DOI: 10.1002/ejic.201100360

# "Click" Assembly of Carborane-Appended Polymers and Stabilization of Gold and Palladium Nanoparticles

**Liyuan Liang,[a] Amalia Rapakousiou,[a] Lionel Salmon,[b] Jaime Ruiz,[a] Didier Astruc,*[a] Barada Prasanna Dash,[c] Rashmirekha Satapathy,[c] James W. Sawicki,[c] and Narayan S. Hosmane*[c]**

**Keywords:** Carboranes / Polymers / Click chemistry / Polystyrene / Nanoparticles

*o*-Carborane was covalently linked to the side chain of a polystyrene polymer by the "click" reaction to provide a carborane-appended polystyrene polymer. The initial step involved the radical polymerization of *p*-chloromethylstyrene with AIBN followed by replacement of the chloro units by azido groups; the final step employed the $Cu^I$-catalyzed Huisgen-type "click" reaction between the azidomethyl-appended polystyrene polymer and the ethynyl-terminated carborane unit yielding the desired carborane-appended polystyrene. Size exclusion chromatography (SEC) of this carborane-appended polymer showed a polydispersity index (PDI) of 1.52. Dynamic light scattering (DLS) in dichloromethane provided a diameter value of 4.5 nm. The MALDI TOF mass spectrum exhibited a series of single peaks culminating from 16 carborane-appended styrenyl units. The thermogravimetric analysis (TGA) showed the polymer to have good thermal robustness. Polymer-stabilized gold and palladium nanoparticles (AuNPs and PdNPs) were synthesized with sizes determined by TEM to be 2.6 ± 0.4 and 1.7 ± 0.3 nm, respectively. The Miyaura–Suzuki cross-coupling of phenyl iodide with phenylboronoic acid at 22 °C was catalyzed by the polymer-stabilized PdNPs.

## Introduction

Cluster chemistry has attracted considerable interest for over half a century, involving both theoretical and applied aspects.[1,2] Among clusters, carboranes with a high boron content[2] are especially useful for their potential applications in nanomedicine,[3] material science,[4] and organometallic chemistry.[5] Therefore, thermally robust carboranes have been incorporated in nanosystems such as dendrimers,[6] an area pioneered by Newkome,[7] and further exploited by Grimes' group[8] and our groups.[9] It has also been shown that carboranes could be encapsulated in dendrimers in a non-covalent fashion for potential medical applications.[10] Here, we introduce a new approach, the covalent incorporation of carboranes into "click"[11] polymers; indeed polymers are much more rapidly synthesized than dendrimers, which should favor practical usages. In addition, we are taking advantage of these carborane-appended "click" polymers for the stabilization of gold and palladium nanoparticles. Gold nanoparticles (AuNPs)[12] are of fast growing interest for their potential use as nanovectors for the diagnostics and therapy of major diseases,[13] and their combination in composites with boron-rich nanosystems could also be useful. Palladium nanoparticles (PdNPs) are efficient in catalysis,[14] and their stabilization by polymers and dendrimers can provide good catalysts for olefin hydrogenation and cross-carbon–carbon bond formation.[15] "Click" dendrimers are especially appropriate for this catalytic function[16] but analogous studies on catalysis with "click" polymers are rare.[17]

Huisgen-type azide–alkyne $Cu^I$-catalyzed dipolar "click" cycloaddition reactions (CuAAC) have recently been shown to be a remarkable way for connecting organic and bioorganic segments and functions.[11] Therefore, we are using this technique here and wish to report the "click" synthesis, spectroscopic and analytical characterization, and thermal stability of *o*-carborane-appended polymers using a derivative of the carborane *o*-$MeC_2B_{10}H_{10}$.

## Results and Discussion

### Synthesis, Characterization, and Thermal Properties of the Carborane-Appended Polymers

The chloromethyl group is ideal for functionalizing polystyrene polymers, but the classic radical polymerization of *p*-(chloromethyl)styrene (**1**) is marred by side reactions at the chloromethyl group. Initiation using AIBN, however,

---

[a] Institut des Sciences Moléculaires, UMR CNRS N°5255,
Université Bordeaux 1,
33405 Talence Cedex, France
E-mail: d.astruc@ism.u-bordeaux1.fr
[b] Laboratoire de Chimie de Coordination, UPR CNRS N°8241,
31077 Toulouse Cedex 04, France
[c] Department of Chemistry and Biochemistry, Northern Illinois University,
DeKalb, Illinois 60115-2862, USA
E-mail: hosmane@niu.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100360.

was shown to be a possible route that minimizes the side reactions;[18] thus, we have selected this pathway. In a standard procedure,[18] *p*-(chloromethyl)styrene (**1**) underwent radical polymerization in toluene at 80 °C for 24 h with 1% AIBN; the poly[*p*-(chloromethyl)styrene] polymer **2** was purified by the precipitation (five times) from a dichloromethane solution by the addition of methanol. Size exclusion chromatography (SEC) of **2** provided a polydispersity index (PDI) value of 1.26. Nucleophilic replacement of the chloro groups by using sodium azide yielded the azidomethyl-appended polystyrene polymer **3** for which the SEC provided a PDI of 1.34 (see Figure 1, the Experimental Section, and the Supporting Information). The alkynyl *o*-carborane **4** was synthesized by treating the lithiated 1-Me-*o*-carborane with commercially available 4-iodobenzyl bromide. The resulting carboranyl iodo derivative underwent a Pd-catalyzed Sonogashira coupling reaction with trimethylsilylacetylene, and finally deprotection of the TMS group with $K_2CO_3$ yielded the desired alkynyl *o*-carborane **4**.[9a,9c] The click reaction between the azidomethyl-appended polystyrene polymer **3** and the *o*-carborane-containing alkynyl derivative **4** was carried out by using the classical procedure with $CuSO_4$ and a threefold excess of sodium ascorbate as catalyst in THF/water (1:1) at room temperature for 12 h (Scheme 1).

