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Ambient Temperature Synthesis of a Versatile Macromolecular Building Block: Cyclopentadienyl-Capped Polymers

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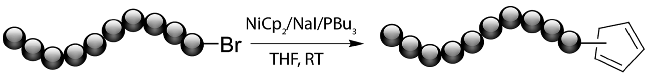
The ability to generate very well-defined end-group functional macromolecules is a central theme in modern polymer synthesis. Arguably being the most convenient and effective technique whereby such structures may be synthesized is controlled radical polymerization (CRP), in particular atom transfer radical polymerization (ATRP)[1] and reversible addition−fragmentation chain transfer (RAFT) polymerization.[2] In the simplest case, the polymerization of a monomer by either of these techniques results in polymer chains bearing precisely controlled end-groups (a halide in the case of ATRP or a thiocarbonylthio moiety in the case of RAFT) which may then be subsequently utilized to polymerize a second monomer, directly yielding the corresponding block copolymer.[3] More recently, however, much attention has been drawn to the use of such technology to impart additional functionality onto the ends of polymer chains, typically within the context of polymer conjugative chemistry (click chemistry).[4]

The use of a CRP process alone or in conjunction with some form of pre- or postpolymerization transformation (such as nucleophilic substitution or esterification) has enabled the generation of a wide variety of polymer chains that bear such functionalities as azide,[5] alkyne,[6] alkene,[7] thiol,[8] hydroxyl,[9] amine,[10] and carboxyl,[11] to name but a few. Now, with the almost ubiquitous presence of click chemistry within the field of CRP, along with a more generic demand for functional polymers, the development of the technologies involved in preparing such functional macromolecules is becoming increasingly important.

Imparting cyclopentadienyl (Cp) functionality onto polymer chains can be a challenging exercise, owing to its high reactivity. Yet, such structures would find enormous applicability in the direct catalyst-free and ambient temperature functionalization of such intensely investigated materials as fullerenes, carbon nanotubes, and graphenes. Unlike other polymer conjugation technologies, the use of Cp-functional polymers in Diels−Alder reactions with the wide variety of available dienophiles would allow one to have precise control over the conditions under which chemical linkages are formed and broken. Recently, the beginnings of this concept were realized in our laboratories with the use of Cp-functional polymers in ultrafast polymer conjugations.[12] Despite this, there have only been very few and rather limited examples of imparting Cp functionality onto polymeric materials reported in the literature.

In organic synthesis, the predominant method for preparing substituted cyclopentadienes has been the nucleophilic substitution of alkyl halides or tosylates with sodium cyclopentadienide (NaCp).[13] Other possibilities include the use of oxycyclopentadienyl dianions[14] or cyclopentadienylmagnesium bromide as a Grignard reagent.[15] In polymer chemistry, there have been numerous reports on the functionalization of chloromethylated polystyrene−divinylbenzene resins with a Cp end-group for use in Diels−Alder reactions with fullerenes.[16] Another approach, reported by Müllen and colleagues,[17] involved the addition of NaCp to poly(styrene) (PS) bearing partial chloromethyl functionality along the polymer chain to yield the corresponding Cp-functional polymer. In a further example from the same authors, dimethylfulvene was added to the lithiated aromatic rings of a PS chain to also impart Cp functionality.[18] As alluded to earlier, we have recently reported the functionalization of PS prepared by ATRP and poly(ethylene glycol) monomethyl ether with NaCp through nucleophilic substitution of the respective bromide and tosylated end-groups.[12]

Scheme 1. General Synthetic Strategy to Cp-Functional Polymers



Although being successful, the above polymeric systems have lacked other chemical functionality that could potentially participate in side reactions with NaCp. Although Dillmore et al.[19] report the addition of NaCp to methyl bromoacetate to yield the corresponding methyl ester functional Cp derivative, NaCp can also participate in a reaction with esters in which the alkoxy substituent is replaced by the Cp anion.[20] NaCp also reacts with other carbonyl containing compounds (ketones and aldehydes) to yield fulvenes.[21] Furthermore, Romdhane et al. presented an excellent model study of the reaction of NaCp with benzyl bromide, the results of which indicated that numerous side reactions take place.[22]

