

Photo-grafting Poly(acrylic acid) onto Poly(lactic acid) Chains in Solution

Jia-Xing Wang, Yan-Bin Huang*, and Wan-Tai Yang

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract Poly(lactic acid) (PLA) is one of the most important bio-plastics, and chemical modification of the already-polymerized poly(lactic acid) chains may enable optimization of its material properties and expand its application areas. In this study, we demonstrated that poly(lactic acid) can be readily dissolved in acrylic acid at room temperature, and acrylic acid can be graft-polymerized onto poly(lactic acid) chains in solution with the help of photoinitiator benzophenone under 254 nm ultraviolet (UV) irradiation. Similar photo-grafting polymerization of acrylic acid (PAA) has only been studied before in the surface modification of polymer films. The graft ratio could be controlled by various reaction parameters, including irradiation time, benzophenone content, and monomer/polymer ratios. This photo-grafting reaction resulted in high graft ratio (graft ratio PAA/PLA up to 180%) without formation of homopolymers of acrylic acid. When the PAA/PLA graft ratio was higher than 100%, the resulting PLA-g-PAA polymer was found dispersible in water. The pros and cons of the photo-grafting reaction were also discussed.

Keywords Photo-grafting; Polymer modification; Poly(acrylic acid); Poly(lactic acid)

Citation: Wang, J. X.; Huang, Y. B.; Yang, W. T. Photo-grafting poly(acrylic acid) onto poly(lactic acid) chains in solution. *Chinese J. Polym. Sci.* 2020, 38, 137–142.

INTRODUCTION

Poly(lactic acid) (also known as polylactide, PLA) is currently the most important polymer in the category of bio-plastics.^[1,2] In addition to its degradability, its monomer lactic acid can be mass- and cost-effectively produced via fermentation from plant starch and lignocellulose, making PLA a sustainable material from renewable sources. More importantly, poly(lactic acid) is a thermoplastic with processability, rigidity, and optical clarity in the same range of currently used polymers such as polystyrene and poly(ethylene terephthalate).^[1,2] Consequently, it is regarded as one of the most promising candidates to substitute these petrochemically-derived polymers, at least in certain application areas such as packaging and textiles.

However, poly(lactic acid) does have certain disadvantages against its wider applications. For example, the glass transition temperature of PLA is around 50–60 °C, making it a brittle material with low heat deformation temperature.^[3] As another example, PLA is biocompatible and, together with its copolymers, it is one of the most extensively used polymers in biomedical applications such as drug delivery, tissue engineering, and medical devices.^[4] Nevertheless, PLA is hydrophobic and has low affinity to cells, resulting in limited range to adjust its biodegradation rate and often requiring surface modification in practice.^[5] Therefore, chemical modifications

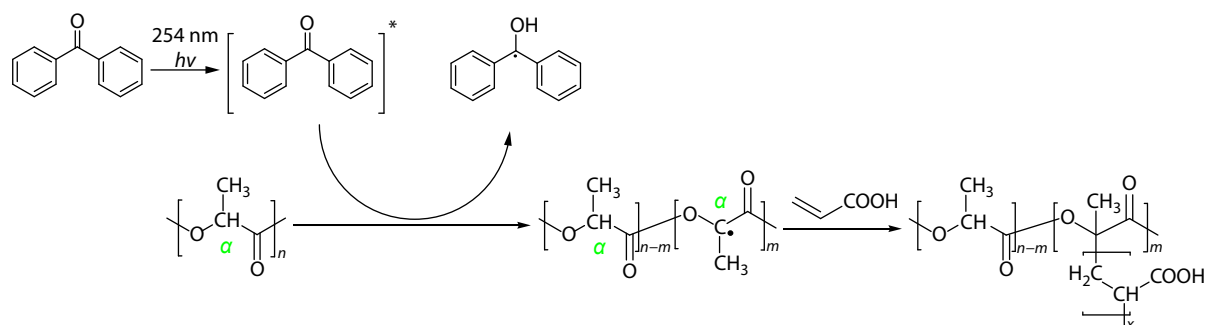
of poly(lactic acid) represent an important route to optimize its material properties and expand its application areas.

