COMMUNICATION

Synthesis of Vinyl Iodide Chain-end Polymers *via* Organocatalyzed Chain-end Transformation

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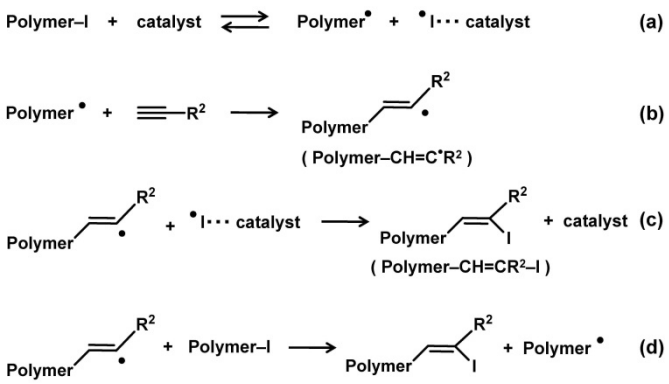
In the presence of alkynes (CH≡C–R^2), iodide chain-end polymers (Polymer–I) were successfully transformed to vinyl iodide chain-end polymers (Polymer–CH=CR^2–I) in a single step *via* organocatalysis. This reaction is completely metal-free and easy to carry out without using special reagents or special conditions. The polymers encompassed polyacrylates and polymethacrylate, and additional functionalities (e.g., OH and CF_3) was also incorporated into the R^2 moiety. The obtained Polymer–CH=CR^2–I further served as a useful precursor for copper-catalyzed cross-coupling reactions with various thiols (R^3–SH) to yield vinyl sulfide chain-end polymers (Polymer–CH=CR^2–SR^3) with various R^3 moieties. Interestingly, under selected conditions, this organocatalysis also offered block-like copolymers containing a conjugated oligo-alkyne segment and a non-conjugated polyacrylate segment. Exploiting the unique structure, the block-like copolymer was used as an efficient dispersant of carbon nanotubes.

Vinyl iodides (R^1–CH=CR^2–I) are useful precursors for metal-catalyzed coupling reactions to form vinyl sulfides,[1] vinyl amides,[2,3] vinyl azides[4] and also for decarboxylative coupling reactions to form sp^3–sp^2 bonds.[5] In polymer chemistry, vinyl iodides have been incorporated in polymer backbones *via* solid-phase polymerizations of diiododiynes[6] and diiodotetraynes,[7] step-growth polymerizations of alkyl diyne and alkyl diiodides,[8] and post-polymerization transformations.[9,10] However, there has been no report for the synthesis of polymers with vinyl iodide at the chain end.

Living (or reversible deactivation) radical polymerization offers polymers with narrow molecular weight distributions.[11–16] The obtained polymers possess a capping agent (X) at the chain end, and X has been converted to various functional groups, yielding chain-end functionalized polymers.[17,18]

Our research group developed an organocatalyzed living radical polymerization using alkyl iodides as initiators (X = iodide) and organic molecules as catalysts.[19–21] An example of the catalyst is tetrabutylammonium iodide ($Bu_4N^+I^-$) (BNI). Mechanistically (Scheme 1a), a polymer-iodide dormant species (Polymer–I) coordinates a catalyst *via* halogen bonding to form a complex (Polymer–I···catalyst), which reversibly generates a propagating radical (Polymer$^\bullet$) and an $^\bullet$I···catalyst complex. Through post-treatment via nucleophilic substitution, the iodide of Polymer–I was transformed to several functional groups, yielding chain-end functionalized polymers.[22-26]

