Supplementary Material (ESI) for Chemical Communications

ELECTRONIC SUPPORTING INFORMATION

Toward the Synthesis of Sequence-controlled Vinyl Copolymers

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Materials and Methods.

Methyl 2-bromopropionate, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), tris[2-(dimethylamino)ethyl]amine (Me6TREN), copper(II) bromide ($CuBr_2$), potassium bromide (KBr) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO), sodium hypochlorite (NaOCl, 14% available chlorine), dimethylaminopyridine (DMAP) and EDC hydrochloride were purchased from Alfa Aesar. Methyl acrylate, copper powder, isopropanol and sodium bicarbonate was purchased from Sinopharm Chemical (China). Allyl alcohol was purchased from Fuchen Chemical (China). Methyl acrylate was distilled before using, and other reagents were used as received without further purification.

^{1}H NMR spectra were recorded on a 300 MHz JOEL spectrometer, using $CDCl_3$ as solvent. ESI mass spectra were recorded on an Agilent 6300 ion trap mass spectrometer, polymer solutions (0.1 mg/mL in methanol, and ammonium formate at a concentration of 20 mM was added to enhance the ionization) were injected at 10uL/min.

Synthesis of PMA support *via* ATRP (1)

Methyl acrylate (5 mL, 55 mmol) was polymerized using methyl 2-bromopronionate (1 mL, 9 mmol) as initiator, and CuBr (13 mg, 0.09 mmol) and PMDETA (19 uL, 0.09 mmol) as catalyst. The reaction was carried out at 30C overnight. After that, the mixture was passed through a neutral alumina column to remove copper catalyst and precipitated in hexane.

The Br end functionality of the produced PMA is confirmed with the ^{1}H NMR and ESI-MS analysis (Figure S1). For example, the m/z = 614.1 / 616.1 is assigned to PMA having 6 repeat units and Br end group, and containing an ammonia ion responsible for ionization (calculated value = 614.18 / 616.18).

Mono addition of PMA to allyl alcohol (2)

PMA (2.0 g) was dissolved in 2.5 mL MeOH, and then reacted with excess allyl alcohol (2.5 mL) catalyzed by Cu/$CuBr_2$/Me_6TREN (18 mg, 0.28mmol /63mg, 0.28 mmol/144uL, 0.56 mmol). The

reaction was carried out at 40 C overnight. Then, the mixture was passed through a neutral alumina column and precipitated in hexane.

The products contained two components, the mono-adducts keeping Br end functionality and PMA which lost the Br end as shown in scheme S1. This was also confirmed by the ESI-MS spectrum (Figure S2), in which the isotope distribution was consistent with the targeted structure. For example, the m/z = 844.4 / 846.4 is assigned to PMA having 8 repeat units, one allyl alcohol unit and Br end group, and containing an ammonia ion responsible for ionization (calculated value = 844.30 / 846.29); the m/z = 880.5 is assigned to PMA having 10 repeat units without Br end containing an ammonia ion (calculated value = 880.42).

Oxidation of mono-adduct (3)

The obtained PMA mono-adduct to allyl alcohol was dissolved in 10 mL acetonitrile, added with 25 mg TEMPO (0.16 mmol). 0.25 g KBr (2.1 mmol) dissolved in 3 mL water was then added to the polymer solution. After cooled with an ice bath, 7.5 mL NaOCl mixed with 2 mL saturated $NaHCO_3$ solution was added dropwise. The reaction was carried out overnight. After neutralized with dilute HCl, the mixture was extracted using diethyl ether for 3 times. The organic solutions were combined, and dried with $MgSO_4$. The solvent was then removed in a rotary evaporator.

The zoomed ESI-MS spectrum with isotope distribution was shown in Figure S3. For example, the m/z = 772.3 / 774.3 is assigned to PMA having 7 repeat units, one acrylic acid unit and Br end group containing an ammonia ion responsible for ionization (calculated value = 772.24 / 774.24).

Esterification with isopropanol (4)

The carboxylic ended product was dissolved in 10 mL dichloromethane, added with 30 mg DMAP (0.25 mmol). After adding 0.3 mL isopropanol (4 mmol), the mixture was cooled with an ice bath. And then 0.6 g EDC·HCl (3 mmol) was added. The reaction was carried overnight. The mixture was washed with dilute HCl, brine and saturated $NaHCO_3$ solution, and then extracted with diethyl ether for 3 times. The

organic solutions were then combined and dried with $MgSO_4$. The solvent was then removed in a rotary evaporator.

The product was also confirmed by the ESI-MS spectrum (Figure S4), in which the isotope distribution was consistent with the targeted structure. For instance, the m/z = 814.4 / 816.4 is assigned to PMA having 7 repeat units, one isopropyl acrylate unit and Br end group containing an ammonia ion responsible for ionization (calculated value = 814.29 / 816.28).