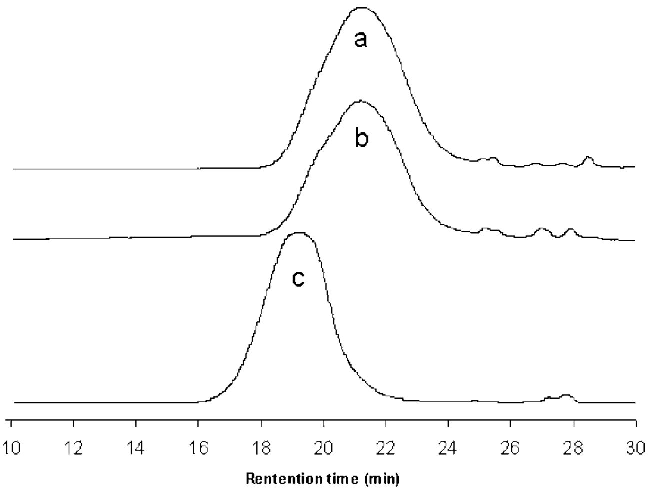
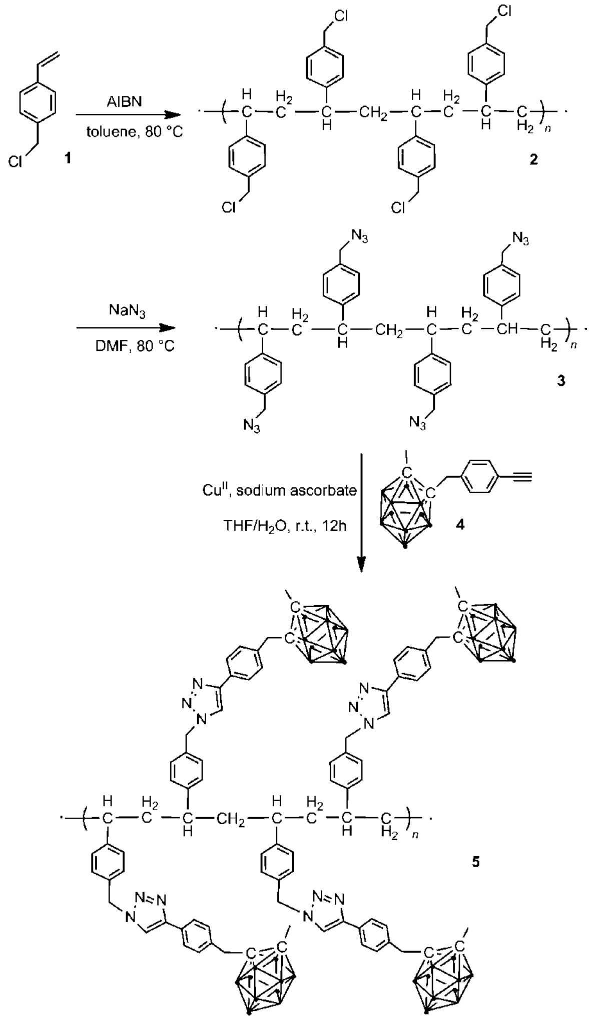


Figure 1. SEC of (a) **2** (PDI = 1.26; $M_n$ 3996; $M_w$ = 5029); (b) **3** (PDI = 1.34; $M_n$ = 4055; $M_w$ = 5443); (c) **5** (PDI = 1.52; $M_n$ = 9343; 14186).

The Cu ions were removed as $[Cu(NH_3)_2(H_2O)_2][SO_4]$ upon reaction with an aqueous ammonia solution, and the new polymer **5** was purified upon precipitation from a dichloromethane solution by the addition of methanol. Acording to this procedure, polymer **5** was obtained as a white powder in 66% yield. Its IR spectrum showed the complete disappearance of the azide band at 2097 $cm^{-1}$ and the band of the alkyne group at 2108 $cm^{-1}$. The $^1H$ NMR spectrum of **5** exhibited the signal for the proton of the triazolyl group at $\delta$ = 7.79 ppm versus TMS in $CDCl_3$ (see the $^1H$ and $^{13}C$ NMR spectra in the Supporting Information). SEC provided a PDI value of 1.52 for **5** (Figure 1).



Scheme 1. Synthesis of the carborane-appended polystyrene polymer **5**.

Elemental analysis also indicated the formation of polymer **5**, and the MALDI TOF mass spectrum showed well-defined individual molecular peaks for polymers containing 9–27 carborane-chain-appended styrenyl units with a maximum intensity around a molecular weight of 6944.76 Da corresponding to the polymer containing 16 carborane-chain-appended styrenyl units. All peaks are separated by 424 Da, which corresponds to the mass of one unit; a residue of 160 Da remains. This residue corresponds to the polymer termini, that is, a $CMe_2CN$ radical from the initiating radical and a methylenestyryl radical provided by radical Cl abstraction from *p*-(chloromethyl)styrene followed by coupling to the other polymer end. These two radicals correspond to 163 Da (Figure 2). The apparent $M_n$ and $M_w$ values provided by SEC (Figure 1) are much larger than those obtained by MALDI-TOF mass spectrometry, but as usual the calibration was carried out with polystyrene. There also is an increase of the polydispersities from **2** to **5** reflecting the fact that the reactions of the polymers are not quantitative and thus introduce defects.