In the present work, instead of nucleophilic substitution, we explored an organocatalyzed radical addition of alkynes to yield vinyl iodide chain-end functionalized polymers. Polymer–I and an organic catalyst (BNI) generate Polymer$^\bullet$ and I$^\bullet$···catalyst (Scheme 1a). Polymer$^\bullet$ adds to an alkyne (CH≡C–R^2) to form a vinyl radical species (Polymer–CH=C$^\bullet$$R^2$) (Scheme 1b), which subsequently reacts with I$^\bullet$···catalyst to give the vinyl iodide chain-end functionalized polymer (Polymer–CH=CR^2–I) (Scheme 1c). Polymer–CH=C$^\bullet$$R^2$ can also abstract iodide from Polymer–I *via* a radical chain transfer to generate Polymer–CH=CR^2–I (Scheme 1d).[27] Because the vinyl-iodide bond is too strong to be cleaved by the studied catalyst (BNI), we are able to obtain Polymer–CH=CR^2–I in a stable manner. Notably, this approach is free from metal, since the catalyst (BNI) is organic. This approach was amenable to various polymers including functional polyacrylates and polymethacrylates. A scientific interest is the regulation in the number of alkyne units added



Scheme 1. (a) Reversible activation of Polymer–I to Polymer$^\bullet$, (b) addition of Polymer$^\bullet$ to alkyne, and (c and d) formation of vinyl iodide chain-end polymer.

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Table 1. Reactions of Polymer–I with CH≡C–R^2.

Entry	Polymer–I[a]	CH≡C–R^2 [b]	$[CH{\equiv}C{-}R^2]_0$/ $[Polymer{-}I]_0/[BNI]_0$	T (°C)	t (h)	Diglyme (solvent)	Polymer–I Remaining[c]	Polymer–$(CH{=}CR^2)_m$–I[c]					
								m = 1	2	3	4	5	6
1	PBA–I	PA	10 / 1 / 1	110	6	50 wt%	9%	84%	7%	-	-	-	-
2	PBA–I	PA	10 / 1 / 2	110	14	50 wt%	5%	86%	9%	-	-	-	-
3	PBA–I	PA	30 / 1 / 1	110	6	50 wt%	8%	79%	13%	-	-	-	-
4	PBA–I	PA	60 / 1 / 1	110	6	30 wt%	9%	72%	19%	-	-	-	-
5	PBA–I	PA	100 / 1 / 1	110	6	None	12%	47%	19%	7%	9%	6%	-
6	PBA–I	PA	100 / 1 / 1	110	6	50 wt%	6%	63%	16%	5%	5%	5%	-
7	PBA–I	PA	300 / 1 / 10	110	14	None	14%	23%	16%	12%	14%	13%	8%
8	PMEA–I	PA	10 / 1 / 2	110	14	50 wt%	0%	90%[d]	-	-	-	-	-
9	PMMA–I	PA	100 / 1 / 10	70	14	None	41%	50%	9%	-	-	-	-
10	PBA–I	EBA	10 / 1 / 2	110	14	50 wt%	8%	92%	-	-	-	-	-
11	PBA–I	TFT	10 / 1 / 2	110	14	50 wt%	7%	84%	9%	-	-	-	-
12	PBA–I	EBP	10 / 1 / 2	110	14	50 wt%	10%	79%	11%	-	-	-	-
13	PBA–I	PEG-alkyne	10 / 1 / 2	110	14	50 wt%	Average m value = 2.1 units[e]						

[a] PBA–I = poly(butyl acrylate)-iodide (M_n = 4000 and $Đ$ = 1.19), PMEA–I = poly(2-methoxyethyl acrylate)-iodide (M_n = 6200 and $Đ$ = 1.25), and PMMA–I = poly(methyl methacrylate)-iodide (M_n = 4200 and $Đ$ = 1.19). [b] PA = phenylacetylene, EBA = 4-ethynylbenzylalcohol, TFT = 4-ethynyltrifluorotoluene, EBP = 4-ethynylbiphenyl, and PEG-alkyne = 3-(polyethylene glycol monomethyl ether)-prop-1-yne. [c] Estimated based on the peak intensity ratio in MALDI-TOF-MS. [d] The remaining 10% is an unidentified product. [e] Estimated using ^{1}H NMR.

