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Conjugated Polymers

Highly Efficient Benzannulation of Poly(phenylene ethynylene)s**

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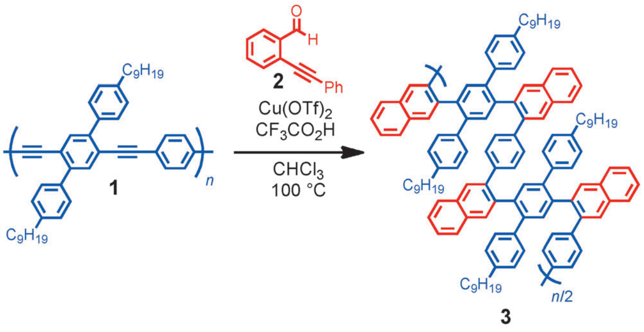
Macromolecules linked by single bonds between aromatic substituents, that is, polyphenylenes, have attracted great interest for use in organic light-emitting diodes (OLEDs)[1] and other optoelectronic devices,[2] as structurally rigid dendrimers,[3] for isolating[4] or organizing chromophores,[5] and as soluble precursors of nanostructured forms of graphene.[6] *Para-* and *meta*-linked polyphenylenes with high molecular weight are synthesized through transition-metal-catalyzed cross-coupling approaches, some of which proceed through chain-growth mechanisms.[7] Only a few oligomeric *ortho*-linked phenylenes have been reported[8] as a result of poor cross-coupling efficiency during the polymerization. Longer *o*-polyphenylenes are interesting because they can adopt specific helical conformations induced by steric interactions along the polymer backbone[8,9] and can be oxidized to soluble, structurally precise graphene nanoribbons.[10] New strategies for accessing *o*-polyphenylenes, particularly those that tolerate additional aromatic substituents, are therefore of great utility.

Here we report a versatile and efficient approach to prepare polymers of high molecular weight containing *o*-substituted arylene linkages through a cycloaddition reaction at each alkyne function of a poly(phenylene ethynylene) (PPE). PPEs are attractive precursors because of their structural versatility, functional-group tolerance, and efficiency of polymerizations. However, their alkyne moieties are notably unreactive and have only been reduced to methylene[11] or *cis*-vinylene groups prior to this study.[12] This benzannulation strategy (Scheme 1) is the first reported efficient cycloaddition performed along a conjugated polymer backbone,[13] and it tolerates bulky aromatic substituents adjacent to the alkyne moieties, thus suggesting that it will be applicable to a broad range of crowded aromatic architectures.



Scheme 1. Benzannulation of each alkyne of a substituted poly(phenylene ethynylene) **1** provides polyphenylene **3**.

Yamamoto and co-workers reported a Cu(OTf)$_2$-catalyzed benzannulation of diphenylacetylene with *o*-(phenylethynyl)benzaldehyde **2** to produce 2,3-diphenylnaphthalene,[14] but this transformation has not previously been employed for polymer modification. We first evaluated its feasibility for PPE benzannulation using dialkyne **4** (Figure 1), a model compound similar in structure to PPE **1**. Compound **4** reacts rapidly (in as little as 30 min) and efficiently with **2** in the presence of catalytic amounts of Cu(OTf)$_2$ and excess trifluoroacetic acid (CF$_3$CO$_2$H) at 100 °C to provide the doubly benzannulated product **5** in 98 % yield of isolated product. Yamamoto and co-workers found that some alkyne-containing substrates form more than 10 % of a naphthyl ketone side product (Figure 1 b, inset)