The average size of polymer **5** in a dichloromethane solution was determined by dynamic light scattering (DLS)

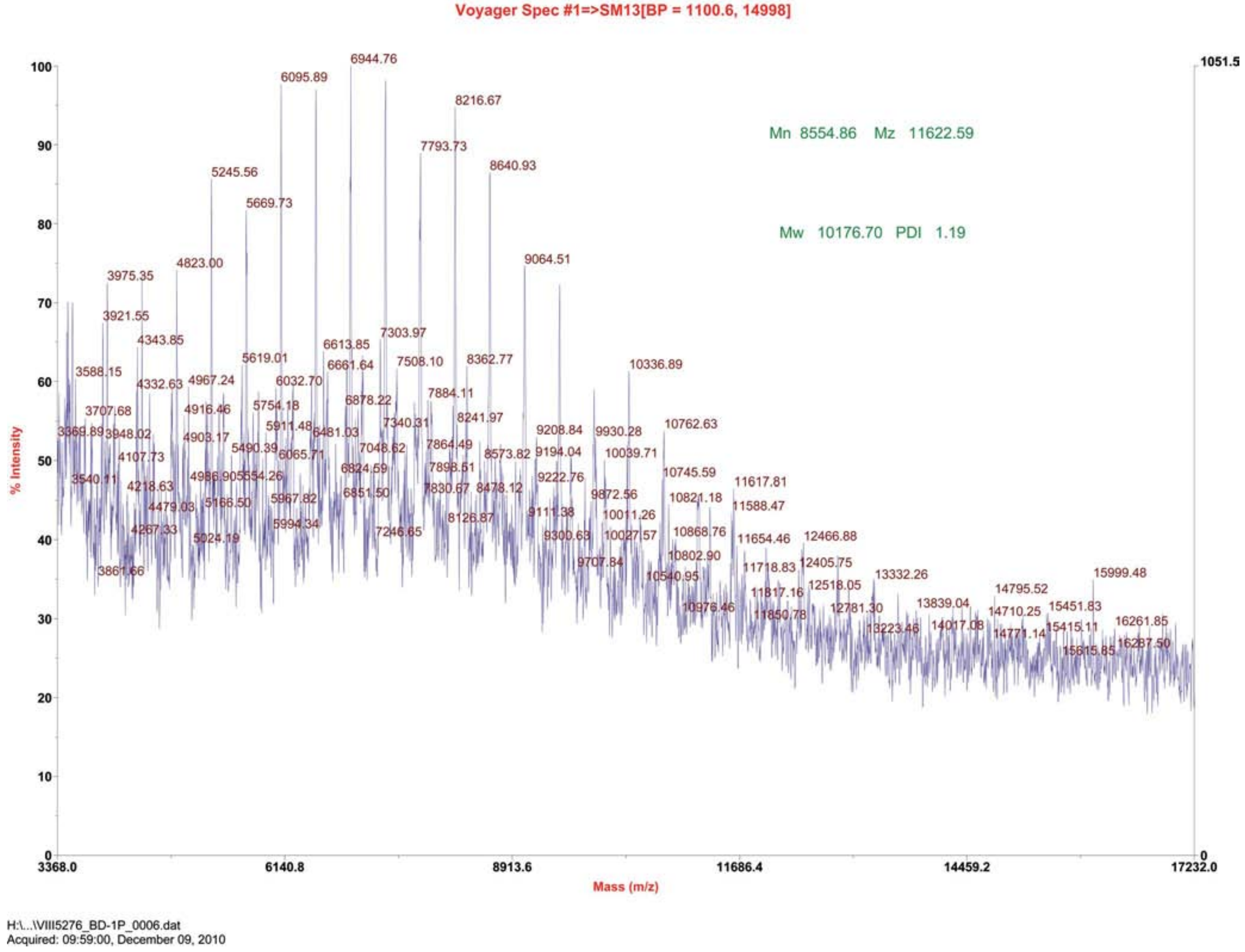


Figure 2. MALDI-TOF spectrum of **5**.

yielding an average diameter of 4.5 nm (volume average, with a dispersity of 0.25). The thermogravimetric analysis (TGA) exhibited two decomposition steps. The first mass loss (up to 5%) started at around 100 °C, probably because of the decomposition of the aliphatic chain. The second mass loss started sharply at around 340 °C, and 10% mass loss occurred at 377 °C. About 73% mass of the sample was retained even at 700 °C showing the thermal robustness of the carborane polymer (Figure 3).

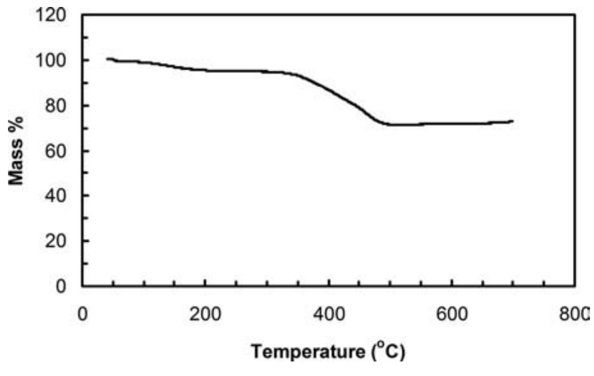


Figure 3. Thermogravimetric analysis of **5**.

