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Full Paper

Graft Copolymers with Polyamide Backbones via Combination of Passerini Multicomponent Polymerization and Controlled Chain-growth Polymerization

Xin-Xing Deng,[A] *Yang Cui,*[A] *Yao-Zong Wang,*[A] *Fu-Sheng Du,*[A] *and Zi-Chen Li*[A,B]

[A]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.
[B]Corresponding author. Email: zcli@pku.edu.cn

We report a facile 'grafting from' approach to graft copolymers with polyamide backbones and controlled vinyl polymer or polyester side chains. Two polyamides with in situ-formed pendant bromide or hydroxyl groups were obtained by Passerini-based multicomponent polymerization. They were used respectively to initiate the atom-transfer radical polymerization of vinyl monomers or the ring-opening polymerization of lactones to generate two new types of graft copolymers. One of the important features of the method is that the pendant initiators are generated in situ from non-branching monomers, and they are linked to the polymer backbone by ester bonds. Therefore, the vinyl polymer side chains could be detached from the backbones, and their structures could thus be fully characterized. Moreover, multicomponent polymerization and atom-transfer radical polymerization can even be carried out in a one-pot manner.

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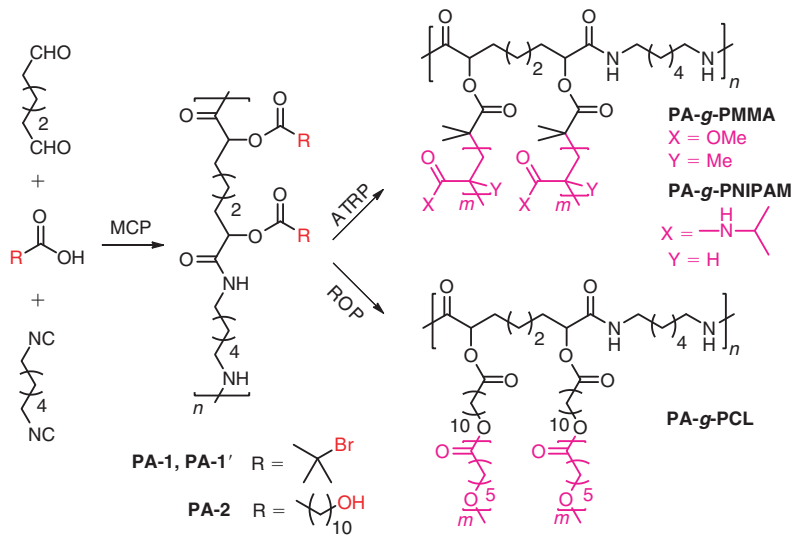
Introduction

Graft copolymers with distinctive backbones and side chains have played important roles in many fields like biomaterials, absorbents, detergents, and separation materials.[1,2] Three general approaches, grafting from, grafting on, and grafting through, have been developed to synthesize a wide range of graft copolymers. The main chains can be constructed by either step-growth polymerization or chain-growth polymerization, while the side chains are usually from chain-growth polymerization of vinyl monomers or ring monomers. The development of living or controlled radical polymerization has advanced this field far, in particular for graft copolymers with carbon–carbon main chains from vinyl monomers, and even bottle brush-shaped polymers.[2] When the polymer main chains are formed from step-growth polymerization like polycondensation or polyaddition, the three general synthetic approaches are not always straightforward. In most cases, a complicated procedure coupled with protection and deprotection is necessary. Successful examples are the 'grafting through' synthesis of polyamide-*g*-poly(methyl methacrylate) (PA-*g*-PMMA) via polycondensation of dicarboxyl-terminated PMMA macromonomers with diamines;[3] the 'grafting onto' approach via formation of polyester or polyurethane main chains containing pendant alkynes and subsequent click reactions with the azido-terminated polymers;[4] and the 'grafting from' approach via construction of backbones from monomers containing branching structures and followed by free radical polymerization.[5] Our efforts focus on developing conceptually new 'grafting from' strategies that can give facile access to graft polymers with backbones formed by the step-growth polymerization of easily available monomers without branching structures under mild conditions. In particular, we are interested in the preparation of polyamides with different functional groups or side chains.[6]

Multicomponent reactions (MCRs) such as the Mannich reaction, isocyanide-based multicomponent reactions (IMCRs), A^3 coupling, and Cu-catalyzed three-component reactions, have attracted considerable interest owing to their exceptional synthetic efficiency: the inherent formation of several bonds in a one-pot reaction and one-step conversion.[7] Various MCRs have been utilized for linear polymer synthesis.[8–13] However, limited by monomer scope and/or poor functional group tolerance, only a few polymers with functional side groups can be synthesized by the above multicomponent polymerizations (MCPs).

The Passerini reaction, a three-component reaction as well as an efficient atom-economical reaction, plays an important role in many fields.[7a,14] When applied in polymer chemistry, three outstanding characteristics make the Passerini reaction promising: high efficiency, which offers chances for the synthesis of high-molecular-weight polymers; formation of an ester–amide sequence during reaction, which makes the synthesis of sequence-regulated polymers realizable; and branching structures formed during reaction, which offer new access to branched and/or functional polymers. Recently, Meier and coworkers reported the synthesis of linear polyesters using the



Scheme 1. Synthesis of graft copolymers via construction of the PA backbones by multicomponent polymerization (MCP) followed by atom-transfer radical polymerization (ATRP) or ring-opening polymerization (ROP).