In principle, poly(lactic acid) can be modified through two routes: one is copolymerization with monomers such as glycolide and caprolactone,^[6] and the other is grafting other polymers onto the already-formed poly(lactic acid) chains. For example, Critchfield *et al.*^[7] and Wu *et al.*^[8] both reported graft polymerization of acrylic acid and other vinyl monomers onto polyester chains in the melt state by adding free radical initiators (*i.e.*, benzoyl peroxide, BPO). Ideally, the thermally-decomposed free radical initiators would abstract hydrogens from the poly(lactic acid) chains and result in polymer free radicals to initiate the graft polymerization of acrylic acid. However, the use of thermal initiation and conventional initiators will unavoidably generate acrylic acid homopolymers.

In this study, we propose to use the well-studied photoinitiator benzophenone (BP) and photo-grafting polymerize acrylic acid (AA) onto poly(lactic acid) chains (Scheme 1): (1) As a Norrish Type II photoinitiator, the ultraviolet-excited benzophenone predominately goes through the hydrogen abstraction process instead of decomposing into two free radicals.^[9] In the presence of poly(lactic acid) chains, the most likely reaction site is the hydrogen on the tertiary carbons, though hydrogens on the methyl groups are also possible candidates. The hydrogen-abstracting reaction results in PLA radicals and benzophenone ketyl radicals. The polymer radicals will initiate the graft polymerization of acrylic acid, while the ketyl radicals, due to its steric hindrance, are known un-

* Corresponding author, E-mail: yanbin@tsinghua.edu.cn

Received May 12, 2019; Accepted May 25, 2019; Published online September 12, 2019



Scheme 1 Proposed reaction scheme of photo-grafting poly(acrylic acid) onto poly(lactic acid) chains.

able to initiate polymerization.^[10–12] (2) Compared with the hydrogens on the PLA chains, those on the acrylic acid monomers need much higher energy to be abstracted, which minimizes the possibility of chain transfer to monomers and subsequent initiation of acrylic acid homo-polymerization.^[13] (3) We accidentally found out that poly(D,L-lactic acid) can be easily dissolved in acrylic acid at high concentration (at least 1:1 by weight) at room temperature, thus avoiding the use of heat throughout the reaction and minimizing the thermal initiation of acrylic acid homo-polymerization.

It should be noted that photo-grafting of various vinyl monomers (including acrylic acid) on the poly(lactic acid) material surface has been extensively studied as an efficient surface modification technology.^[14,15] Nonetheless, to the best of our knowledge, photo-grafting onto poly(lactic acid) chains in the bulk solution has not been reported.

EXPERIMENTAL

Materials

Poly(lactic acid) (PLA), composed of 50% L-lactide and 50% D-lactide, was used as supplied by Sigma-Aldrich Co., USA. Acrylic acid (AA), from Shanghai Macklin Biochemical Co., was purified by vacuum distillation before use. Benzophenone (BP) was used as supplied by Shanghai D&B Biological Science and Technology Co., China.

Synthesis of PLA-g-PAA

In a typical experiment, 200 mg of PLA and 100 mg of BP were dissolved in 1 g of acrylic acid at room temperature. The solution was transferred in a 1-mm-deep groove on a glass plate and covered with 3-mm-thick quartz glass. Then, the solution was placed as close as possible under UV-irradiation (254 nm, 120 W, CEL-LB70, Zhong Jiao Jin Yuan Co., China) for 1 h. Afterwards, the sample was washed twice in ethanol to remove AA and BP, and dried for 24 h in a vacuum oven at room temperature. To study the effect of different reaction parameters on the grafting ratio, reactions were carried out with different reaction times (5 min, 10 min, 30 min, 40 min, and 1 h), different BP contents (1%, 2%, 5%, and 10% by weight of the AA amount), and different ratios of AA/PLA (1, 2.5, 5, and 10) in the reaction mixtures.

Characterizations

¹H-nuclear magnetic resonance (¹H-NMR), solid-state ¹³C-nuclear magnetic resonance (ss ¹³C-NMR), and DOSY-NMR spectroscopies were used to confirm the chemical structures. ¹H-NMR

and DOSY-NMR (at 50 °C) tests were conducted on a JOEL JNM-ECA600 nuclear magnetic resonance spectrometer. Deuterated *N,N*-dimethylformamide (DMF-d₇) was used as the solvent. Analysis of the obtained spectra was performed using the MestReNova software. ¹³C-NMR analysis was conducted using a JNM-ECZ600R ¹³C-NMR spectrometer at 150 MHz.