## Stabilization of Gold and Palladium Nanoparticles

### *Gold Nanoparticles*

The addition of $HAuCl_4$ to polymer **5** leads to the complexation of $Au^{III}$ by the 1,2,3-triazolyl ligands of the polymer, as monitored by the change in the UV/Vis spectrum (Figure 4). This is followed by the reduction of $Au^{III}$ to $Au^0$ atoms that assemble in the AuNPs and are then stabilized by the triazolyl ligands of the polymer (weak electronic interaction) and by the overall polymer framework (steric stabilization). Indeed, after addition to the polymer **5**, $HAuCl_4 \cdot 3H_2O$ was reduced by $NaBH_4$ in THF/water to AuNPs in the presence of the carborane-appended polymer **5** at room temperature in 1 min, as indicated by the color change from yellow ($Au^{III}$ band at 322 nm in the UV/Vis spectrum) to purple (plasmon band[12] with a maximum at 521 nm); the polymer **5** stabilized purple AuNP solution was stable for several days (Scheme 2).

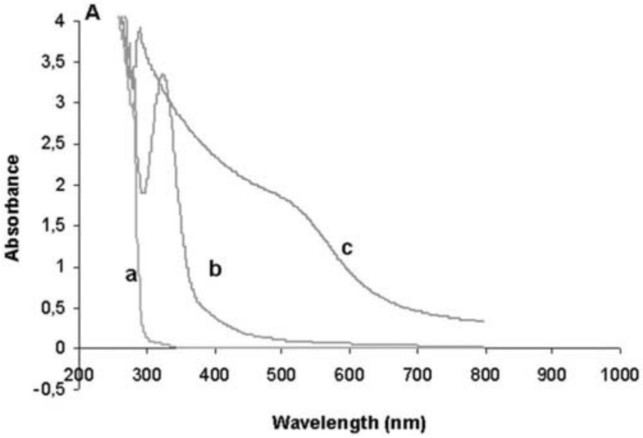


Figure 4. UV/Vis spectra of the THF/$H_2O$ solution of the polymer **5**: (a) alone; (b) after addition of $HAuCl_4$; (c) after reduction of $Au^{III}$ by $NaBH_4$ to AuNPs (plasmon band: 521 nm).

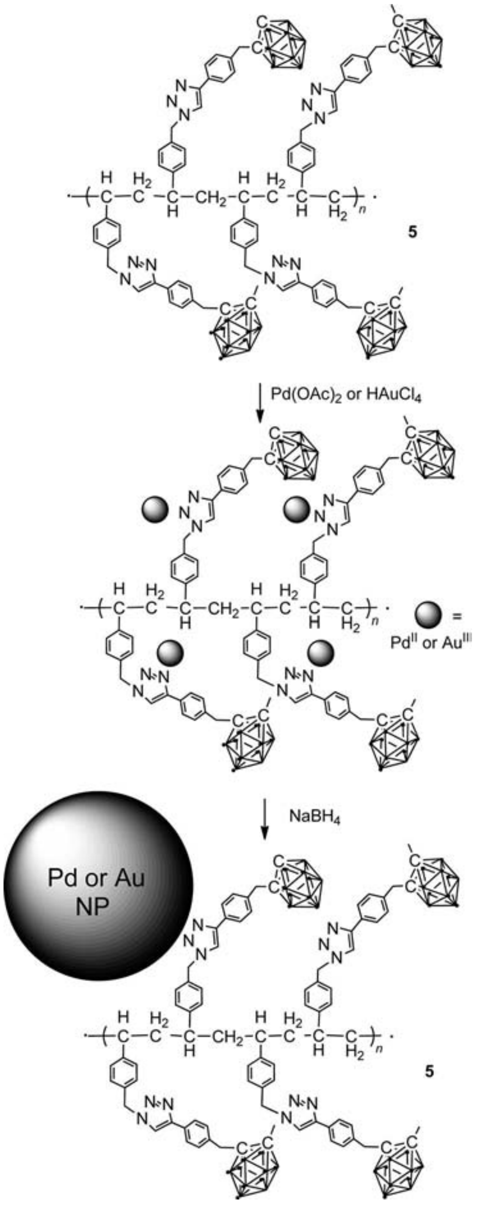
Figure 4 shows the change in the UV/Vis spectrum of polymer **5** upon the addition of $HAuCl_4·3H_2O$, then the reductant. Analysis by TEM indicated a diameter of 2.6 ± 0.4 nm, as shown in Figure 5.

### *Palladium Nanoparticles*

$Pd(OAc)_2$ was reduced by methanol to $Pd^0$ assembling in PdNPs in the presence of a $CHCl_3$ solution of polymer **5** at room temperature in 12 h, as indicated by the color change from yellow to brown after this time. The reaction was monitored by UV/Vis spectroscopy, which showed no new bands, but that the band corresponding to $Pd(OAc)_2$ at 400 nm disappeared. Analysis by TEM showed a diameter of 1.7 ± 0.3 nm (Figure 6).

## Catalytic Properties of the Palladium Nanoparticles

The $CHCl_3$/MeOH solution of PdNPs was used in catalytic amount for the Miyaura–Suzuki cross-coupling reaction between iodobenzene and phenylboronic acid to test



Scheme 2. Complexation of the 1,2,3-triazole groups of polymer **5** by $Pd^{II}$ or $Au^{III}$ followed by reduction of the metal ions to metal atoms that agglomerate in nanoparticles stabilized by the polymer.