Passerini reaction.[15] Asymmetric dendrimers have also been prepared by this reaction.[16] Our group extended the use of the Passerini reaction and developed a new MCP for preparing sequence-regulated poly(ester amide), polyamide with various functional groups, star copolymers, and photolabile polymers.[6d,17]

Herein, we report for the first time the synthesis of graft copolymers from monomers without branching structures via construction of the polymer backbones by Passerini-based MCP (Scheme 1). This general approach can provide access to graft copolymers with PA backbones from easily available monomers, even in a one-pot manner. Combination of Passerini-based MCP of hexane-1,6-dial, 1,6-diisocyanohexane, and 2-bromoisobutyric acid, followed by the in situ-formed 2-bromoisobutyrate-initiated atom-transfer radical polymerization (ATRP) of methyl methacrylate (MMA) and *N*-isopropylacrylamide (NIPAM), two graft copolymers, **PA-*g*-PNIPAM** and **PA-*g*-PMMA**, were obtained. The living nature of ATRP can control the molecular weight and polydispersity of the side chain polymers. As the polymer side chains were linked to the PA backbones via ester groups, PMMA and PNIPAM could be detached from the PA main chain and characterized separately. Alternatively, when hydroxyl side groups were introduced into the backbone, **PA-*g*-poly (ε-caprolactone) (PCL)** could be easily synthesized via the ring-opening polymerization (ROP) of ε-caprolactone.

Experimental

Materials

Silica gel (200–300 mesh, Yantai Chemical Research Institute), alkali alumina (200–300 mesh, Sinopharm Chemical Reagent Co. Ltd.), sodium periodate ($NaIO_4$; analytical grade (AR), Xi Long Chemical Co. Ltd.), 1,6-diisocyanohexane (Aldrich, >98 %), 10-undecynoic acid (96 %, Alfa Aesar), 2-bromoisobutyric acid (98 %, Alfa Aesar), 2,2′-bipyridine (bpy, 98 %, Alfa Aesar), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, 96 %, Alfa Aesar), 11-hydroxyundecanoic acid (98 %, Alfa Aesar), *trans*-cyclohexane-1,2-diol (98 %, Alfa Aesar), 1,6-diaminohexane (AR, Beijing Chemical Co. Ltd.), ethyl formate (chemical pure (CP), Sinopharm Chemical Reagent Co. Ltd.), were used as received. *N*, *N*-dimethylformamide (DMF; AR, Beijing Chemical Co. Ltd.) was refluxed with KOH and distilled under reduced pressure. Dichloromethane (CH_2Cl_2; AR, Beijing Chemical Co. Ltd.) and triethylamine (AR, Beijing Chemical Co. Ltd.) were refluxed with CaH_2 and distilled before use. Caprolactone (CL, 99 %, J&K) was distilled under reduced pressure. Cuprous chloride and cuprous bromide (CuBr, >99 %, Aldrich) were washed with acetic acid, methanol, and diethyl ether and dried under vacuum. *N*-Isopropylacrylamide (98 %, Shanghai Wujing Chem. Co. Ltd) was recrystallized three times from a mixture of benzene and *n*-hexane (1 : 3 v/v). Methyl methacrylate (99 %, Aldrich) was passed through a basic alumina column to remove the inhibitor and then distilled from CaH_2 under vacuum before use. Tris(2-(dimethylamino) ethyl) amine (Me_6TREN) was synthesized according to a literature method.[18]

Measurements

The number-average molecular mass (M_n) and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC) equipped with a Waters 2414 refractive index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel HT columns (HT2, HT3, HT4). The columns were thermostatted at 35°C, and THF was used as an eluent at a flow rate of 1.0 mL min^{-1}. Calibration was made against narrowly dispersed polystyrene (PSt); the obtained data were processed on professional software.

^1H NMR (400 or 300 MHz) spectra were recorded in $CDCl_3$ on a Bruker ARX-400 spectrometer or a Varian Gemini 300 spectrometer with tetramethylsilane (TMS) as the internal reference for chemical shifts.

Synthesis of Hexane-1,6-dial[19]

To a vigorously stirred suspension of chromatographic grade silica gel (105 g, 1.75 mol) in CH_2Cl_2 (500 mL) was added dropwise an aqueous solution of $NaIO_4$ (0.65 M, 105 mL, 68.2 mmol). A solution of *trans*-cyclohexane-1,2-diol (6.08 g, 52.3 mmol) in CH_2Cl_2 (200 mL) was then added, and the reaction was stirred for 24 h. The mixture was filtered on sintered glass, and the silica gel was thoroughly washed with CH_2Cl_2.

Evaporation of the solvent afforded the *title compound* as a colourless oil. No further purification was necessary. Yield 75 %. δ_H ($CDCl_3$, ppm) 9.78 (t, 2H, CHO), 2.49 (m, 4H, CH_2CHO), 1.67 (m, 4H, CH_2).

Synthesis of ***PA-1***

Hexane-1,6-dial (0.114 g, 1.00 mmol), 2-bromoisobutyric acid (0.334 g, 2.00 mmol), 1,6-diisocyanohexane (0.136 g, 1.00 mmol), and $CHCl_3$ (1 mL) were added to a 25-mL Schlenk flask and subjected to one freeze–pump–thaw cycle. The mixture was stirred at 40°C, and after 48 h, the reaction mixture was precipitated into diethyl ether to obtain a brown solid (yield 94 %; M_n, 12.5 kDa; PDI, 2.29).

Kinetics Study of the Backbone Formation

Hexane-1,6-dial (0.114 g, 1.00 mmol), 2-bromoisobutyric acid (0.334 g, 2.00 mmol), 1,6-diisocyanohexane (0.136 g, 1.00 mmol), and $CDCl_3$ (1 mL) were added to a 5-mL Schlenk flask and subjected to one freeze–pump–thaw cycle. The mixture was stirred at 40°C. Samples were taken out at the desired time for the ^{1}H NMR and GPC analysis.