A comparatively little explored method to achieve Cp functionalization is the use of nickelocene ($NiCp_2$) as the substituting agent. Characterized by a rather covalent Ni−Cp bond, $NiCp_2$ may be considered to be a much less harsh reagent when compared to NaCp, which is much more ionic in nature. $NiCp_2$ has been successfully used in the synthesis of highly crowded Cp derivatives,[23] Cp ligands bearing fluorinated "ponytails",[24] and has been proven to be efficient in the preparation of Cp-functional polymeric supports (such as Merrifield's resin).[25] The decision to use $NiCp_2$ in these applications was borne out of consideration of the various ill-desired side reactions that are encountered via the use of NaCp. To the best of our knowledge, selective substitution of halogenated esters via the $NiCp_2$ route has not been reported.

Herein, we demonstrate the effectiveness of $NiCp_2$ in quantitatively converting a variety of bromide end-functional polymers into the corresponding Cp functional polymers at ambient temperature without any side product formation (Scheme 1). PS, poly(methyl methacrylate) (PMMA), poly(methyl acrylate) (PMA), and poly(isobornyl acrylate) (P*i*BoA) were prepared via low conversion ATRP to ensure high bromide functionality. In the case of PS, the bromide functionality was confirmed by ^{1}H NMR spectroscopy; for the remaining polymers, both ^{1}H NMR spectroscopy and electron spray ionization mass spectrometry (ESI-MS) were utilized for characterization.

Extrapolating from our previous efforts,[12] Cp-functionalization of the above synthesized polymers was initially attempted by using the NaCp route. As expected, the PS-Br **1** cleanly underwent the transformation into the PS-Cp **5**, as verified by ^{1}H NMR spectroscopy. However, treatment of PMMA-Br **2**, P*i*BoA-Br **3**,

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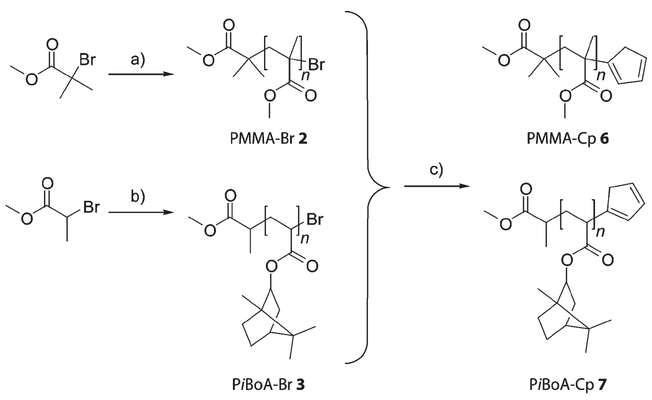
Scheme 2. Synthesis of PMMA-Cp 6 and P*i*BoA-Cp 7[a]



[a] Reactants and conditions: (a) ATRP of methyl methacylate, $Cu^IBr/Cu^{II}Br$/bpy, acetone, 50 °C; (b) ATRP of isobornyl acrylate, Cu^IBr/PMDETA, EtOAc, 77 °C; (c) $NiCp_2/NaI/PBu_3$, THF, RT, bpy = 2,2′-bipyridine, PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine.

Table 1. Polymer Characterization

polymer	$M_{n,GPC}$[a] [g mol^{-1}]	PDI[b]
PS-Br **1**	1600	1.06
PMMA-Br **2**	2700	1.09
P*i*BoA-Br **3**	4200	1.22
PMA-Br **4**	2800	1.29

[a] Molecular weights determined against PS standards for PS, P*i*BoA, and PMA and against PMMA standards for PMMA. [b] Polydispersity index.

and PMA-Br **4** with NaCp did not yield the corresponding Cp polymers. A more in-depth discussion of these findings may be found in the Supporting Information.