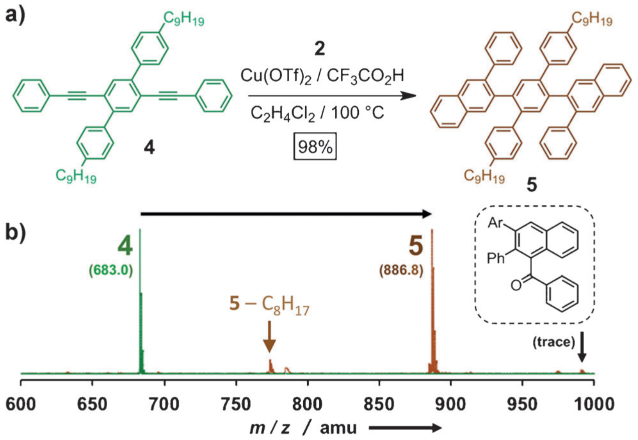


Figure 1. Model study of the benzannulation strategy. a) Subjection of terphenyl-containing dialkyne **4**, a molecular compound similar in structure to PPE **1**, to the Cu(OTf)$_2$-catalyzed benzannulation.
b) MALDI-TOF mass spectra of dialkyne **4** and benzannulated product **5**. Inset: structure of a possible naphthyl ketone side product based on previous reports of the benzannulation reaction,[14] observed only as a trace impurity in the mass spectrum.

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under the Cu(OTf)$_2$-catalyzed benzannulation conditions, although this side reaction was not observed for the substrate diphenyl acetylene.[14] If present in our system, this side reaction would induce defects along the polyphenylene backbone. Fortunately, **4** forms little or no naphthyl ketone side products ($<1\%$), as judged by the high yield of isolated product **5**, as well as by NMR and Fourier transform infrared (FTIR) spectroscopy (see the Supporting Information), and thin-layer chromatography.

A comparison of the MALDI-TOF mass spectra of **4** and **5** also indicates the high efficiency of the reaction. After benzannulation, a strong signal for the doubly benzannulated product **5** is observed. The weak signal in the spectrum at 773.6 mass units corresponds to a fragmentation product of **5**. The only signals corresponding to benzannulation side products are weaker: the naphthyl ketone at 990.6 mass units and monoannulated product at 784.6 mass units. These by-products were formed in trace amounts and were not observed by other analytical methods. In summary, this model study confirms the potential of this reaction for polymer modification.

The *p*-terphenyl-*alt*-phenyl PPE **1** was obtained by copolymerizing the appropriate terphenyl dialkyne monomer and 1,4-diiodobenzene under Sonogashira cross-coupling conditions. A substoichiometric amount of a monofunctional aryl iodide, 4-iodoanisole, was used to control the molecular weight and the identity of the end-group of the polymer. Nevertheless, at molecular weights approaching 100 kDa, **1** is insoluble in the reaction mixture and partially precipitates during the polymerization. As a result, we obtained a bimodal molecular-weight distribution ($M_n = 7.85$ kDa; PDI $= 3.53$; $D_p = 12$) by size-exclusion chromatography (SEC), consisting of a main peak for polymers of low molecular weight with a shoulder for polymers of high molecular weight (Figure 2).

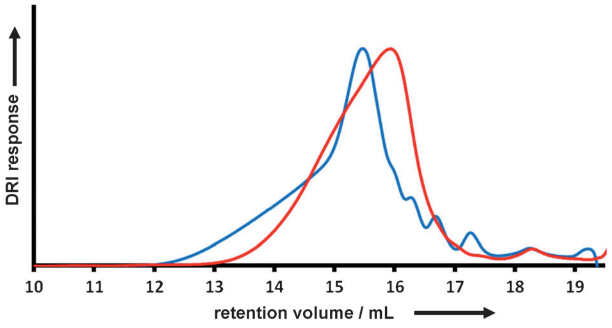

Figure 2. Differential refractive index (DRI) response of SEC traces of PPE **1** (blue) and polyphenylene **3** (red).

These molecular weights were determined by multi-angle light scattering, a direct measure of the polymer mass that does not rely on comparisons to polymer standards of questionable applicability. Despite its broad molecular-weight distribution, we did not separate **1** into fractions of high and low molecular weight because we found that the shorter chains were easily removed by precipitation after the benzannulation step. We estimate the D_p of the high-molecular-weight fraction of **1** to be approximately 59, making it an appropriate system in which to evaluate our synthetic approach.