Synthesis of ***PA-g-PMMA***

PA-1 (0.0292 g, containing 0.100 mmol Br), MMA (1.00 g, 0.010 mol), CuBr (0.0143 g, 0.100 mmol), and THF (4 mL) were added to a 25-mL Schlenk flask and subjected to three freeze–pump–thaw cycles; then bipyridine (0.0156 g, 0.100 mmol) was added. After three more freeze–pump–thaw cycles, the mixture was stirred at 40°C under an N_2 atmosphere. After 7 h, the reaction mixture was passed through a column packed with Al_2O_3 to remove the copper salt. The solution was then poured into diethyl ether, producing a white precipitate. The precipitate (**PA-*g*-PMMA**) was collected and vacuum-dried (yield 23 %; M_n, 82.0 kDa; PDI, 1.31).

Methanolysis of ***PA-g-PMMA***

PA-g-PMMA (0.10 g, ~0.04 mmol ester groups), NaOH (0.010 g, 0.25 mmol), and CH_3OH (4 mL) were added to a 10-mL flask and stirred at 30°C. After 12 h, the solution was concentrated under vacuum to give a white solid. The solid was dissolved in THF (2 mL). The solution was then poured into pentane (20 mL), producing a white precipitate. The precipitate was collected and vacuum-dried (yield 81 %; M_n, 5.9 kDa; PDI, 1.29).

Synthesis of ***PA-g-PNIPAM***

PA-1 (0.0292 g, 0.100 mmol Br), NIPAM (1.13 g, 0.010 mol), CuCl (0.0098 g, 0.100 mmol), and 2-propanol (2 mL) were added to a 25-mL Schlenk flask and subjected to three freeze–pump–thaw cycles; then Me_6TREN (0.0230 g, 0.100 mmol) was added. After three more freeze–pump–thaw cycles, the mixture was stirred at 30°C under an N_2 atmosphere. After 16 h, the reaction mixture was passed through a column packed with Al_2O_3 to remove the copper salt. The solution was then poured into diethyl ether, producing a white precipitate. The precipitate (**PA-*g*-PNIPAM)** was collected and vacuum-dried (yield 44 %; M_n, 87.3 kDa; PDI, 1.52).

Hydrolysis of ***PA-g-PNIPAM***

PA-g-PNIPAM (0.10 g, ~0.07 mmol ester groups), NaOH (0.020 g, 0.50 mmol), and CH_3OH/H_2O (1 : 1, 4 mL) were added to a 10-mL flask and stirred at 30°C. Hydrochloric acid (0.50 mL, 1 mol L^{-1}) was added to neutralize the solution after stirring for 12 h. The solution was concentrated under vacuum to give a white solid. The solid was dissolved in THF (2 mL). The solution was then poured into diethyl ether (20 mL), producing a white precipitate. The precipitate was collected and vacuum-dried (yield 82 %; M_n, 5.9 kDa; PDI, 1.16).

One-pot Synthesis of ***PA-g-PNIPAM′*** *and Subsequent Hydrolysis*

Hexane-1,6-dial (0.114 g, 1.00 mmol), 2-bromoisobutyric acid (0.334 g, 2.00 mmol), 1,6-diisocyanohexane (0.136 g, 1.00 mmol), and $CDCl_3$ (1 mL) were added to a 25-mL Schlenk flask and subjected to one freeze–pump–thaw cycle. The mixture was stirred at 40°C under an N_2 atmosphere. During the polymerization, several samples were taken out for GPC and ^{1}H NMR analysis. The solvent was removed under vacuum after stirring for 48 h, and a brown solid (**PA-1′**) was obtained (yield > 99 %; M_n, 9.2 kDa; PDI, 2.10). After taking out most of the solid, 0.0292 g of **PA-1′** (0.100 mmol Br) remained, and NIPAM (1.13 g, 0.010 mol), CuCl (0.0098 g, 0.100 mmol), and 2-propanol (2 mL) were added to the Schlenk flask and subjected to three freeze–pump–thaw cycles; then Me_6TREN (23.0 mg, 0.100 mmol) was added. After three more freeze–pump–thaw cycles, the mixture was stirred at 30°C under an N_2 atmosphere. After 16 h, the reaction mixture was passed through a column packed with Al_2O_3 to remove the copper salt. The solution was then precipitated in diethyl ether, and a white solid (**PA-g-PNIPAM′**) was obtained and vacuum-dried (yield 43 %; M_n, 98.9 kDa; PDI, 1.27). **PA-g-PNIPAM′** (0.10 g, ~0.06 mmol ester groups), NaOH (0.020 g, 0.50 mmol), and CH_3OH (4 mL) were added to a 10-mL flask and stirred at 30°C. Hydrochloric acid (0.50 mL, 1 mol L^{-1}) was added to neutralize the solution after stirring for 12 h. The solution was concentrated under vacuum to give a white solid. The solid was dissolved in THF (2 mL). The solution was then poured into diethyl ether (20 mL), producing a white precipitate. The precipitate (**PNIPAM′**) was collected and vacuum-dried (yield 75 %; M_n, 8.6 kDa; PDI, 1.14).

Synthesis of ***PA-2***

PA-2 was synthesized following the same procedure as for **PA-1**, except that 11-hydroxyundecanoic acid was used as the starting material (yield 93 %; M_n, 11.2 kDa; PDI, 4.19).