In need of an alternate pathway, the use of $NiCp_2$ as the source of the Cp unit was considered. The overall strategy for two selected examples is depicted in Scheme 2. It has previously been encountered that in performing the chloride/bromide to Cp transformation with $NiCp_2$ alone sluggish reaction times or indeed no reaction at all can be observed. However, it has been documented that the addition of triphenylphosphine and sodium iodide as a halogen metathesis reagent (if required) greatly enhances the alkylation reaction.[24,25] As such, this approach was applied in the present circumstance. The results for PMMA-Br **2** and P*i*BoA-Br **3** will be discussed in detail here; the Supporting Information contains details concerning the PS-Br **1** (see Figure S5 for ^{1}H NMR spectra) and PMA-Br **4** (see Figure S8 for the ESI-MS spectra). The molecular weight assessments for the starting polymers are included in Table 1.

In a typical experiment, the bromide-terminated polymer, sodium iodide (6.0 equiv), and, in our case, tributylphosphine (PBu_3, 2.0 equiv) were dissolved in anhydrous THF under a nitrogen atmosphere. To the resulting mixture, a solution of $NiCp_2$ (4.0 equiv) also in anhydrous THF was added, and the now green solution was allowed to stir overnight at ambient temperature. The progression of the reaction is characterized by the change in solution color to deep purple and the precipitation of nickel(II) bromide. It was interesting to observe that the change from green to purple occurred within the space of seconds for the poly(acrylates), a few minutes for the poly(methacrylate), and a few hours for the poly(styrene). At the end of the reaction, the mixture was passed through a short column of basic alumina and precipitated in an appropriate solvent. Chloroform solutions of the recovered polymers were then subjected to a water wash, after which the purified polymers were recovered once again by precipitation. This procedure was also performed on a 10 g scale with identical results.

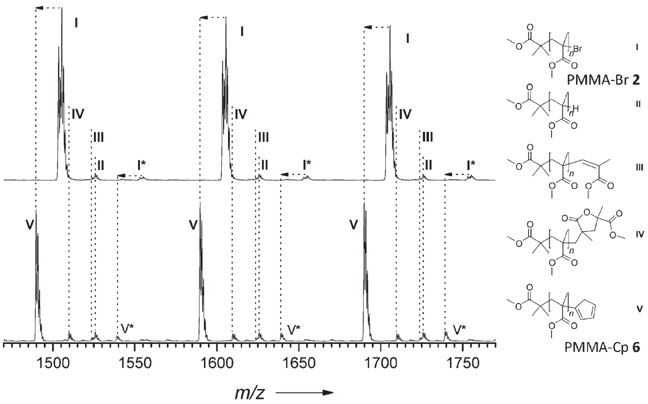


Figure 1. ESI-MS spectra of PMMA-Br **2** and PMMA-Cp **6**. Note the clear change in the isotopic pattern from bromide terminated species to Cp-terminated species that occurs (see further Figure S6).