The second mono addition of PMA to allyl alcohol (5)

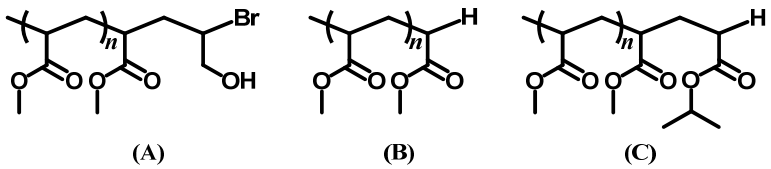
The esterified product was dissolved in 2.5 mL MeOH. And the addition reaction was carried out the same as the first mono addition step mentioned above.

The products contained three components, the mono-adducts keeping Br end functionality, the product **(4)** without the Br end and PMA without the Br end as shown in Scheme S1. This was also confirmed by the ESI-MS spectrum (see in Figure S5), in which the isotope distribution was consistent with these structures. For instance, the m/z = 786.4 / 788.4 is assigned to PMA having 6 repeat units, one isopropyl acrylate unit, one allyl alcohol unit and Br end group containing an ammonia ion responsible for ionization (calculated value = 786.29 / 788.29).

Purification of product (3).

The purification was carried out through a reverse phase HPLC, added with little ammonia, using methanol and water (70:30) as mobile phase. The purified product **(3)** was confirmed by ESI-MS analysis.

Scheme S1. Polymer structure of mono-adducts **2** with Br end group **(A)**, PMA without Br end group **(B)** and product 4 without Br end group **(C)**.



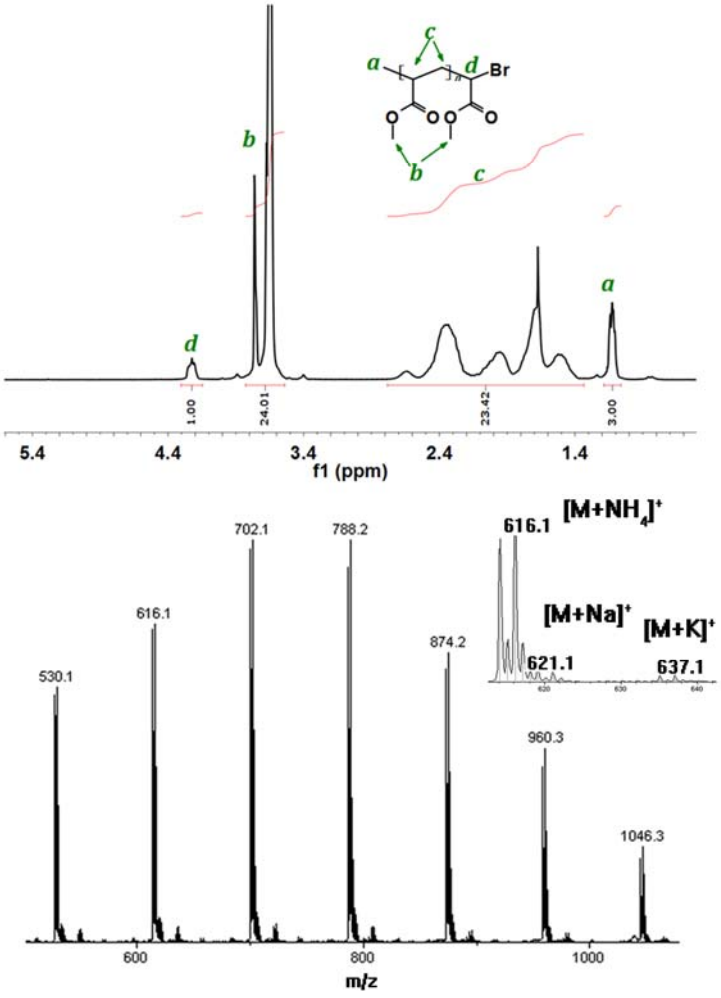


Figure S1. ^{1}H NMR and ESI-MS spectrum of PMA support. Br functionality calculated from integration ratio of peak ***d*** and ***a*** in ^{1}H NMR was almost 1; the isotope distribution of MS was also consistent with the expected pattern.

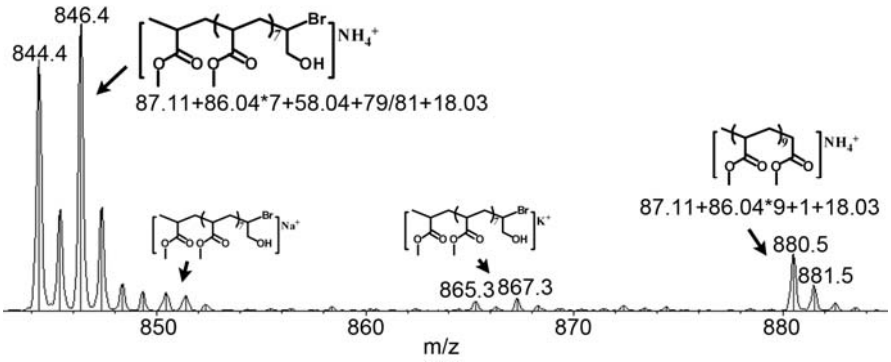


Figure S2. Zoomed ESI-MS spectrum of product **(2)**.