Synthesis of ***PA-g-PCL***

PA-2 (0.0397 g, 0.1 mmol OH) was dissolved in dry THF (4 mL) in a 50-mL dry flask under an inert atmosphere. Then toluene (40 mL) and CL (1.14 g, 10 mmol) were added. After two freeze–pump–thaw cycles, $Sn(Oct)_2$ (0.0004 g, dissolved in toluene) was added into the flask via syringe. The mixture was gently refluxed under nitrogen at 110°C. After 2 h, excess cold methanol was poured into the solution to terminate the reaction and precipitate the product. The white precipitate was collected by filtration, redissolved in THF, and the solution was then poured into diethyl ether, producing a white precipitate. The precipitate (**PA-*g*-PCL**) was collected and vacuum-dried (yield 54 %; M_n, 119.2 kDa; PDI, 1.56).

Results and Discussion

All the starting materials, except hexane-1,6-dial, which was synthesized according to a literature method (Fig. S1),[19] are commercially available. We first conducted the polymerization of hexane-1,6-dial, 2-bromoisobutyric acid, and 1, 6-diisocyanohexane (molar ratio 1 : 2 : 1) in chloroform at 30°C

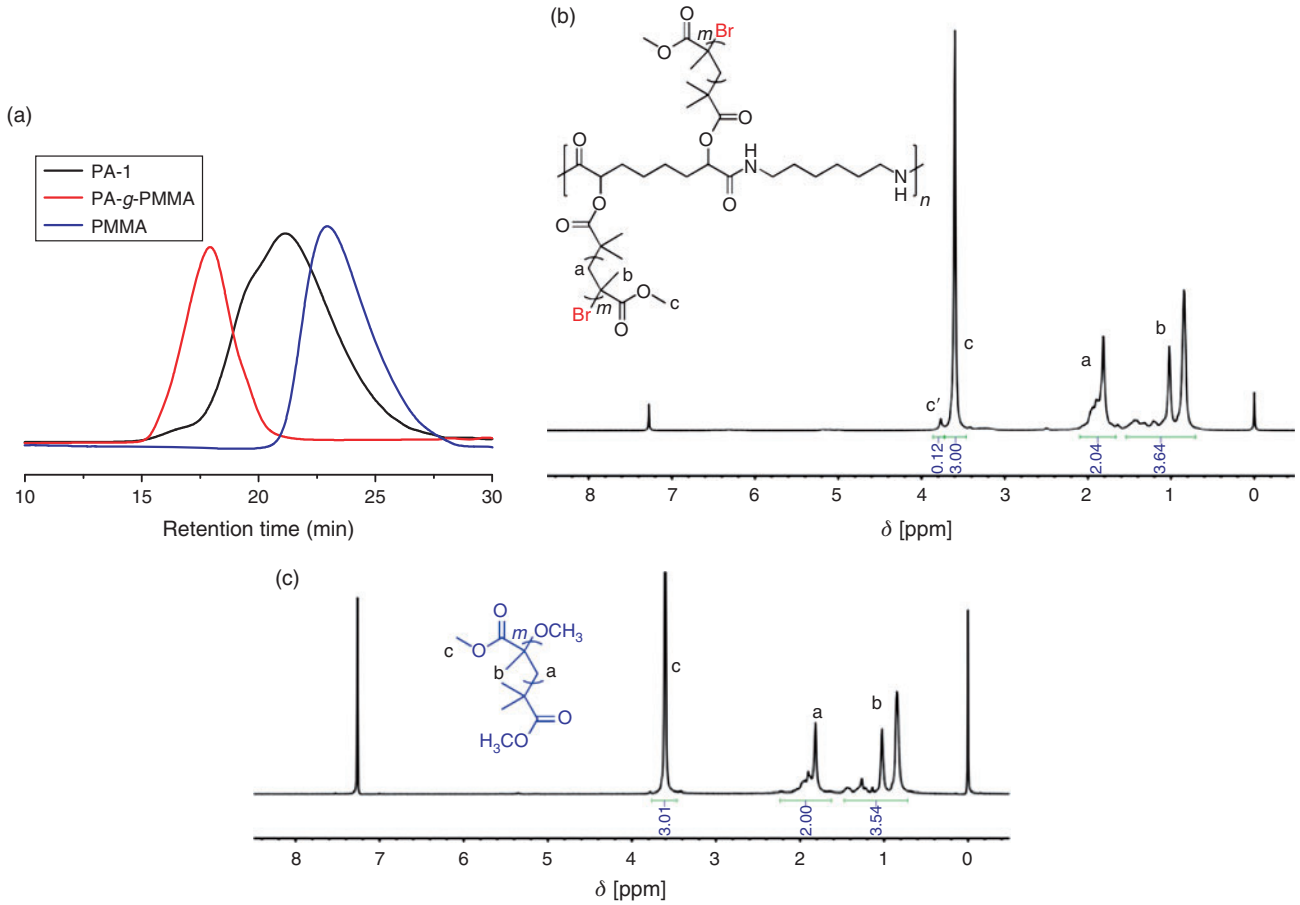


Fig. 1. Gel permeation chromatography (GPC) traces of **PA-1**, **PA-*g*-PMMA** and PMMA (a); ^{1}H NMR spectra of **PA-*g*-PMMA** (b); and PMMA (c).

