Synthesis of Poly(vinylacetylene) Block Copolymers by Atom Transfer Radical Polymerization

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The preparation of well-ordered nanostructured carbon materials has attracted interest due to their potential in a number of applications including energy storage devices,[1] sensors,[2] and electronics devices.[3] Recently, a novel low-cost route to prepare well-defined nanocarbon materials was developed based on the pyrolysis of block copolymers that contains a carbon precursor block such as polyacrylonitrile (PAN) and a sacrificial block (e.g., poly(*n*-butyl acrylate).[4−8] The resulting carbon structures rely on the self-organization of block copolymers to form well-ordered morphologies,[9] and fabrication conditions which can be controlled in the nanoscale by defining the relative compositions of each block. Carbons derived from PAN precursors, however, also contain up to 7% nitrogen, which results in defect sites that affect the electronic properties of the materials. This fact led us to explore other types of block copolymers that could result in the preparation of pure carbon structures.

Poly(vinylacetylene) (PVA), a polymer that structurally resembles PAN without the inherent nitrogen group, may possess the potential to give similar nanostructured materials with high carbon yield without the presence of preformed n-type dopants. There have been a few reports on the preparation of PVA from simple conjugated enyne molecules by cationic polymerization,[10] anionic polymerization,[11−14] thermal polymerization,[13] or conventional free radical polymerization.[15−17] The anionic polymerization of VA derivatives including 2-methyl derivatives of VA exhibit a living-like character.[18,19] Thermal treatment of PVA in the temperature range of 150−400 °C resulted in the formation of conjugated cross-linked materials with moderate electrical conductivity and thermal stability.[10] However, controlled polymerization of vinylacetylene remains challenging due to its conjugated character and side reactions related to the presence of pendant acetylene group and the acidic acetylene proton. The difficulty in polymerizing vinylacetylene has limited the investigation of PVA-containing materials as effective high yield carbon precursors for nanostructured carbon systems.

In order to prepare well-defined block copolymers that contain PVA, we decided to investigate controlled/living radical polymerization (CRP) techniques.[20] Atom transfer radical polymerization (ATRP),[21−26] one of the most widely used CRP methods, is a powerful tool for the preparation of well-defined polymers with predetermined molecular weight, low polydispersity, and high degrees of functionality. Here we report the first CRP of vinylacetylene and synthesis of block copolymers containing poly(vinylacetylene) segments via ATRP. The active acetylenic hydrogen atom in vinylacetylene was substituted with the trimethylsilyl group in order to prevent 1,4-polymerization and Cu(I)-catalyzed coupling reactions. It was found that conducting the homopolymerization of trimethylsilyl-protected vinylacetylene (VATMS) at lower temperature prevented side reactions and gave a well-controlled polymer with low polydispersity. The more robust process, activators regenerated by electron transfer (ARGET) ATRP,[27,28] was also successfully utilized to polymerize VATMS. Based on these homopolymerization studies, block extension of poly(methyl methacrylate) (PMMA) macroinitiators with VATMS was performed, providing the first example of well-defined block copolymers with PVA segments.

VATMS was prepared according to the reported method.[17] ATRP of VATMS was carried out using CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy)[29] as the catalyst (Table 1, entries 1−4). Since PVATMS has relatively low polarity, a 50% v/v mixture of anisole or acetone was used as a solvent for polymerization of VATMS in order to dissolve the catalyst and polymer. ^{1}H NMR spectroscopy was used to follow monomer conversion by comparing integral ratios between monomer and solvent, while the molecular weight and the molecular weight distribution were estimated by gel permeation chromatography (GPC) with tetrahydrofuran as an eluent. GPC calibration using PMMA standards overestimates the molecular weight of PVATMS as a result of significantly different hydrodynamic volumes, as is the case with polyacrylonitrile,[30] giving molecular weights ∼2 times larger than those calculated by ^{1}H NMR.

When the reaction was carried out at 90 °C, the polymerization was less controlled, showing a low-molecular-weight shoulder in GPC traces with increasing polydispersity (Table 1, entry 1, Figure S1). Also, the first-order kinetic plot of the ATRP of VA-TMS showed curvature above 40% conversion. These results indicated that the radical concentration decreased during the reaction due to some side reactions. Several side reactions could be considered: (1) copolymerization with acetylenic, vinylic, and allenic polymers by 1,2-, 3,4-, and 1,4-addition, respectively; (2) an outer-sphere electron transfer (OSET) reaction[31] where growing radicals react with Cu(I) catalyst to produce carbanion which can abstract a proton; (3) an elimination reaction to produce HBr; (4) termination reactions due to plausible low values of the propagation rate constant. The ^{13}C NMR measurements revealed the absence of vinylic and allenic structures, indicating selective polymerization by 1,2-addition and negligible contribution of side reactions (1). However, when the reaction targeting low molecular weight polymer was followed by ^{1}H NMR (Table 1, entry 2), the content of bromine end-group functionality decreased during the polymerization, demonstrating in the loss of dormant chain ends (possible reactions 2, 3, and 4).