PPE **1** was benzannulated under similar conditions as the model compound **5** (3 equiv of **2** per alkyne, 3 equiv CF_3CO_2H, 0.05 equiv Cu(OTf)$_2$), after which polyphenylene **3** was isolated by precipitation from CH_2Cl_2 into acetone, followed by Soxhlet extraction using acetone as the liquid phase. SEC analysis of the acetone-insoluble material showed a monomodal distribution of chain sizes, the molecular weight and polydispersity ($M_n = 39.6$ kDa, PDI $= 1.65$, $D_p = 49$) of which correspond to the benzannulation of the higher-molecular-weight portion of **1**. Steric hindrance along the polymer backbone prevents **3** from adopting a planar conformation and it is far more soluble in organic solvents than **1**. Despite its higher molecular weight, polyphenylene **3** is retained longer by the SEC columns relative to its PPE precursor **1**, which we attribute to the polymer adopting a more compact solvated structure as a consequence of its steric demands (Figure 2). As a result, the polymer chains of **3** adopt smaller hydrodynamic volumes than random-coil polymer chains of comparable molecular weight. This explanation is consistent with recent findings that oligomeric *o*-phenylenes adopt specific helical conformations as a consequence of their crowded structure.[8,15]

According to a molecular dynamics (MD) simulation, polyphenylene **3** adopts a compact structure in organic solvent. MD provides an atomically explicit representation of the dynamics of the system under the influence of inter- and intramolecular forces. A 24-unit polymer chain of **3** was simulated along with 11,740 1,2-dichlorobenzene solvent molecules using the OPLS-AA force field[16] within the LAMMPS software package[17] (see the Supporting Information for complete details). The resulting structure of the polymer was highly contorted with several distinct conformations at each monomer unit, which contribute to the compact structure of the solvated polymer in solution. In each monomer unit, we determined eight dihedral angles that affect the local conformation of the polymer and thus investigated their disposition. Preferred angles were found by locating peaks in histograms generated by the data; Gaussian distributions were fitted to each peak to estimate an average angle value as well as a standard deviation (Supporting Information, Table S2). From left to right in Figure 3, the three most common conformations of polymer **3** have lengths of 5.8, 9.6, and 7.2 Å per repeat unit, respectively. Even though **3** does not fold into a single or small number of well-defined conformers, as do *o*-phenylene oligomers, many of the rotations of its aromatic rings are correlated, as evidenced by their specific ranges of energetically favorable dihedral angles. These simulations are consistent with the otherwise anomalous shift to higher SEC retention times when **1** is benzannulated to **3**.

The efficiency of the benzannulation of PPE **1** was characterized using a full complement of spectroscopic measurements. The inability of adjacent aromatic rings in **3** to adopt coplanar conformations induces a significant blue shift in its UV/Vis absorption spectrum relative to its PPE precursor **1**. The λ_{max} of **3** is blue-shifted by 140 nm compared to that of **1** (Figure 4a) and its spectrum is strikingly similar to

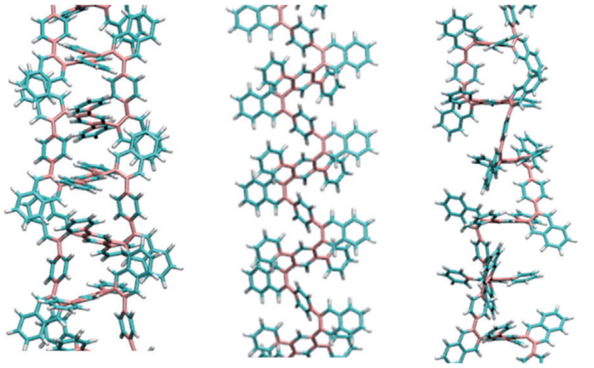

Figure 3. Illustration of the three most common conformations in the simulation of several repeat units of polymer **3** in the presence of 1,2-dichlorobenzene solvent. Truncated polymer structures are shown with their *n*-nonyl side-chains omitted for clarity.

that of benzannulated model compound **5** (Figure 4a). In addition, the absorption spectrum of model compound **4** shows an intense band with defined vibrational structure from 325–375 nm (Figure 4a). If the benzannulation were inefficient, residual alkyne-containing subunits would cause **3** to absorb in this region or at longer wavelengths, yet **3** does not absorb strongly within this spectral range.