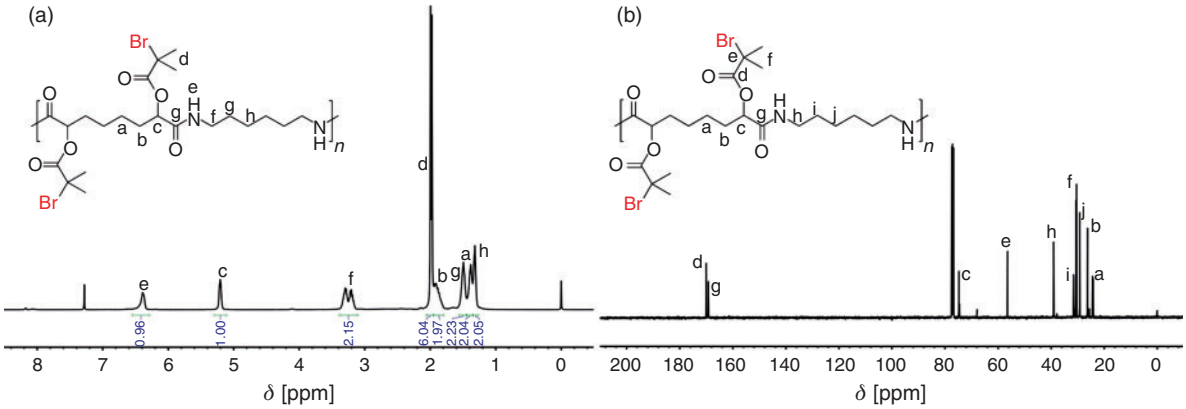


Fig. 2. ^{1}H NMR (a); and ^{13}C NMR (b) spectra of **PA-1**.

according to our previous procedure.[6d,17] A kinetics study showed the rapid conversion of monomers (Fig. S2), and after 48 h, **PA-1** was obtained in 94 % yield (M_n = 12.5 kDa, PDI = 2.29) (Fig. 1a). The structure of **PA-1** was confirmed by the ^{1}H NMR and ^{13}C NMR spectra (Fig. 2).

The ATRP of MMA initiated by **PA-1** was then conducted in THF at 40°C ([MMA]$_0$/[Br of **PA-1**]$_0$/[CuBr]$_0$/[bpy]$_0$ = 100 : 1 : 1 : 1). A preliminary experiment showed that polymers with M_n = 43.7 kDa and PDI = 1.79 were obtained after 2 h (Fig. S3) at 4 % conversion of MMA. By increasing the polymerization time to 7 h, **PA-*g*-PMMA** with M_n = 82.0 kDa and PDI = 1.31 was obtained at 23 % conversion of MMA (Table 1, Fig. 1a). The GPC trace shows that the obtained polymer had much a higher apparent molecular mass than that of the **PA-1** precursor, indicating the formation of graft copolymers (Fig. 1a). The structure of **PA-*g*-PMMA** was confirmed by the ^{1}H NMR spectrum shown in Fig. 1b. The methyl protons of the side 2-bromoisobutyrate groups of **PA-1** appearing at 2.1 ppm completely disappeared in **PA-*g*-PMMA**, and the main chain protons were invisible in the spectrum, indicating the complete reaction of the attached initiators. As one feature of the graft copolymers, the side PMMA chains were connected to the PA main chain via ester linkages. Therefore, these PMMA chains could be easily detached from the main chain via methanolysis of **PA-*g*-PMMA** in methanol/NaOH at 30°C for 12 h, and PMMA was obtained in 81 % yield. The GPC trace of the

Table 1. Summary of gel permeation chromatography (GPC) data of the polymer backbones, graft copolymers and side chains
PDI, polydispersity index

Backbones			Graft copolymers			Side chains		
	M_n [kDa]	PDI		M_n [kDa]	PDI		M_n [kDa]	PDI
PA-1	12.5	2.29	**PA-*g*-PMMA**	82.0	1.31	PMMA	5.9	1.29
PA-1			**PA-*g*-PNIPAM**	87.3	1.52	PNIPAM	5.9	1.16
PA-1′	9.2	2.10	**PA-*g*-PNIPAM′**	98.9	1.27	PNIPAM′	8.6	1.14
PA-2	11.2	4.19	**PA-*g*-PCL**	119.2	1.56	PCL[A]	–	–

[A]The PCL side chains could not be selectively detached from backbones.