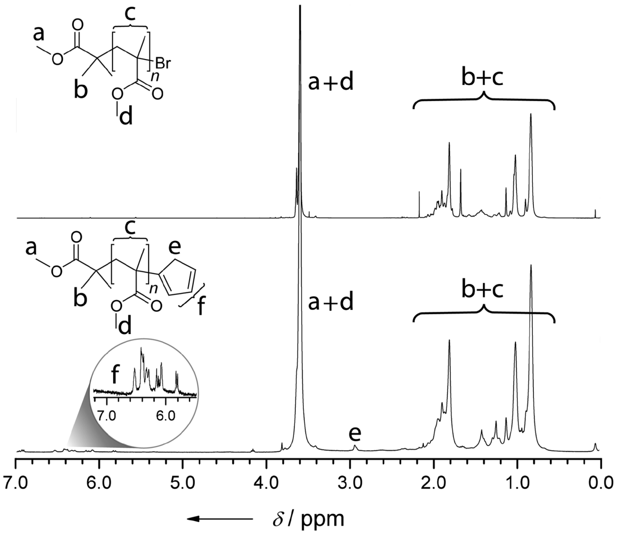


Figure 2. ^{1}H NMR spectra of PMMA-Br **2** and PMMA-Cp **6**. The M_n determined by integration (2800 g mol^{-1}) is in good agreement with the GPC value, thus further confirming the efficiency of the transformation. The ratio of the integrals of peaks **f**:**e**:[**a** + **d**] is 3:2:81.

Figure 1 shows the ESI-MS spectra of the starting PMMA-Br **2** alongside that of the reaction product, PMMA-Cp **6**. The dominant species in the spectrum of the starting material is clearly the required bromide-terminated polymer. One may also observe the presence of a small quantity of impurities, all but one of which can be assigned to inescapable side products of the ATRP process and have been previously encountered in the literature.[26] The remaining unidentified product may be inferred to be another bromide-terminated species, based upon the characteristic isotopic pattern of its signal. Regardless, the ATRP-derived side products are of no significance in our investigation of this concept. After the transformation, the signals for all bromide-terminated species are observed to shift to lower *m*/*z* values in accordance with the formation of the desired Cp-functional species. Specific molecular ion assignments are presented in the Supporting Information.

The results of ^{1}H NMR spectroscopic analysis (Figure 2) reveal that Cp functionality has indeed been imparted to the polymer chain by virtue of the appearance of characteristic signals at 6.6−5.8 and 2.9 ppm. It should be noted that although the reaction product contains a mixture of the 1-, 2-, and

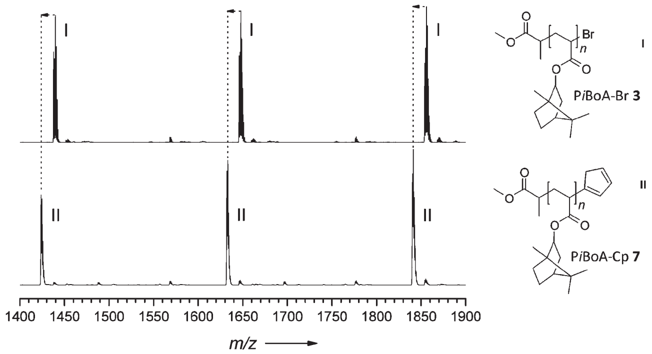


Figure 3. ESI-MS spectra of P*i*BoA-Br **3** and P*i*BoA-Cp **7**. Note the clear change in the isotopic pattern from bromide-terminated species to Cp-terminated species that occurs (see further Figure S7).

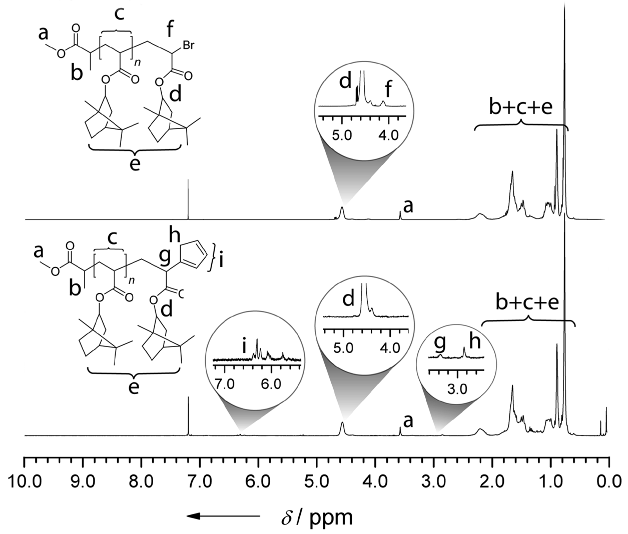


Figure 4. ^{1}H NMR spectra of P*i*BoA-Br **3** and P*i*BoA-Cp **7**. The M_n determined by integration (4500 g mol^{-1}) is in good agreement with the GPC value, thus further confirming the efficiency of the transformation. The ratio of the integrals of peaks **i**:**h**:**g**:**d** is 3:2:1:21.