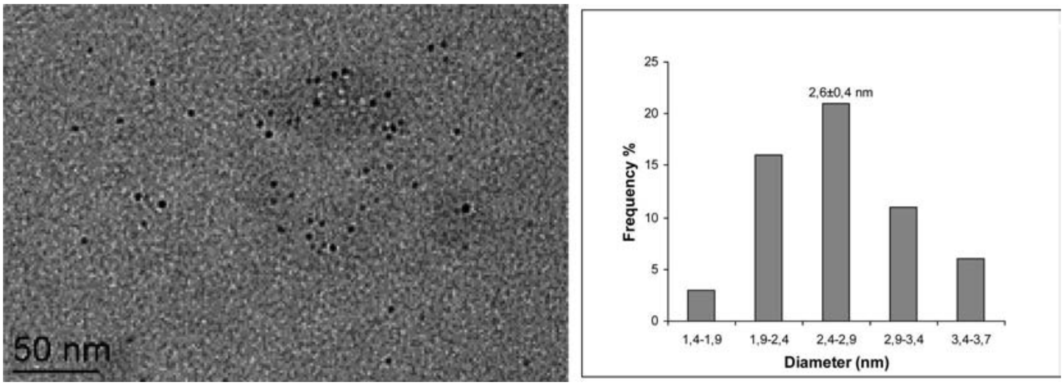


Figure 5. TEM of the AuNPs stabilized by polymer **5**.

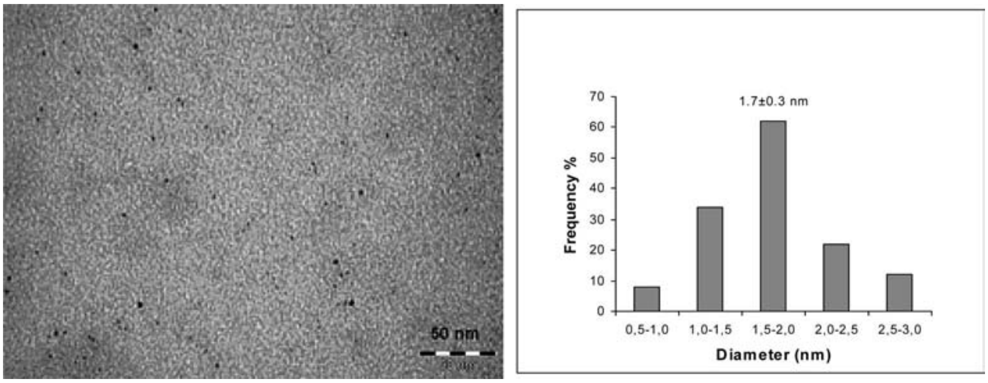


Figure 6. TEM of the PdNPs stabilized by polymer **5**.

the catalytic performances of the PdNPs under these conditions. At 22 °C, the yields of the PdNP-catalyzed cross-coupled product were 13, 23, and 62% by using 0.01, 0.1, and 1% Pd, respectively; these values are much smaller than the yields and turnover numbers obtained at 25 °C by using PdNPs stabilized by other triazolyl-appended polystyrene polymers in EtOH/$H_2O$.[17] The PdNPs are small enough to be efficient, but the modest results obtained here show the importance of the structure of the appended chain in such catalytic reactions by using substituted 1,2,3-triazolyl-appended polystyrene polymers.

## Conclusion

The facile synthesis of carborane-appended polymers is of interest towards further use and applications, because such syntheses are much more rapid and convenient than those of dendrimers that are covalently or supramolecularly assembled. One potential use includes nanoparticle stabilization. The combination of gold nanoparticles and boron-rich clusters within the same nanosystems, achieved here for the first time, could be of further use for the design of nanovectors for diagnostics and boron neutron capture + AuNP photo-thermal therapy against cancer and other major diseases. The stabilization of PdNPs led to catalytic data that were modest compared to those obtained with other triazolyl-appended polystyrene polymers. More studies on related systems are necessary to understand the factors that optimize the catalytic efficiency of nanoparticles stabilized by "clicked" polymers.

## Experimental Section

**General Data:** Reagent-grade toluene was dried with Na foil and distilled from sodium benzophenone under argon immediately prior to use. All other solvents (THF, dichloromethane, methanol, DMF) and chemicals were used as received. $^{1}$H NMR spectra were recorded at 25 °C with a Bruker AC 200 or 300 (200 or 300 MHz) spectrometer. $^{13}$C NMR spectra were obtained in the pulsed FT mode at 75 MHz with a Bruker AC 300 spectrometer, and the $^{11}$B NMR spectra were recorded at 160.5 MHz with a Bruker AC 500 spectrometer. All the chemical shifts are reported in parts per million ($\delta$, ppm) with reference to $Me_4Si$ (TMS) for the $^{1}$H and $^{13}$C NMR spectra and with reference to $BF_3{\cdot}Et_2O$ for the $^{11}$B NMR spectra. Mass spectra were recorded with an Applied Biosystems Voyager-DE STR-MALDI-TOF spectrometer. The DLS measurements were carried out with a Malvern Zetasizer 3000 HSA instrument at 25 °C at an angle of 90°. IR spectra were recorded with an ATI Mattson Genesis series FT-IR spectrophotometer. UV absorption and emission spectra were measured with a Perkin–Elmer Lambda 19 UV/Vis spectrometer and a Hitachi F-2500 fluorescence spectrophotometer, respectively. TGA was performed with a Perkin–Elmer Pyris 1 analyzer at a heating rate of 5 °C/min under argon. SEC of the polymers was performed with a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian (series RI-3) refractive index detector and a JASCO 875 UV/Vis absorption detector, with THF as the mobile phase. Gas chromatography data were recorded with a Hewlett Packard 5890 Series II gas chromatograph, equipped with a Stabilwax (Crossband Carbowax-PEG) column and a flame ionization detector. For all substrates, helium was used as the carrier gas. The injector and detector temperatures were 240 °C. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon Villeurbanne, France.