In order to prevent, or significantly reduce, such side reactions, we investigated several techniques which increase control of the polymerization of VATMS. One strategy involved reducing radical concentration during ATRP to decrease termination reactions and elimination reactions. For instance, lowering the reaction temperature can reduce radical concentration during ATRP and thus reduce contribution of side reactions. Indeed, the reaction carried out at 60 °C improved the control of ATRP of VATMS (Table 1, entry 3), while the reaction at

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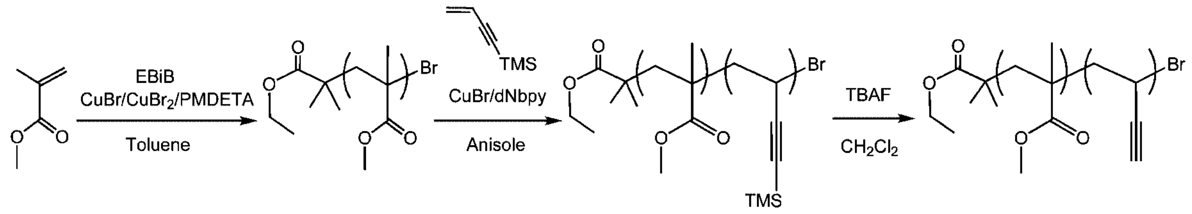
Table 1. ATRP of Trimethylsilylvinylacetylene

	molar ratio									
entry	EBiB/VATMS	Cu	ligand	solvent	temp (°C)	time (h)	conv^a	$M_{n,theor}$	$M_{n,exp}$	M_w/M_n^{a}
1	1/100	CuBr 1	dNbpy 2	anisole	90	7	39	5000	3300^a 7000^b	1.40
2	1/20	CuBr 0.5	dNbpy 1	acetone-d_6	40	24	59	17,00	1900 3000	1.07
3	1/100	CuBr 1	dNbpy 2	anisole	60	90	36	4700	3700^a 5100^b	1.33
4	1/100	CuBr 1	dNbpy 2	anisole	20	150	44	5700	5900^a 13000^b	1.14
5^c	1/100	$CuBr_2$ 0.01	TPMA/Sn(EH)$_2$ 0.03/0.01	anisole	40	300	57	7300	11000^b	1.50
6^c	1/200	$CuBr_2$ 0.01	TPMA/Sn(EH)$_2$ 0.03/0.01	anisole	40	224	35	8900	12800^b	1.17

^{a} Based on ^{1}H NMR spectra. ^{b} Based on GPC using PMMA standards. ^{c} ARGET ATRP.

Scheme 1. Preparation of PMMA-*b*-PVA Block Copolymer



20 °C yielded PVATMS with low polydispersity (1.14) after 150 h (Table 1, entry 4).

Furthermore, we reduced Cu metal concentration, which could cause side reactions,[32] by employing ARGET ATRP, where the reaction is conducted with a significantly lower concentration of Cu metal in the presence of a reducing agent such as tin(II) 2-ethylhexanoate (Sn(EH)$_2$).[27,28] During the reaction, the reducing agent constantly regenerates the Cu(I) species from Cu(II), compensating for the loss of ATRP activator by side reactions and other impurities such as oxygen or various other radical inhibitors. Therefore, radical termination reactions and Cu metal-participating side reactions can be minimized in this method.

Figure S2 presents a kinetic plot of the ARGET ATRP of VATMS (reaction conditions: [VATMS]:[EBiB]:[CuBr$_2$]:[TPMA]:[Sn(EH)$_2$] = 100:1:0.01:0.03:0.1; T = 40 °C, in 50% v/v anisole). The reaction followed linear first-order kinetics, showing a constant concentration of active species for up to 300 h. As a result, a sample of PVATMS, molecular weight (M_n = 12 800) with low polydispersity (M_w/M_n = 1.17), was prepared (Table 1, entries 5 and 6). The side reactions that caused the loss of the halide-dormant species are still not clear. However, lowering the reaction temperature and using ARGET ATRP significantly increased the control of VATMS polymerization.