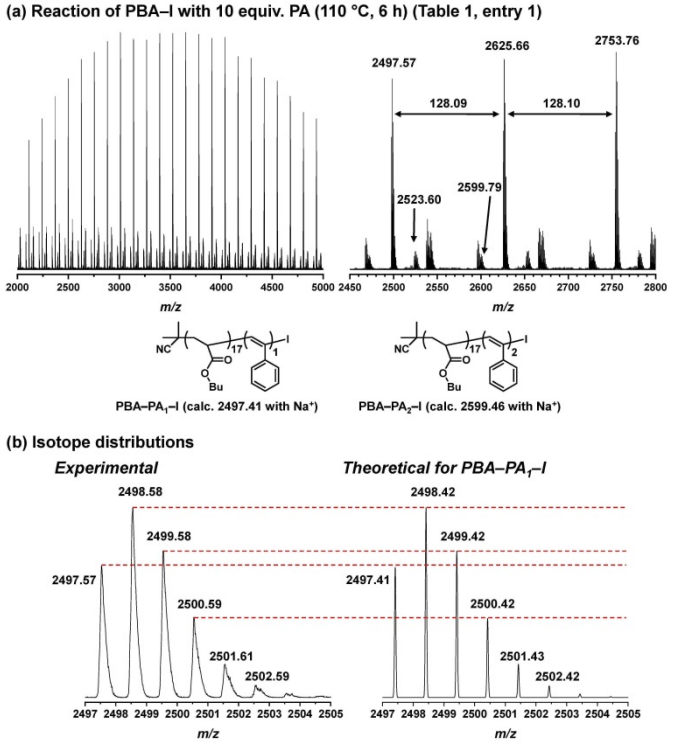

Fig. 1. (a) MALDI-TOF-MS spectrum of the polymer after reaction of PBA–I with PA (Table 1, entry 1) and (b) its experimentally observed isotope distribution and the theoretical isotope distribution of PBA–PA_1–I

to the chain end. In selected conditions, (nearly) single alkyne addition was achieved to form Polymer–CH=CR^2–I. Additional functionalities (e.g., OH and CF_3) can also be incorporated in R^2, yielding unique polymers double-functionalized with a vinyl iodide and an additional R^2 functionality. Moreover, Polymer–CH=CR^2–I can serve as a useful precursor for various coupling reactions with small molecules, polymers, and solid surfaces. The present paper shows cross-coupling reactions of Polymer–CH=CR^2–I with thiols (R^3–SH) to yield vinyl sulfide chain-end polymers (Polymer–CH=CR^2–SR^3) with several R^3 moieties. Multiple alkyne addition was also achieved by increasing the concentration of the alkyne, yielding interesting block-like copolymers with a non-conjugated (polyacrylate) segment and a conjugated (oligo-acetylene) segment. Exploiting the unique structure, the block-like copolymer was used as an efficient dispersant of multi-walled carbon nanotubes.

We synthesized a poly(butyl acrylate)-iodide (PBA–I) in the polymerization of butyl acrylate (BA) (monomer, 100 equiv.) using 2-iodo-2-methylpropionitrile (CP–I) (alkyl iodide initiator, 1 equiv.) and BNI (catalyst, 4 equiv.) at 110 °C for 6 h (ESI). The obtained polymer possessed the CP group at the initiating chain end and iodide at the growing chain end. After the purification *via* reprecipitation twice, we obtained a PBA–I with M_n = 4000 and $Đ$ (= M_w/M_n) = 1.19, where M_n and M_w are the number-average and weight-average molecular weights, respectively, and $Đ$ is dispersity. By the ^{1}H NMR analysis, the iodide-chain-end fidelity was estimated to be 98% (93–100% with experimental error) (ESI).