**Synthesis of Linear Poly[*p*-(chloromethyl)styrene] (2):** *p*-(Chloromethyl)styrene (**1**) (2.17 g, 14.2 mmol) was dissolved in dry toluene (40 mL) and AIBN (0.12 g, 0.7 mmol) added under nitrogen. The reaction mixture was stirred at 80 °C for 24 h. The toluene was removed under vacuum, and the crude product was washed with methanol and precipitated five times from $CH_2Cl_2$/methanol. The poly[*p*-(chloromethyl)styrene] **2** was obtained as a white powder in 53.9% yield (1.17 g). $^{1}$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.12, 6.56 (m, Ar), 4.53 (s, $CH_2$-Cl), 1.77, 1.47 ($CH$ and $CH_2$ of polymer chain) ppm. $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 145.2 ($C$q of Ar), 135.0 ($C$q-$CH_2$), 128.6, 128.0 ($C$H of Ar), 46.4 ($C$H$_2$-Cl), 40.4 ($C$H$_2$ and $C$H of polymer chain) ppm. SEC: PDI = 1.26, $M_n$ = 3996, $M_w$ = 5029.

**Synthesis of Linear Poly[*p*-(azidomethyl)styrene] (3):** In a Schlenk flask, poly[*p*-(chloromethyl)styrene] (**2**) (2.5 g, 0.5 mmol) was dissolved in DMF (20 mL) and $NaN_3$ (1.6 g, 24.6 mmol) added. The mixture was heated at 80 °C for 24 h before the suspension was extracted three times with diethyl ether/$H_2O$; the organic phase was dried with $Na_2SO_4$, filtered, and the solvents were evaporated. Poly[*p*-(azidomethyl)styrene] **3** was obtained as a white waxy product in 84.6% yield (2.2 g). $^{1}$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.05, 6.53 (m, Ar), 4.25 (s, $CH_2$-$N_3$), 1.72, 1.46 (s, $CH$ and $CH_2$ of polymer chain) ppm. $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 145.4 ($C$q of Ar), 134.9, 132.7 ($C$q-$CH_2$), 128.0 ($C$H of Ar), 54.7 ($C$H$_2$-$N_3$), 40.3

($CH_2$ and $CH$ of polymer chain) ppm. IR: $\tilde{\nu}$ = 2097 (azido band) $cm^{-1}$. SEC: PDI = 1.34, $M_n$ = 4055, $M_w$ = 5443.

**Synthesis of the Carborane-Appended Polymer 5:** The azidomethyl-appended polystyrene polymer **3** (50 mg, 9.54 µmol, 1 equiv.) and ethynylated carborane derivative **4** (128 mg, 472 µmol, 1.5 equiv. per branch) were dissolved in THF. $CuSO_4$ was added (1.5 equiv. per branch, 1 M aqueous solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (3 equiv. per branch, 1 M aqueous solution) to obtain a 1:1 THF/water ratio. The solution was stirred at 25 °C under nitrogen overnight. After removal of the THF under vacuum, $CH_2Cl_2$ and an aqueous ammonia solution were added. The mixture was stirred for 1 h to remove all the Cu ions trapped inside the polymer as $[Cu(NH_3)_2(H_2O)_2][SO_4]$. The organic phase was washed three times with water, dried with $Na_2SO_4$, and the solvent was removed under vacuum. The product was precipitated twice with $CH_2Cl_2$/MeOH, and a white powder was obtained (90 mg, 66%). The IR spectrum shows the disappearance of the band at 2097 $cm^{-1}$ characteristic of the azide function and the band at 2108 $cm^{-1}$ for the terminal alkyne group. $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ = 7.79 (3 H, C*H* of triazole and C*H* of Ar-cluster), 7.17 (2 H, C*H* of Ar-cluster), 6.81, 6.30 (4 H, C*H* of Ar of styrenyl), 5.33 (2 H, $CH_2$-triazole), 3.40 (2 H, $CH_2$-cluster), 2.12 ppm (3 H, cluster-$CH_3$). $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ = 147.2(*C*q of triazole), 145.1(*C*q of Ar), 134.96 (*C*q of Ar-cluster), 130.9, 125.8 (*C*H of Ar-cluster), 127.9 (*C*H of Ar-polymer chain), 120.6 (*C*H of triazole), 75.1(*C* of cluster), 53.8(Ar-$CH_2$-triazole), 40.8 (*C*H and $CH_2$ of polymer chain), 23.6 ppm (cluster-$CH_3$). $^{11}B$ NMR ($CDCl_3$, 160.5 MHz): $\delta$ = –5.9 and –10.5 (typical for *o*-carborane) ppm. SEC: PDI = 1.52, $M_n$ = 9343, $M_w$ = 14186. $C_{693}H_{957}B_{330}N_{99}$ (14242.2): calcd. C 58.44, H 6.77; found C 59.01, H 6.99. DLS: Radius $r$ = 4.5 nm.