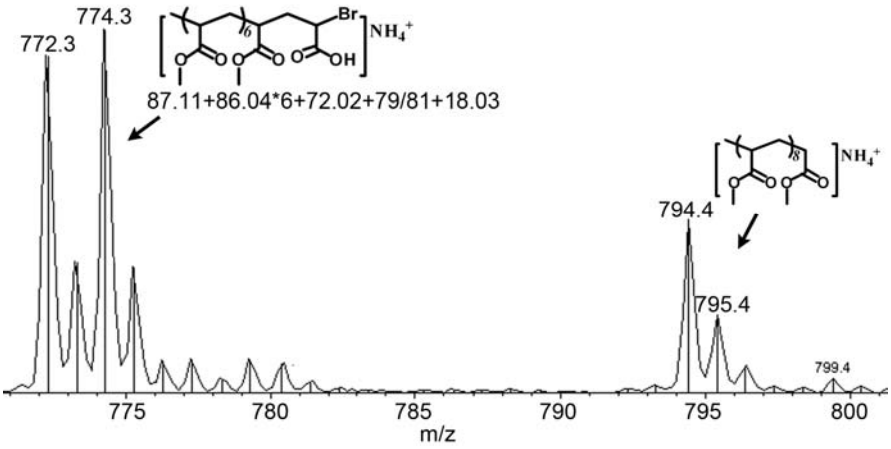


Figure S3. Zommed ESI-MS spectrum of product **(3)**.

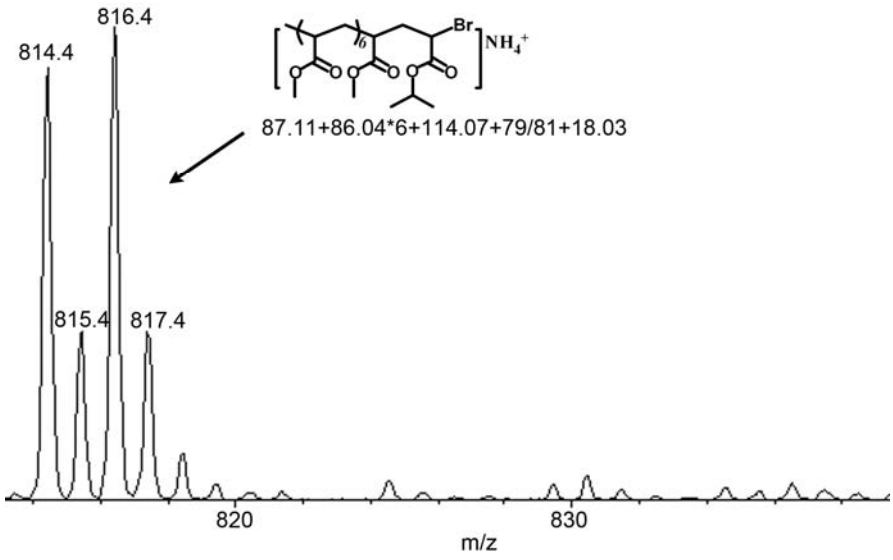


Figure S4. Zoomed ESI-MS spectrum of product **(4)**.

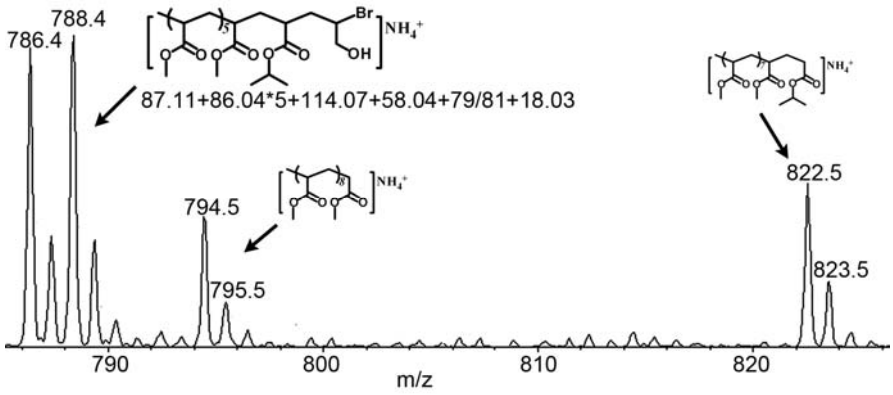


Figure S5. Zoomed ESI-MS spectrum of product **(5)**.