We conducted the chain-end transformation by heating a mixture of PBA–I (1 equiv.), phenylacetylene (PA) (CH≡C–R^2 with R^2 = phenyl, 10 equiv.), and BNI (1 equiv.) in diglyme (solvent, 50 wt%) at 110 °C for 6 h (Table 1, entry 1). After the reaction, the polymer was purified using a preparative gel permeation chromatography (GPC) and then analyzed with matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) (Fig. 1a) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as a matrix and sodium trifluoroacetate (NaTFA) as an additive salt. The polymer can possess ^{12}C and ^{13}C atoms. For simplicity, the theoretical masses discussed below and the experimental masses given in the figures (MALDI-TOF-MS

spectra in Fig. 1a and ESI) are those without ^{13}C atom (*i.e.*, with only ^{12}C atoms). In Fig. 1a, a main series of peaks appeared at 2497.57, for example, with regular intervals of 128.09 (BA unit). The peak at 2497.57 closely matches the theoretical mass (2497.41) of the desired vinyl iodide chain-end species (PBA–PA_1–I), where the subscript is the number of the PA unit. The theoretical mass is calculated by 68.05 + 128.0838×*n* + *Y* + 22.99, where 68.05, 128.0838, *Y*, and 22.99 are the masses of the initiating CP group, BA, the terminal chain-end group, and Na^+, respectively, and *n* is the number of the BA unit. The experimental isotope distributions perfectly matched the theoretical distributions (Fig. 1b), confirming the generation of PBA–PA_1–I. A small peak observed at 2599.79 (Fig. 1a) is attributed to the polymer containing two PA units (PBA–PA_2–I) (theoretical mass = 2599.46), and another small peak observed at 2523.60 (Fig. 1a) is attributed to the unreacted PBA–I.

From the peak intensity ratio, we estimate that 84% of PBA–I was successfully converted to PBA–PA_1–I, 7% of PBA–I was converted to PBA–PA_2–I, and 9% of PBA–I remained unreacted (Table 1, entry 1). It should be noted that the intensity ratio may not be the same as that of the actual amounts of the species and should be viewed as an estimate. We also assume that the molecular weight of the polymer chain does not significantly affect the chain-end transformation reaction. There were other minor peaks in the spectrum (Fig. 1a), which were assigned to PBA with a lactone ring end group (PBA-Lac) (theoretical mass = 2595.64), BA macromonomer (PBA–ene) (theoretical mass = 2537.64), and PBA with a hydroxyl chain end (PBA–OH) (theoretical mass = 2541.63). They seemed to be generated during the synthesis of PBA–I or the MALDI-TOF-MS analysis (Fig. S4a in the ESI). Because their peaks were small and we focus on the post-transformation of PBA–I, the peak intensities of PBA–ene, PBA–OH and PBA–Lac are excluded from the calculations in the present paper. Thus, the values given in Table 1 are estimates on these assumptions.

In order to reduce the unreacted PBA–I, we increased the reaction time from 6 h to 14 h and the amount of the catalyst (BNI) from 1 equiv. to 2 equiv. (Table 1, entry 2). Although the complete consumption was not attained, the unreacted PBA–I was reduced from 9% to 5%. PBA–PA_1–I was formed in an 86% yield with 9% of PBA–PA_2–I. Thus, the desired PBA–PA_1–I was successfully obtained in a high yield (86%).

We increased the amount of PA from 10 (Table 1, entry 1) to 30, 60, 100 and 300 equivalents (Table 1, entries 3–7). In these cases, the addition of multiple PA units to PBA$^\bullet$ (Scheme 1b) is likely to occur before PBA–PA$^\bullet$ is capped with iodide (Schemes 1c and 1d). In fact, with an increase in the amount of PA, a larger amount of PBA–PA_2–I (with two PA units) was generated (from a 7% yield to a 19% yield). Interestingly, with 100 and 300 equivalents of PA, PBA–PA_m–I polymers with 2, 3, 4, 5 and 6 PA units were obtained, where *m* is the number of the PA units (Table 1, entries 5–7 and Figs. S8–10 in the ESI). These polymers are block-like copolymers with a non-conjugated (PBA) segment and a conjugated (oligo-PA) segment. The absence (Table 1, entry 5) and presence (Table 1, entry 6) of the solvent (diglyme) gave similar results, but the presence of the solvent slightly increased the yield of the single addition product (PBA–PA_1–I) and decreased the yields of the multiple addition products because of the dilution of PA.