**Preparation of Gold Nanoparticles (AuNPs) with the Carborane-Appended Polymer 5:** Solution A contained polymer **5** (10 mg) dissolved in THF (20 mL; $c = 3.5 \times 10^{-5}$ mol/L). Solution B contained $HAuCl_4 \cdot 3H_2O$ (20 mg) dissolved in $H_2O$ (20 mL; $c = 2.5 \times 10^{-3}$mol/L). To record the UV/Vis spectra of the nanoparticles, the baseline was established in a THF/$H_2O$ mixture (2 and 0.9 mL, respectively). The UV/Vis spectrum of **5** containing $Au^{III}$ was obtained by mixing solution A (2 mL) and solution B (0.9 mL, 1 equiv. $HAuCl_4$ per branch). The $Au^{III}$ species in the yellow reaction mixture was reduced to $Au^0$ by the addition of an aqueous solution of $NaBH_4$ (2.5 mol. equiv. per Au in 2 mL) under ambient conditions during 1 min; a purple solution was immediately obtained. The excess $NaBH_4$ was not removed. This purple color remained persistent at room temperature during several days.

**Preparation of Palladium Nanoparticles (PdNPs) with the Carborane-Appended Polymer 5 and Catalysis of the Miyaura–Suzuki Reaction**

(1) Solution A contained polymer **5** (10 mg) dissolved in $CHCl_3$ (28 mL; $c = 2.5 \times 10^{-5}$ mol/L). Solution B contained $Pd(OAc)_2$ (20 mg) dissolved in $CHCl_3$ (20 mL; $c = 4.45 \times 10^{-3}$ mol/L). To record the UV/Vis spectra of the nanoparticles, the baseline was established in a $CHCl_3$/MeOH mixture (2 and 1 mL, respectively). The UV/Vis spectrum of **5** with $Pd^{II}$ was obtained upon mixing solution A (2.8 mL) with solution B [0.5 mL, 1 equiv. $Pd(OAc)_2$ per branch] and MeOH (1.7 mL); the color of the solution changed from light yellow to dark brown after stirring for 12 h. No new band was observed in the spectrum; however, the band for $Pd(OAc)_2$ at 400 nm disappeared.

(2) In a Schlenk flask, a solution of **5** (1 mg, $7 \times 10^{-8}$ mol) was prepared in a $CHCl_3$/MeOH mixture, and a yellow solution of $Pd(OAc)_2$ (1 mg/mL in $CHCl_3$) was added dropwise under nitrogen [$V_{CHCl3}/V_{MeOH}$ = 2:1; $c$(Pd) = $4.6 \times 10^{-4}$ mol/L]. After stirring at 20 °C overnight, the color of the solution turned from yellow to brown, which indicated the formation of PdNPs. NaOAc, phenyl boronic acid, and iodobenzene were added under nitrogen, and the Miyaura–Suzuki reaction was carried out at 20 °C. After 24 h, the mixture was extracted with $CH_2Cl_2/H_2O$, the organic phase was dried with $Na_2SO_4$, filtered through silica gel to remove the PdNPs, and injected into the gas chromatograph. The results are indicated in the Results and Discussion section.

**Supporting Information** (see footnote on the first page of this article): $^1H$, $^{13}C$, and $^{11}B$ NMR and IR spectra of the polymers.

## Acknowledgments

We thank Dr. R. Djeda (ISM, Talence) and N. Guidolin (LPCO, Pessac) for helpful assistance in the synthesis and SEC work, respectively. Financial support from the Universities Bordeaux 1, the Centre National de la Recherche Scientifique, the Agence Nationale pour la Recherche (ANR-07-CP2D-05-01), and the National Science Foundation (CHE-0906179 & CHE-0840504) are gratefully acknowledged. Additional support to N. S. H. from the Alexander von Humboldt Foundation and the award from the NIU Inaugural Board of Trustees Professorship (N. S. H.) are also hereby acknowledged.

---

[1] T. P. Fehlner, J.-F. Halet, J.-Y. Saillard, *Molecular Clusters*, Cambridge University Press, Cambridge, **2007**.

[2] a) M. F. Hawthorne, *Acc. Chem. Res.* **1968**, *1*, 281–288; b) K. F. Purcel, J. C. Kotz, *Inorganic Chemistry*, Holt-Saunders, London, **1977**, pp. 980–1008; c) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Heidelberg, **2007**, pp. 67–76.

[3] J. F. Valliant, K. J. Guenther, S. Arienne, *Coord. Chem. Rev.* **2002**, *232*, 173–230; Z. Yinghuai, A. T. Peng, K. Carpenter, J. A. Maguire, N. S. Hosmane, M. J. Takagaki, *J. Am. Chem. Soc.* **2005**, *127*, 9875–80; M. C. Parrott, E. B. Marchington, J. F. Valliant, A. Adronov, *J. Am. Chem. Soc.* **2005**, *127*, 12081–12089; D. Astruc, E. Boisselier, C. Ornelas, *Chem. Rev.* **2010**, *110*, 1857–1959.

[4] J. Plesek, *Chem. Rev.* **1992**, *92*, 269–78; R. N. Grimes, *J. Chem. Educ.* **2004**, *81*, 657–672.

[5] Y. Zhu, K. Y. Cheng, J. A. Maguire, N. S. Hosmane, *Curr. Chem. Biol.* **2007**, *1*, 141–149.