5-substituted cyclopentadienes, only the chemical structure for the 1-isomer is presented for reasons of brevity.

Similar success was also achieved in the case of P*i*BoA. Figure 3 shows the ESI-MS spectra recorded for the starting P*i*BoA-Br **3** and the substitution product P*i*BoA-Cp **7**. Comparable to the PMMA example, a number of unidentified side products are present resulting from the ATRP process; however, these are present in very minor quantities. Nevertheless, a clear and complete transformation is observed. A comparison of the experimental and theoretical *m*/*z* values is presented in the Supporting Information.

The above substitution was further confirmed via ^{1}H NMR spectroscopy, the results of which are presented in Figure 4. The signal for the proton (in α position to the bromide terminus) appearing at 4.1 ppm is observed to completely shift to 3.4 ppm after the substitution. The characteristic Cp signals at 6.4−5.8 and 2.9 ppm are also clearly observed, nicely complementing the ESI-MS analysis and thus proving the efficient functionalization of the polymer.

As a further test of the efficient transformations, a comparative gel permeation chromatography (GPC) analysis was performed between PMMA-Br **2** and PMMA-Cp **6** and between P*i*BoA-Br **3** and P*i*BoA-Cp **7**. As a diene, cyclopentadiene is very reactive such that it readily dimerizes at ambient temperature via a Diels−Alder mechanism. Thus, there is potential for the presently investigated Cp-capped polymers to also undergo some degree of dimerization, a phenomenon which would be readily observable in a GPC analysis. Figure 5 shows such an analysis. It is very clear that no dimerization has occurred in either system, which is consistent with our earlier findings.[12]

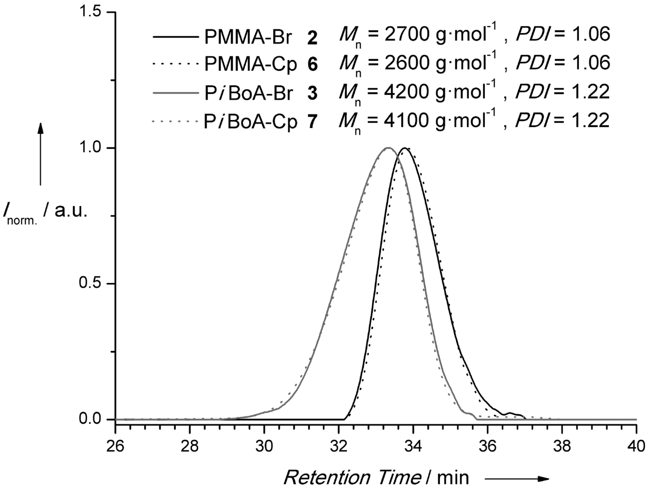


Figure 5. Overlay of GPC traces of PMMA-Br **2** and PMMA-Cp **6** (black) and of P*i*BoA-Br **3** and P*i*BoA-Cp **7** (gray).

In summary, we have presented a selective, efficient, and mild strategy for equipping a variety of polymer chains (prepared via ATRP) with a highly reactive Cp moiety. The numerous side reactions that can occur in the presence of NaCp are avoided, and more importantly, the multitude of ester functional groups that exist in poly(acrylates) and poly(methacrylates) have been shown to be essentially inert to the functionalization system employed. We envisage that such provision of Cp-functional polymers would bring the concept of ambient temperature and catalyst-free conjugation to a broader platform.

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Supporting Information Available: All experimental procedures, additional NMR spectra, and ESI-MS spectra/analyses concerning the present investigation. This material is available free of charge via the Internet at http://pubs.acs.org.

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