Trends observed in the photoemission spectra of **1**, **3**, **4**, and **5** are also consistent with the interpretation that efficient benzannulation of **1** occurred (Figure 4b). The emission of PPE **1** shows well-known components of both isolated and aggregated PPE with local maxima at 426 nm and 447 nm, respectively.[18] Upon benzannulation, the maximum emission blue-shifted by 22 nm but also broadens significantly. Emission over a similarly broad wavelength range was observed by Hartley and co-workers in a series of *o*-phenylene oligomers, which was attributed to emission from two different conformational states.[8a] FTIR spectroscopy of **3** showed increased C(sp^2)–H stretches at 3030 cm^{-1} from the newly installed naphthalene rings (Supporting Information, Figure S27), as well as significant changes in the 500–1500 cm^{-1} region that suggest major modifications to the structure of **3** relative to its PPE precursor **1**. In summary, UV/Vis, fluorescence, and FTIR spectroscopy are each consistent with efficient benzannulation of PPE **1**.

Finally, an isotopic-labeling study also provided direct evidence for the high efficiency of the benzannulation reaction. A sample of PPE **1** with ^{13}C-enriched alkyne moieties was prepared by employing [$^{13}C_2$]trimethylsilylacetylene in the synthesis of the dialkyne monomer. The most intense resonances in ^{13}C NMR spectrum of this sample (Figure 5a) are centered at 92.8 ppm and correspond to the ^{13}C-enriched alkyne moieties. The three small resonances at 128.3, 129.3, and 131.5 ppm correspond to aromatic carbon atoms with naturally abundant amounts of ^{13}C, and occur at identical chemical shifts as the three most intense aromatic resonances in the spectrum of unlabeled **1** (Supporting Information, Figure S10). After benzannulation, the signals of the ^{13}C-enriched alkyne moieties were shifted cleanly to a broad peak centered at 139.5 ppm, and no residual alkyne resonances are visible above the baseline (Figure 5b). Both the ^{1}H and ^{13}C NMR spectra of the ^{13}C-labeled and unlabeled benzannulated polymer obtained at room temperature show peak broadening as a consequence of hindered rotation about the newly installed 2,3-disubstituted naphthalene moieties, consistent with the above MD simulations. ^{13}C NMR spectra obtained in $C_2D_2Cl_4$ sharpen at higher temperatures, such that the nonequivalent ^{13}C-enriched carbon signals are resolved. These resonances are shown in a partial spectrum obtained at 135 °C as an inset of Figure 5b, and complete spectra obtained in 10° increments between 25–135 °C are provided in the Supporting Information (Figures S24 and S25). These resonances are coupled to one another, as determined by a 2D-INADEQUATE experiment (Supporting Information, Fig-

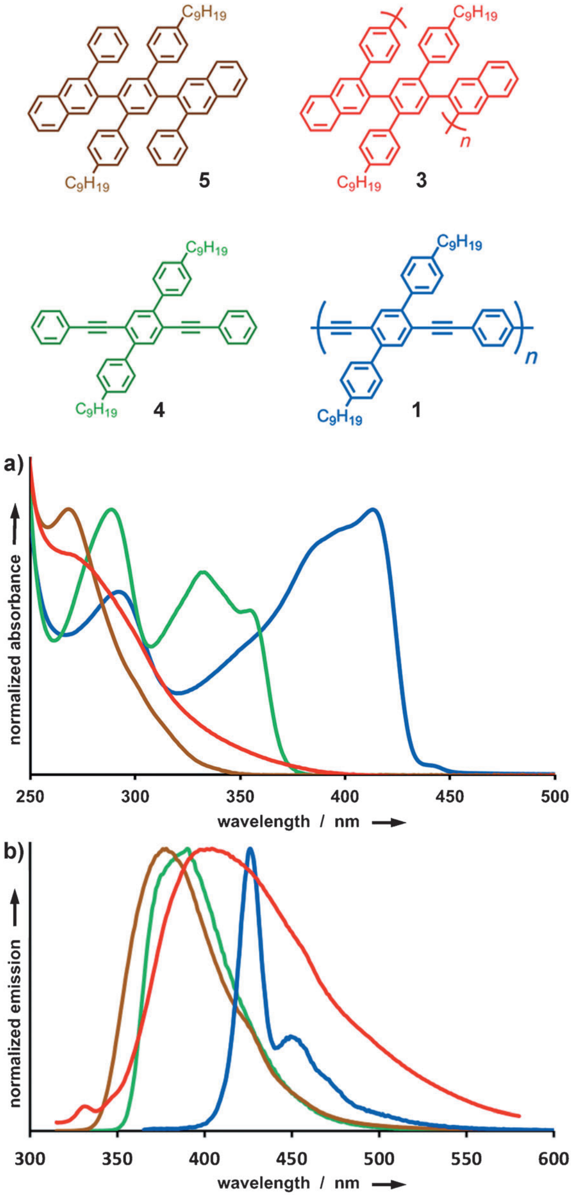

Figure 4. Characterization of the benzannulation of PPE **1**. a) UV/visible absorption, and b) photoemission spectra of PPE **1**, benzannulated polymer **3**, dialkyne **4**, and its benzannulation product **5**. The steric congestion of **3** reduces the effective conjugation length, shifting the absorbance of the polymer to higher energy.