[6] a) G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons. Concepts, Syntheses, Applications*, Wiley-VCH, Weinheim, **2001**; b) *Dendrimers and other Dendritic Polymers* (Eds.: D. A. Tomalia, J. M. J. Fréchet), Wiley, Amsterdam, **2001**; c) G. R. Newkome, C. Shreiner, *Chem. Rev.* **2010**, *110*, 6338–6442; d) D. Astruc, *C. R. Acad. Sci., Ser. IIb* **1996**, *322*, 757–766.

[7] G. R. Newkome, C. N. Moorefield, J. M. Keith, G. R. Baker, G. S. Escamilla, *Angew. Chem.* **1994**, *106*, 701; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 666–668; For a recent review, see: S.-H. Hwang, C. D. Shreiner, C. N. Moorefield, C. N. Newkome, *New J. Chem.* **2007**, *31*, 1192–1217.

[8] H. Yao, R. N. Grimes, M. Corsini, P. Zanello, *Organometallics* **2003**, *22*, 4381–4383.

[9] a) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *Org. Lett.* **2008**, *10*, 2247–2250; b) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *Chem. Commun.* **2009**, 3267–3269; c) B. P. Dash, R. Satapathy, E. R. Gaillard, J. A. Maguire, N. S. Hosmane, *J. Am. Chem. Soc.* **2010**, *132*, 6578–6587; d) B. P. Dash, R. Satapathy, J. A. Maguire, N. S. Hosmane, *Organometallics* **2010**, *29*, 5230–5235; R. Djeda, J. Ruiz, R. Satapathy, B. P. Dash, N. S. Hosmane, *Inorg. Chem.* **2010**, *49*, 10702–10709.

[10] a) G. Wu, R. F. Barth, W. Yang, M. Chatterjee, W. Jjarks, M. J. Ciesielki, R. A. Fenstermaker, *Bioconjugate Chem.* **2004**, *15*,

185–194; b) R. Shukla, T. P. Thomas, J. L. Peters, A. M. Desai, J. Kukowska-Latallo, A. K. Patri, A. Kotlyar, J. R. Baker, *Bioconjugate Chem.* **2006**, *17*, 1109–1115; c) G. Wu, R. F. Barth, M. Swidall, A. K. Bandyopadhyaya, W. Jjarks, B. Khorsandio, T. E. Blue, A. K. Ferketich, M. Yang, G. A. Christoforidis, T. J. Sferra, P. J. Binns, K. J. W. Riley, M. J. Ciesielki, R. A. Fenstermaker, *Clin. Cancer Res.* **2007**, *13*, 1260–1268.

[11] V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem.* **2002**, *114*, 2708; *Angew. Chem. Int. Ed.* **2002**, *41*, 2596–2600; C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064; M. Meldal, C. W. Tornøe, *Chem. Rev.* **2008**, *108*, 2952–3015; M. Meldal, *Macromol. Rapid Commun.* **2008**, *29*, 1016–1051.

[12] a) *Nanoparticles* (Ed.: G. Schmid), Wiley-VCH, Weinheim, **2004**; b) M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293–346.

[13] a) P. Jain, I. H. El-Sayed, M. A. El-Sayed, *Nanotoday* **2007**, *2*, 18–29; b) C. J. Murphy, A. M. Gole, J. W. Stone, P. N. Sisco, A. M. Alkilany, E. C. Goldsmith, S. C. Baxter, *Acc. Chem. Res.* **2008**, *41*, 1721–1730; c) S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res.* **2008**, *41*, 1842–1851; d) E. Boisselier, D. Astruc, *Chem. Soc. Rev.* **2009**, *38*, 1759–1782.

[14] a) R. Bönnemann, R. Richards, *Eur. J. Inorg. Chem.* **2001**, *10*, 2455–2480; b) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757–3778; c) D. Astruc, F. Lu, J. Ruiz, *Angew. Chem.* **2005**, *117*, 8062; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852–7872; d) N. T. S. Phan, M. van der Sluys, C. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; e) J. G. de Vries, *Dalton Trans.* **2006**, 421–429; f) D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884–1894; *Nanoparticles and Catalysis* (Ed.: D. Astruc), Wiley-VCH, Weinheim, **2007**.

[15] a) R. M. Crooks, L. Zhao, V. Sun, L. Chechik, K. Yeung, *Acc. Chem. Res.* **2001**, *34*, 181–190; b) R. W. J. Scott, O. M. Wilson, R. M. Crooks, *J. Phys. Chem. B* **2005**, *109*, 692–704.

[16] a) C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, *Chem. Commun.* **2007**, 4946–4948; b) A. K. Diallo, C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, *Angew. Chem.* **2007**, *119*, 8798; *Angew. Chem. Int. Ed.* **2007**, *46*, 8644–8648; c) C. Ornelas, L. Salmon, J. Ruiz, D. Astruc, *Adv. Synth. Catal.* **2008**, *350*, 837–845; d) D. Astruc, C. Ornelas, J. Ruiz, *Acc. Chem. Res.* **2008**, *41*, 841–856.

[17] C. Ornelas, A. K. Diallo, J. Ruiz, D. Astruc, *Adv. Synth. Catal.* **2009**, *351*, 2147–2154.

[18] a) For a general review on the radical polymerization of *p*-(chloromethyl)styrene, see: M. Camps, M. Chatzopoulos, J.-P. Monthéard, *Polym. Rev.* **1982**, *22*, 343–407; b) see also: J.-P. Monthéard, C. Jegat, M. Camps, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1999**, *C39*, 135–174; c) C. Lin, I. Gitsov, *Macromolecules* **2010**, *43*, 3256–3267.

Received: April 5, 2011