After the successful homopolymerization of VATMS at low temperature, the synthesis of block copolymers of PMMA-*b*-PVATMS was then investigated (Scheme 1). PVATMS prepared by ATRP can be used as a macroinitiator for further chain extension. However, when PVATMS macroinitiator obtained by ARGET ATRP (M_n = 12 800, M_w/M_n = 1.17) was used, the block extension with MMA was poorly controlled and gave a copolymer with a bimodal profile in GPC traces (Figure S3). As mentioned above, PVATMS loses terminal bromine functionalities by aforementioned side reactions, producing dead chains.

Therefore, block extension of PMMA with VATMS was attempted. The PMMA macroinitiator was prepared by ATRP using ethyl 2-bromoisobutyrate (EBiB) as an initiator and yielded PMMA with M_n = 15 000 and M_w/M_n = 1.17. Chain extension of PMMA with VATMS was conducted by ATRP using CuBr/dNbpy as the catalyst at 40 °C. GPC profiles during the chain extension were monomodal, which indicated the successful synthesis of a block copolymer by extension of PMMA with VATMS. The block copolymer containing 28 wt % of VATMS was subsequently desilylated by reaction with TBAF in CH_2Cl_2. After desilylation, the proton signal of the TMS groups disappeared, and the characteristic ≡C−H proton was observed in the ^{1}H NMR spectrum (Figure S4). Also, the FT-IR spectrum of the desilylated block copolymer showed the presence of an acetylene C−H stretching vibration peak at 3300 cm^{-1} (Figure S5). Furthermore, the block copolymer exhibited exothermic peaks in the temperature range from 200 to 350 °C characteristic of stabilization of the carbon precursor by cross-linking in PVA, whereas there was no peak in this region detected in the block copolymer before deprotection.

In conclusion, we report successful synthesis of PVATMS from trimethylsilyl-protected vinylacetylene via ATRP and ARGET ATRP when conducted at lower temperature. Furthermore, a PMMA-*b*-PVATMS block copolymer was prepared by ATRP, followed by desilylation to give the first example of a PMMA-*b*-PVA block copolymer. The thermal properties and morphology of vinylacetylene-containing polymers are currently under investigation, and the potential of block copolymers as

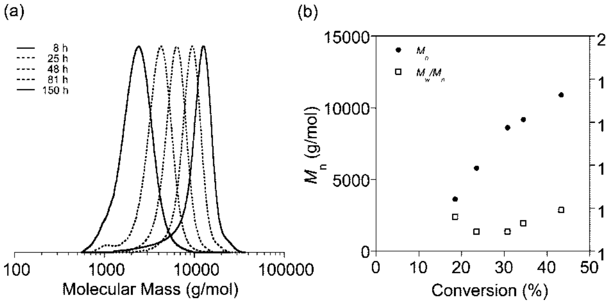


Figure 1. Evolution of GPC traces (a) and evolution of molecular weights and M_w/M_n with monomer conversion (b) for ATRP of VATMS at 40 °C. Reaction conditions: [VATMS]:[EBiB]:[CuBr]:[dNbpy] = 100:1:1:2; solvent: anisole.

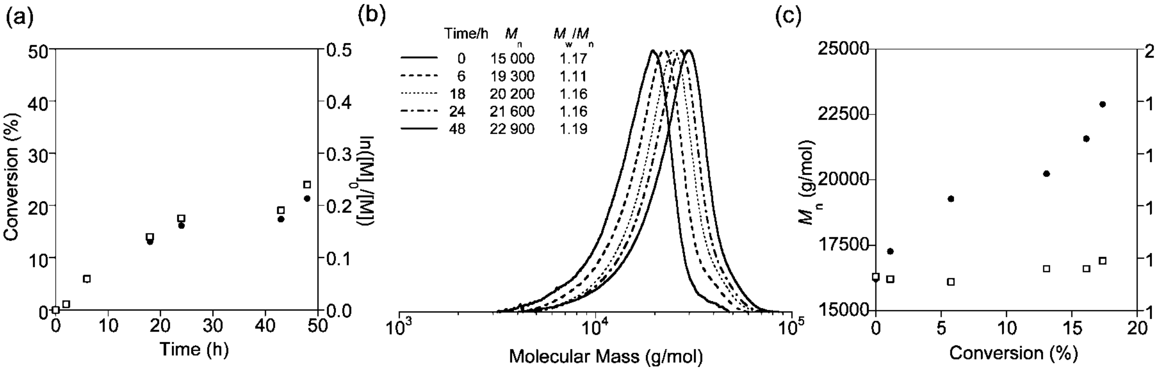


Figure 2. Block extension of PMMA with VATMS by ATRP: kinetics (a) and evolution of SEC traces (b); dependence of molecular weights and molecular weight distribution (c).

precursors for carbon-containing nanostructured materials will be explored.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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