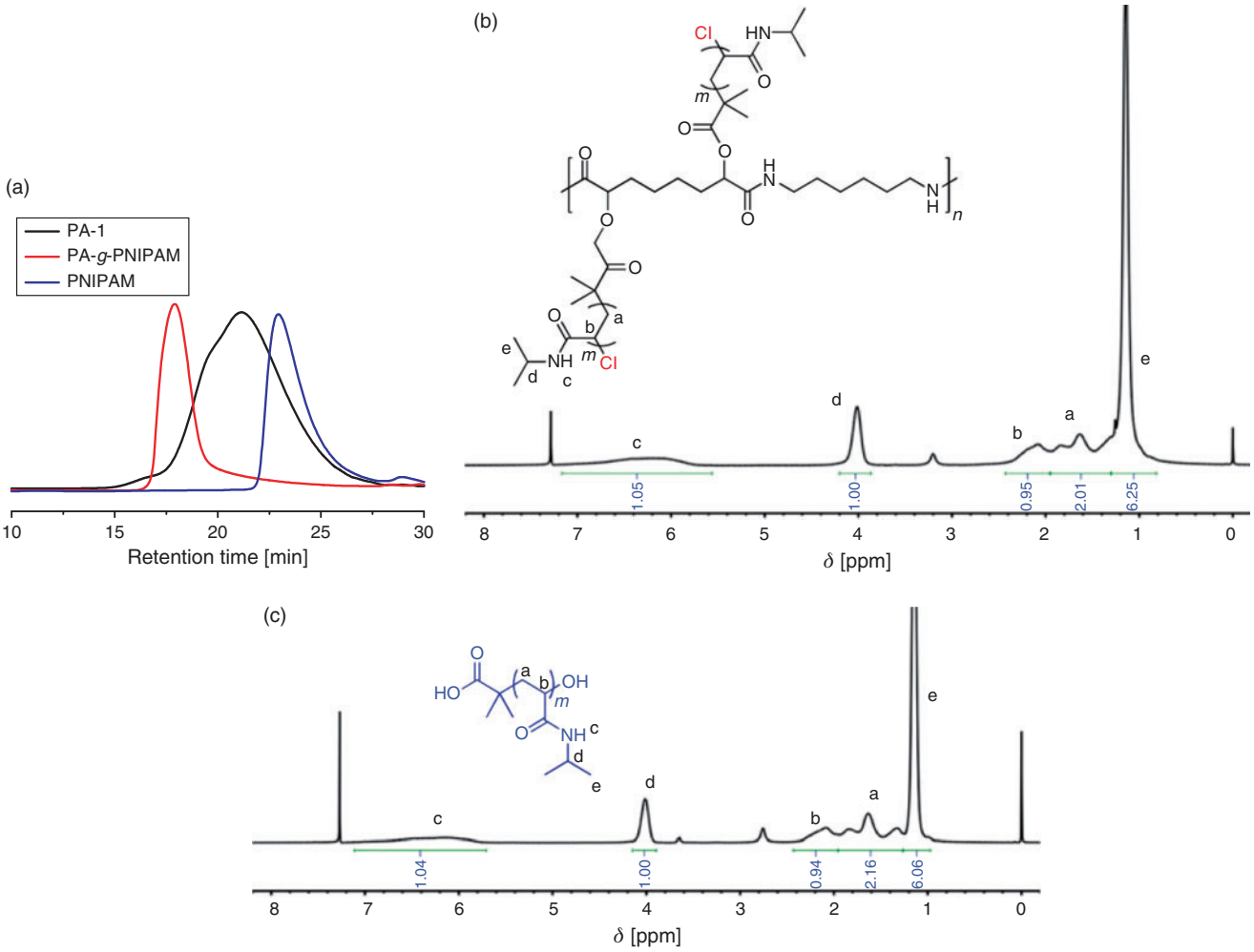


Fig. 3. Gel permeation chromatography (GPC) traces of **PA-1**, **PA-*g*-PNIPAM**, and PNIPAM (a); ^{1}H NMR spectra of **PA-*g*-PNIPAM** (b); and PNIPAM (c).

formed PMMA is shown in Fig. 1a; it gives a PMMA with $M_n = 5.9$ kDa and PDI = 1.29. This low PDI compared with the graft copolymers implies that the ATRP of MMA occurred in a controlled manner. The ^{1}H NMR spectrum of the detached PMMA shown in Fig. 1c also confirmed the structure.

Similarly, the ATRP of NIPAM initiated by **PA-1** was conducted in 2-propanol at 30°C ($[NIPAM]_0/[Br \text{ of } \mathbf{PA_1}]_0/[CuCl]_0/[Me_6TREN]_0 = 100:1:1:1$).[20] After 16 h, the GPC trace of the resulting polymer shifted to a higher apparent molecular mass, and a graft copolymer, **PA-*g*-PNIPAM**, with $M_n = 87.3$ kDa and PDI = 1.52, was obtained at 44 % conversion of NIPAM (Table 1, Fig. 3a). The structure of **PA-*g*-PNIPAM** was confirmed by its ^{1}H NMR spectrum (Fig. 3b).

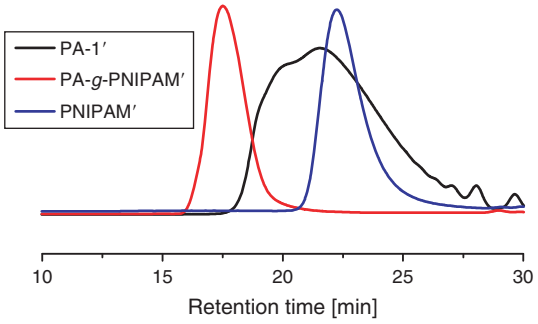


Fig. 4. Gel permeation chromatography (GPC) traces of **PA-1′**, **PA-*g*-PNIPAM′**, and **PNIPAM′**.

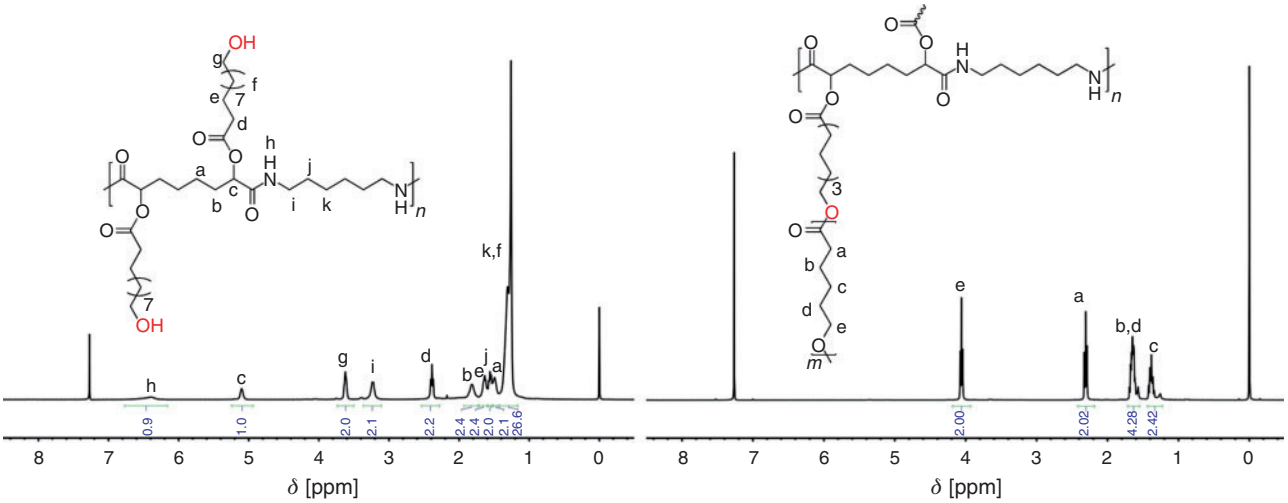


Fig. 5. ^{1}H NMR spectra of **PA-2** and **PA-*g*-PCL**.