The scope of the polymer was extended to a functional polyacrylate, *i.e.*, poly(2-methoxyethyl acrylate)-iodide (PMEA–I), which is a biocompatible polyacrylate. 90% of PMEA–I was successfully converted to vinyl iodide chain end PMEA (Table 1, entry 8). We further extended the polymer scope from polyacrylates to a polymethacrylate, *i.e.*, poly(methyl methacrylate)-iodide (PMMA–I). The reaction of PMMA–I and PA yielded the vinyl iodide species in a 59% yield (PMMA–PA_1–I (50%) and PMMA–PA_2–I (9%)) (Table 1, entry 9). Further increases in the reaction time and the amounts of BNI and PA did not give a greater yield. The generated PMMA$^\bullet$ radical seemed less reactive with PA than the polyacrylate radicals. We preliminarily tested a polystyrene-iodide (PSt–I) but did not observe the expected vinyl iodide chain-end polymers, possibly because of the low reactivity of the generated PSt$^\bullet$ radical with PA.

We also incorporated functional groups in the R^2 moiety of Polymer–CH=CR^2–I. For PBA–I, we used 4-ethynylbenzyl alcohol (EBA) with a hydrophilic OH group (R^2 = –PhCH_2OH), 4-ethynyl-trifluorotoluene (TFT) with a super-hydrophobic fluorinated group (R^2 = –PhCF_3), 4-ethynylbiphenyl (EBP) with a biphenyl group (R^2 = –PhPh), and 3-(polyethylene glycol monomethyl ether)-prop-1-yne (PEG-alkyne) (M_n = 400) with a biocompatible hydrophilic PEG group (R^2 = –PEG). The desired vinyl iodide chain-end PBAs with OH, CF_3, and biphenyl functionalities in the R^2 moiety were obtained in high (79–92%) yields (Table 1, entries 10–12). For PEG-alkyne, because PEG has a molecular weight distribution, MALDI-TOF-MS was not effective to determine the yield. Thus, we used ^1H NMR and determined the average *m* value to be 2.1 (Table 1, entries 13 and Fig. S14 in the ESI).

The obtained PBA–PA_m–I (Table 1, entry 2, with *m* = 0 (5%), *m* = 1 (86%), and *m* = 2 (9%)) was utilized in copper catalyzed cross-coupling reactions with thiols (R^3–SH) to form vinyl sulfide chain-end polymers (PBA–PA_m–S–R^3). The MALDI-TOF-MS analysis showed that the coupling with dodecanethiol (R^3 = –$C_{12}H_{25}$) yielded a vinyl sulfide chain-end polymer bearing the long alkyl ($C_{12}H_{25}$) chain in a high yield (85%) (*m* = 1 and 2), while a small amount of PBA–PA_1–I (*m* = 1) was unreacted (10%) and PBA–I (*m* = 0) was converted to unidentified species (5%) (Table 2, entry 1). The coupling with mercaptoethanol (R^3 = –C_2H_4OH) yielded vinyl a sulfide chain-end polymer with the OH functionality (*m* = 1 and 2) in a 46% yield (Table 2, entry 2). The coupling with poly(ethylene glycol) methyl ether thiol (R^3 = –PEG) (M_n = 800) yielded a vinyl sulfide chain-end polymer with ca. 0.6 PEG segments on average (Table 2, entry 3 and Fig. S19 in the ESI). These results demonstrate that PBA–PA_m–I works a useful precursor for the post reaction. In addition, we used 2-phenylethanethiol (R^3 = –$C_2H_4C_6H_5$) and 3,6-dioxa-1,8-octanedithiol (R^3 = –$(C_2H_4O)_2C_2H_4$SH), but they gave low (22%) and zero yields, respectively (Figs. S17 and S18 in the ESI).