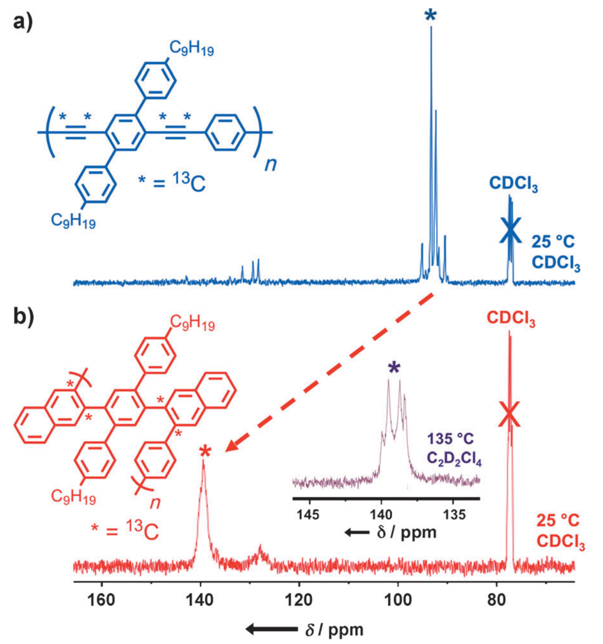

Figure 5. Partial ^{13}C NMR spectra (CDCl$_3$, 100 MHz, RT) of a) ^{13}C-enriched **1**, which was benzannulated to provide b) ^{13}C-enriched **3**. The resonances of the enriched carbon atoms (*) shift to the aromatic region of the spectrum, and no resonances corresponding to residual alkynes are observed. Inset: partial ^{13}C NMR spectrum of **3** (CD$_2$Cl$_4$, 125 MHz, 135 °C) obtained at increased temperature shows resolution and coupling of the two resonances of nonequivalent ^{13}C-enriched carbons.

ure S26). These isotopic labeling experiments, together with the spectroscopic and SEC characterization of polymer **3**, unambiguously demonstrate that this unprecedented transformation of PPE **1** proceeds specifically and efficiently.

In conclusion, we have demonstrated a new approach to prepare otherwise inaccessible polyphenylene architectures using a Yamamoto-type benzannulation reaction. This finding is also the first example of an efficient cycloaddition reaction performed along a conjugated polymer backbone. The high specificity and efficiency of the reaction for polymer modification were characterized using isotopic labeling, and supported by absorption, photoemission, and FT-IR spectroscopy, as well as a study of a model compound. Notably, the benzannulation reaction tolerates additional aromatic substituents adjacent to each alkyne, producing a highly crowded polyphenylene with limited conformational freedom, as determined by size-exclusion chromatography and molecular dynamics simulations. We intend to apply this approach to synthesize a wide variety of congested architectures, such as contorted polycyclic aromatic hydrocarbons, polyarylene dendrimers, and graphene nanoribbons and quantum dots.