This graft copolymer can also be hydrolyzed to liberate the PNIPAM side chains; the GPC trace of PNIPAM shown in Fig. 3a gives a polymer with $M_n = 5.9$ kDa and PDI = 1.16. This polymer was pure PNIPAM as confirmed by the ^{1}H NMR spectrum shown in Fig. 3c. Thus, the graft polymerization of NIPAM was also a controlled polymerization.

Next, we tested the one-pot two-step synthesis of **PA-*g*-PNIPAM′**. The MCP of hexane-1,6-dial, 2-bromoisobutyric acid, and 1,6-diisocyanohexane was conducted in $CHCl_3$ at 40°C. An aliquot was taken out periodically for GPC and NMR measurements. From the kinetics study, we know that the conversion of the functional groups was over 95 % after 48 h. A polymer sample (**PA-1′**, $M_n = 9.2$ kDa, PDI = 2.10) was obtained (Table 1, Fig. 4), and the structure was confirmed to be essentially the same as **PA-1** (Fig. S4). At this stage, the solvent was removed under vacuum, and 2-propanol was added to dissolve the resulting polymers, followed by the addition of NIPAM, CuCl, and Me_6TREN. The solution was further treated under normal ATRP conditions, and was allowed to polymerize at 30°C for 16 h to get the graft copolymer, with $M_n = 98.9$ kDa and PDI = 1.27 (Table 1, Fig. 4). Again, the structure of this **PA-*g*-PNIPAM′** was confirmed by ^{1}H NMR spectra (Fig. S5), and after hydrolysis, **PNIPAM′** was recovered (Fig. 4; M_n 8.6 kDa, PDI 1.14; Fig. S5). Thus, the one-pot synthesis of graft copolymers was achieved.

Finally, a combination of Passerini-based MCP and ROP of CL yielded **PA-*g*-PCL** (Table 1). When ROP initiated by **PA-2** was conducted in toluene, the GPC trace of the resulting polymer shifted to a higher apparent molecular weight, and a graft copolymer, **PA-*g*-PCL**, was obtained at 72 % conversion of CL (Fig. S6). The structures of **PA-2** and **PA-*g*-PCL** were confirmed by ^{1}H NMR (Fig. 5). Thus, Passerini-based MCP can also be used to construct backbones that are suitable for the ROP of lactones.

Conclusions

We have demonstrated a conceptually new approach to graft copolymers with polyamide backbones and vinyl polymers or polyesters as the side chains. The process was a 'grafting from' strategy via the combination of Passerini MCP and controlled chain-growth polymerization of vinyl monomers and lactones. The branching structures with initiating activity were formed in situ during the MCP, and were connected to the polyamide main chain via ester linkages. This feature makes the recovery and characterization of the side chains possible. The easy accessibility of monomers together with the advantage of functional group tolerance offers an interesting new access to grafting copolymers with polyamide backbones. Further extending the synthetic scope of Passerini MCP is under way in our laboratory.

Supplementary Material

Synthetic schemes (Scheme S1–S3), ^{1}H NMR spectra and GPC traces (Figs S1–S6) are all available on the Journal's website.

Acknowledgements

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References

[1] (a) D. W. Jenkins, S. M. Hudson, *Chem. Rev.* **2001**, *101*, 3245. doi:10.1021/CR000257F
(b) A. Bhattacharya, B. N. Misra, *Prog. Polym. Sci.* **2004**, *29*, 767. doi:10.1016/J.PROGPOLYMSCI.2004.05.002
(c) C. Feng, Y. J. Li, D. Yang, J. H. Hu, X. H. Zhang, X. Y. Huang, *Chem. Soc. Rev.* **2011**, *40*, 1282. doi:10.1039/B921358A

[2] (a) M. F. Zhang, A. H. E. Müller, *J. Polym. Sci. A Polym. Chem.* **2005**, *43*, 3461. doi:10.1002/POLA.20900
(b) S. S. Sheiko, B. S. Sumerlin, K. Matyjaszewski, *Prog. Polym. Sci.* **2008**, *33*, 759. doi:10.1016/J.PROGPOLYMSCI.2008.05.001

[3] (a) Y. Yamashita, Y. Chujo, H. Kobayashi, Y. Kawakami, *Polym. Bull.* **1981**, *5*, 361.
(b) Y. Chujo, H. Kobayashi, Y. Yamashita, *Polym. J.* **1988**, *20*, 407. doi:10.1295/POLYMJ.20.407

[4] (a) D. Fournier, F. Du Prez, *Macromolecules* **2008**, *41*, 4622. doi:10.1021/MA800189Z
(b) L. Billiet, D. Fournier, F. Du Prez, *J. Polym. Sci. A Polym. Chem.* **2008**, *46*, 6552. doi:10.1002/POLA.22966

[5] B. Ochiai, Y. Kato, T. Endo, *Macromolecules* **2009**, *42*, 8001. doi:10.1021/MA901834D

