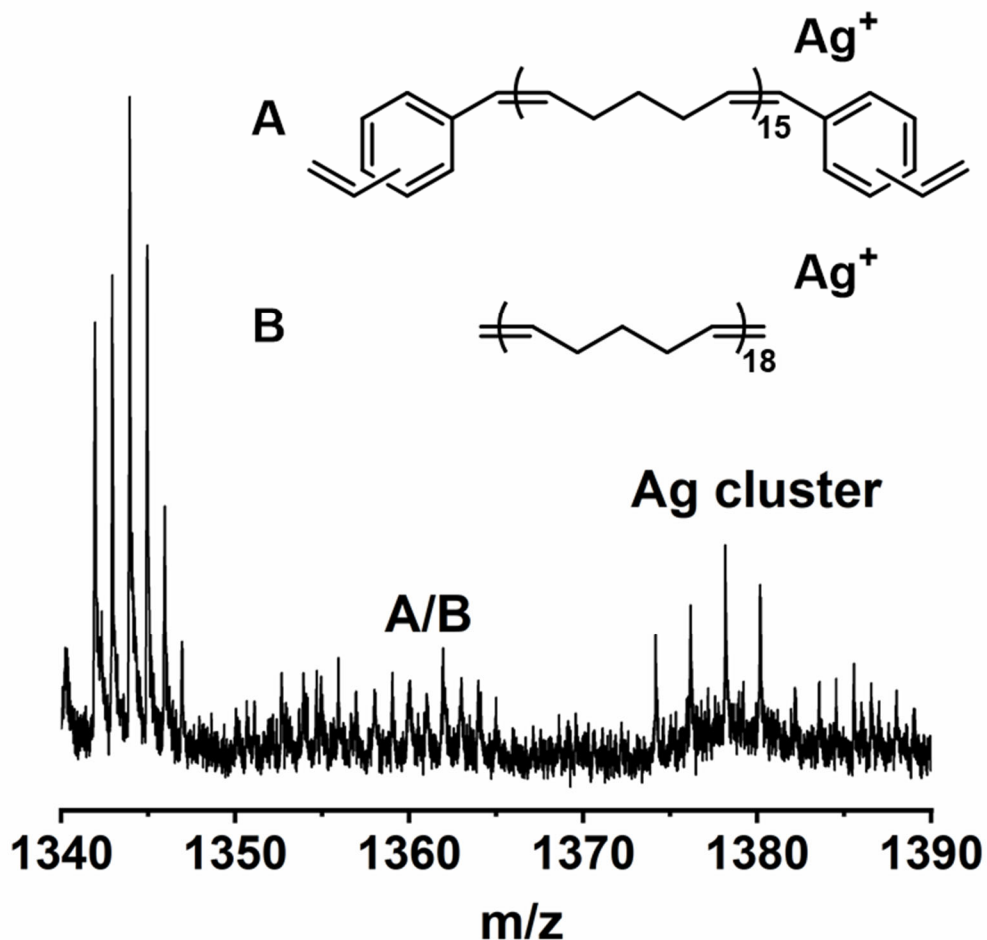


Figure S4. Expanded-scale version of the central region in the inset of Figure S3, showing the presence of weak peaks at m/z near 1362 g/mol. Note that the strong peak in this figure (near 1344 g/mol) is the “minor peak” in Figure S3, so the weak peaks near 1362 g/mol have an intensity only $\sim 1\%$ of that of the major peaks in the inset of Figure S3. Positions of these weak peaks are consistent with the presence of homotelechelic PCP (both dimethylidene-ended and distyryl-ended, which coincidentally have identical m/z , modulo the mass of the CP repeat unit).

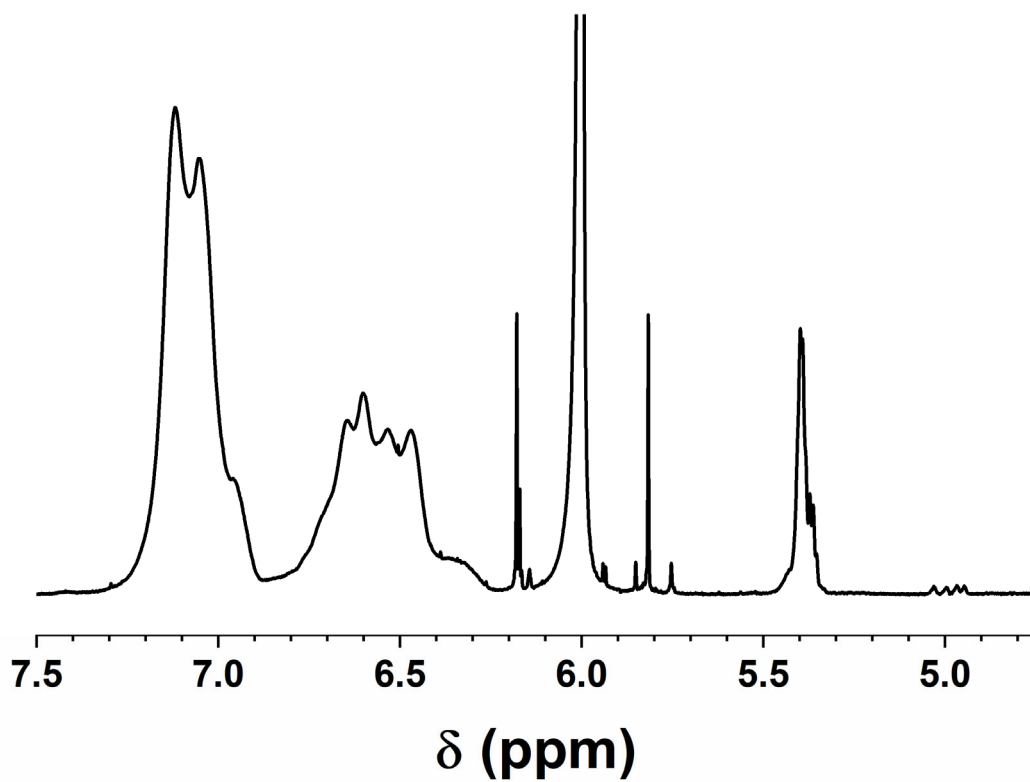


Figure S5. ^1H NMR spectrum (in TCE) of purified comb copolymer, after two precipitations into isooctane. From the areas of the PCP olefinic peaks near 5.4 ppm (2 protons per CP mer), and the aromatic resonances from 6.3-7.2 ppm (5 protons per styrene mer), a composition of 10.4 wt% PCP (89.6 wt% PS) is calculated for the comb copolymer. Note that this assigns the styryl unit at the macromonomer terminus to be “PS” in the comb, and ignores the outer portions of the PCP chain (such as carbons a, b, c in the inset of Figure S2, which do not resonate near 5.4 ppm in the comb); hence, the fraction of the comb derived from the macromonomer is slightly greater than the 10.4 wt% PCP in the comb (approximately 11.6 wt%, which was the macromonomer incorporation level used in the calculation of the styrene radical reactivity ratio r_s).

References

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