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[1] A. C. Grimsdale, K. Leok Chan, R. E. Martin, P. G. Jokisz, A. B. Holmes, *Chem. Rev.* **2009**, *109*, 897–1091.
[2] C. Li, M. Liu, N. G. Pschirer, M. Baumgarten, K. Müllen, *Chem. Rev.* **2010**, *110*, 6817–6855.
[3] D. Türp, T.-T.-T. Nguyen, M. Baumgarten, K. Müllen, *New J. Chem.* **2012**, *36*, 282–298.
[4] a) T. Qin, J. Ding, L. Wang, M. Baumgarten, G. Zhou, K. Müllen, *J. Am. Chem. Soc.* **2009**, *131*, 14329–14336; b) S. Bernhardt, M. Kastler, V. Enkelmann, M. Baumgarten, K. Müllen, *Chem. Eur. J.* **2006**, *12*, 6117–6128.
[5] a) T. Weil, T. Vosch, J. Hofkens, K. Peneva, K. Müllen, *Angew. Chem.* **2010**, *122*, 9252–9278; *Angew. Chem. Int. Ed.* **2010**, *49*, 9068–9093; b) S. Bhosale, A. L. Sisson, P. Talukdar, A. Fürstenberg, N. Banerji, E. Vauthey, G. Bollot, J. Mareda, C. Röger, F. Würthner, N. Sakai, S. Matile, *Science* **2006**, *313*, 84–86; c) A. L. Sisson, N. Sakai, N. Banerji, A. Fürstenberg, E. Vauthey, S. Matile, *Angew. Chem.* **2008**, *120*, 3787–3789; *Angew. Chem. Int. Ed.* **2008**, *47*, 3727–3729.
[6] a) Z. Tomović, M. D. Watson, K. Müllen, *Angew. Chem.* **2004**, *116*, 773–777; *Angew. Chem. Int. Ed.* **2004**, *43*, 755–758; b) M. Müller, C. Kübel, K. Müllen, *Chem. Eur. J.* **1998**, *4*, 2099–2109; c) F. Morgenroth, E. Reuther, K. Müllen, *Angew. Chem.* **1997**, *109*, 647–649; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 631–634.
[7] a) K. Okamoto, C. K. Luscombe, *Polym. Chem.* **2011**, *2*, 2424–2434; b) E. L. Lanni, A. J. McNeil, *J. Am. Chem. Soc.* **2009**, *131*, 16573–16579; c) R. Miyakoshi, K. Shimono, A. Yokoyama, T. Yokozawa, *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.
[8] a) J. He, J. L. Crase, S. H. Wadumethrige, K. Thakur, L. Dai, S. Zou, R. Rathore, C. S. Hartley, *J. Am. Chem. Soc.* **2010**, *132*, 13848–13857; b) C. S. Hartley, J. He, *J. Org. Chem.* **2010**, *75*, 8627–8636; c) S. M. Mathew, C. S. Hartley, *Macromolecules* **2011**, *44*, 8425–8432.
[9] E. Ohta, H. Sato, S. Ando, A. Kosaka, T. Fukushima, D. Hashizume, M. Yamasaki, K. Hasegawa, A. Muraoka, H. Ushiyama, K. Yamashita, T. Aida, *Nat. Chem.* **2011**, *3*, 68–73.
[10] L. Dössel, L. Gherghel, X. Feng, K. Müllen, *Angew. Chem.* **2011**, *123*, 2588–2591; *Angew. Chem. Int. Ed.* **2011**, *50*, 2540–2543.
[11] a) A. R. Marshall, U. H. F. Bunz, *Macromolecules* **2001**, *34*, 4688–4690; b) J. B. Beck, A. Kokil, D. Ray, S. J. Rowan, C. Weder, *Macromolecules* **2002**, *35*, 590–593.
[12] R. M. Moslin, C. G. Espino, T. M. Swager, *Macromolecules* **2009**, *42*, 452–454.
[13] The highly electron-rich alkynes of poly(thienyl ethynylenes) undergo additions to tetracyanoethylene or 7,7,8,8-tetracyanoquinodimethane. Conversions of around 25 % of the alkynes are typical. See, for example: Y. Yuan, T. Michinobu, M. Ashizawa, T. Mori, *J. Polym. Sci. Part A* **2011**, *49*, 1013–1020.
[14] N. Asao, T. Nogami, S. Lee, Y. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 10921–10925.
[15] a) A. J. Blake, P. A. Cooke, K. J. Doyle, S. Gair, N. S. Simpkins, *Tetrahedron Lett.* **1998**, *39*, 9093–9096; b) see Ref. [9].
[16] W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.
[17] S. J. Plimpton, *Comp. Phys.* **1995**, *117*, 1–19.
[18] a) C. E. Halkyard, M. E. Rampey, L. Kloppenburg, S. L. Studer-Martinez, U. H. F. Bunz, *Macromolecules* **1998**, *31*, 8655–8659; b) V. E. Williams, T. M. Swager, *Macromolecules* **2000**, *33*, 4069–4073; c) U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605–1644.