[6] (a) K. Marchildon, *Macromol. React. Eng.* **2011**, *5*, 22. doi:10.1002/MREN.201000017
(b) L. Billiet, D. Fournier, F. Du Prez, *Polymer* **2009**, *50*, 3877. doi:10.1016/J.POLYMER.2009.06.034
(c) L. Billiet, X. K. D. Hillewaere, F. E. Du Prez, *Eur. Polym. J.* **2012**, *48*, 2085. doi:10.1016/J.EURPOLYMJ.2012.08.013
(d) Y. Z. Wang, X. X. Deng, L. Li, Z. L. Li, F. S. Du, Z. C. Li, *Polym. Chem.* **2013**, *4*, 444. doi:10.1039/C2PY20927F

[7] (a) A. Dömling, I. Ugi, *Angew. Chem. Int. Ed.* **2000**, *39*, 3168. doi:10.1002/1521-3773(20000915)39:18<3168::AID-ANIE3168>3.0.CO;2-U
(b) A. Jacobi von Wangelin, H. Neumann, D. Gordes, S. Klaus, D. Strubing, M. Beller, *Chem. Eur. J.* **2003**, *9*, 4286. doi:10.1002/CHEM.200305048
(c) V. A. Peshkov, O. P. Pereshivko, E. V. Van der Eycken, *Chem. Soc. Rev.* **2012**, *41*, 3790. doi:10.1039/C2CS15356D
(d) I. Bae, H. Han, S. Chang, *J. Am. Chem. Soc.* **2005**, *127*, 2038. doi:10.1021/JA0432968
[8] E. Tsuchida, T. Tomono, *J. Polym. Sci. A Polym. Chem.* **1973**, *11*, 723. doi:10.1002/POL.1973.170110403
[9] (a) M. Yoneyama, M. Kakimoto, Y. Imai, *Macromolecules* **1988**, *21*, 1908.
(b) S. Oi, K. Nemoto, S. Matsuno, Y. Inoue, *Macromol. Rapid Comm.* **1994**, *15*, 133.
(c) S. Oi, Y. Fukue, K. Nemoto, *Macromolecules* **1996**, *29*, 2694.
[10] (a) T. Yokozawa, K. Takenoya, *Macromolecules* **1996**, *29*, 497. doi:10.1021/MA9510101
(b) L. Niimi, K. Shiino, S. Hiraoka, T. Yokozawa, *Macromolecules* **2002**, *35*, 3490. doi:10.1021/MA011674C
(c) L. Niimi, S. Hiraoka, T. Yokozawa, *J. Polym. Sci. A Polym. Chem.* **2005**, *43*, 5440. doi:10.1002/POLA.21003
[11] (a) N. Miyaki, I. Tomita, T. Endo, *Macromolecules* **1996**, *29*, 6685. doi:10.1021/MA9504431
(b) N. Miyaki, I. Tomita, J. Kido, T. Endo, *Macromolecules* **1997**, *30*, 4504. doi:10.1021/MA9702410
(c) C. K. Choi, I. Tomita, T. Endo, *Macromolecules* **2000**, *33*, 1487. doi:10.1021/MA991459K
(d) B. Ochiai, T. Ogihara, M. Mashiko, T. Endo, *J. Am. Chem. Soc.* **2009**, *131*, 1636. doi:10.1021/JA8070978
[12] E. Ihara, Y. Hara, T. Itoh, K. Inoue, *Macromolecules* **2011**, *44*, 5955. doi:10.1021/MA201037P
[13] I.-H. Lee, H. Kim, T.-L. Choi, *J. Am. Chem. Soc.* **2013**, *135*, 3760. doi:10.1021/JA312592E
[14] (a) M. Passerini, *Gazz. Chim. Ital.* **1921**, *51*, 126.
(b) A. Dömling, *Chem. Rev.* **2006**, *106*, 17. doi:10.1021/CR0505728
(c) A. Dömling, W. Wang, K. Wang, *Chem. Rev.* **2012**, *112*, 3083. doi:10.1021/CR100233R
[15] O. Kreye, T. Toth, M. A. R. Meier, *J. Am. Chem. Soc.* **2011**, *133*, 1790. doi:10.1021/JA1113003
[16] J.-A. Jee, L. A. Spagnuolo, J. G. Rudick, *Org. Lett.* **2012**, *14*, 3292. doi:10.1021/OL301263V
[17] (a) X. X. Deng, L. Li, Z. L. Li, A. Lv, F. S. Du, Z. C. Li, *ACS Macro Lett.* **2012**, *1*, 1300. doi:10.1021/MZ300456P
(b) L. Li, X. W. Kan, X. X. Deng, C. C. Song, F. S. Du, Z. C. Li, *J. Polym. Sci. A Polym. Chem.* **2013**, *51*, 865. doi:10.1002/POLA.26443
(c) A. Lv, X.-X. Deng, L. Li, Z.-L. Li, Y.-Z. Wang, F.-S. Du, Z.-C. Li, *Polym. Chem.* **2013**, *4*, 3659. doi:10.1039/C3PY00382E
(d) L. Li, A. Lv, X. X. Deng, F. S. Du, Z. C. Li, *Chem. Commun.* **2013**, 8549. doi:10.1039/C3CC44557G
[18] M. Ciampolini, N. Nardi, *Inorg. Chem.* **1966**, *5*, 41. doi:10.1021/IC50035A010
[19] S. López, F. Fernandez-Trillo, P. Midon, L. Castedo, C. Saa, *J. Org. Chem.* **2005**, *70*, 6346. doi:10.1021/JO050807F
[20] Y. Xia, X. Yin, N. A. D. Burke, H. D. H. Stöver, *Macromolecules* **2005**, *38*, 5937. doi:10.1021/MA050261Z