The block-like copolymer (with *m* ≤ 6) obtained in Table 1 (entry 7) with non-conjugated (PBA) and conjugated (oligo-PA) segments was used as a dispersant of carbon nanotubes (CNT). The conjugated oligo-PA segment can work as an anchoring

segment to the aromatic CNT surface, and the PBA segment can work as a dispersing segment in an organic solvent. A mixture of multi-walled CNT (1 mg) and a polymer (200 mg) in toluene (8 mL) was sonicated and subsequently stood for 30 min. Fig. 2 shows the images of the mixtures using no polymer (sample A), original PBA–I (sample B), and PBA–PA_m–I (with $m \leq 6$) (sample C) for comparison. As Fig. 2 clearly shows, CNT was well dispersed using PBA–PA_m–I even after the 30 min standing, while CNT almost completely precipitated using no polymer or using PBA–I (without an anchoring segment) after the 30 min standing. The laser diffraction analysis showed that the size of the dispersed CNT was 6.4 μm using PBA–PA_m–I, which was much smaller than those using no polymer (43 μm) and PBA–I (38 μm). These results demonstrate the effective use of the block-like copolymer as a dispersant of CNT.

Table 2. Cross-coupling reactions of PBA–PA_m–I[a] with R^3–SH at 100 °C.

Entry	R^3–SH	*t* (h)	unreacted PBA–PA_m–I[b]	PBA–PA_m–SR^3 [b]
1	$C_{12}H_{25}SH$	24	10% (*m* = 1)[c]	85% (*m* = 1 and 2)[c]
2	HOC_2H_4SH	48	22% (*m* = 1)[d]	46% (*m* = 1 and 2)[d]
3	PEG-SH	48	ca. 0.6 PEG segments on average	

[a] PBA–PA_m–I (with *m* = 0 (5%), *m* = 1 (86%), and *m* =2 (9%)) obtained in Table 1, entry 2. [b] Calculated based on the peak intensity ratio in MALDI-TOF-MS (entries 1 and 2) and calculated using ^{1}H NMR (entry 3). [c] PBA–I (*m* = 0) (5%) was converted to unidentified species. [d] The rest (32%) is a mixture of unidentified (side) products generated from PBA–PA_m–I (*m* = 0–2).

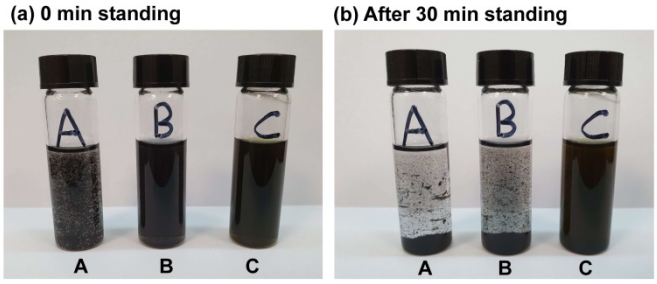

Fig. 2. Images of mixtures of CNT (1 mg) and polymer (0 or 200 mg) in toluene (8 mL); sample A: with no polymer, sample B: with PBA–I (M_n = 4000 and $Đ$ = 1.19 used for the reactions in Table 1), and sample C: with PBA–PA_m–I (Table 1, entry 7) for the (a) 0 min and (b) 30 min standing.

In conclusion, Polymer–I was successfully transformed to Polymer–CH=CR^2–I *via* the organocatalyzed radical addition to alkynes in a metal-free manner. The polymers encompassed polyacrylates and polymethacrylates, and functional groups were also fabricated in R^2. Polymer–CH=CR^2–I further served as a useful precursor in cross-coupling reactions with thiols to generate vinyl sulfide chain-end polymers with additional functional groups. Interestingly, the radical addition method also offered block-like copolymers containing non-conjugated and short conjugated segments by simply increasing the concentration of alkynes in the reaction. The block-like copolymer was exploited as an efficient dispersant of CNT.

Conflicts of interest

There are no conflicts to declare.

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