Molecular weight of PLA-g-PAA was determined using gel permeation chromatography (GPC, Shimadzu Corporation, Japan), equipped with a refractive index detector (RID-10A, Shimadzu Corporation, Japan), a UV detector (SPD-10A, Shimadzu Corporation, Japan), and MZ-Gel SD plus 5.0 μm columns. Chromatographically pure DMF containing 50 mmol/L lithium bromide was used as the eluent at a flow rate of 1.0 mL/min at 50 °C. The number-average molecular weight (*M_n*) was calculated using a calibration curve which was obtained from polystyrene standards.

Water Dispersibility and Self-assembly of PLA-g-PAA

PLA-g-PAA (50 mg) was dissolved in 0.5 mL of DMF, and then 0.01 mL of this solution was dropped into 5 mL of deionized water with stirring. pH was adjusted by adding sodium hydroxide solution and hydrochloric acid. The radius of the PLA-g-PAA suspension particles was determined by ALV/DLS/SLS-5022F Laser Light Scattering System with the He-Ne laser (λ = 632.8 nm). The morphology of PLA-g-PAA suspension particles was observed by transmission electron microscopy (TEM, JEM-2010) operated at an accelerating voltage of 120 kV.

RESULTS AND DISCUSSION

In the proof-of-concept study, the reaction product mixtures of 3 solutions (PLA+BP+AA, PLA+AA, and BP+AA), all of which were irradiated with 254 nm ultraviolet light for 1 h, were directly dissolved in the deuterated DMF and characterized by ¹H-NMR (Fig. 1). In the reaction system containing PLA, BP, and AA (Fig. 1a), besides NMR signals of the initial reaction mixtures, characteristic signals of poly(acrylic acid) at 2.5 ppm (the methine hydrogens in the PAA main chain) were obvious, indicating acrylic acid having been successfully polymerized. In contrast, reaction systems without the photoinitiator BP or the polymer PLA only showed NMR signals of the initial reagent but hardly any noticeable signs of poly(acrylic acid), suggesting that no significant AA homo-polymerization occurred without either PLA or BP. This is in consistent with the proposed photo-grafting reaction mechanism (Scheme 1).

The unreacted AA monomers and BP residuals were easily removed by washing with ethanol. The purified products

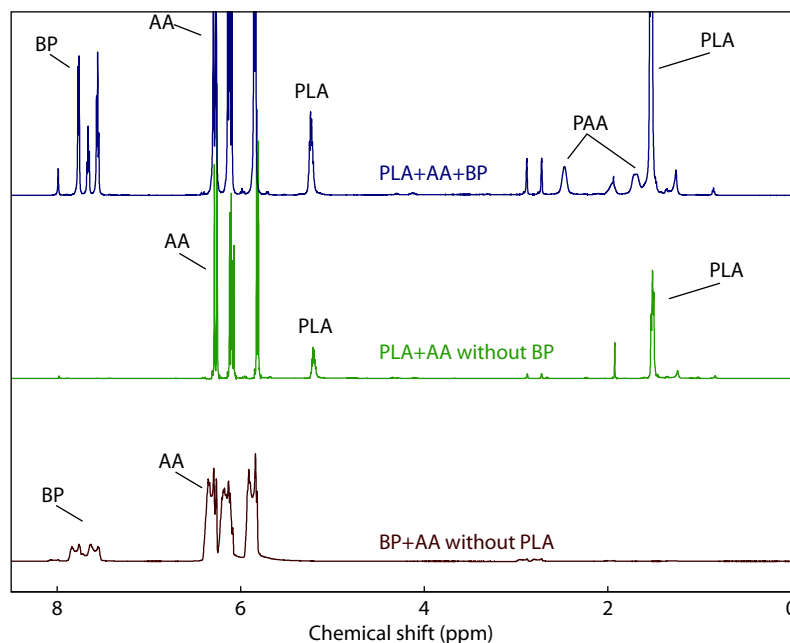


Fig. 1 (From top to bottom) ^1H -NMR spectra of the reaction mixtures of PLA+AA+BP (initial AA/PLA weight ratio of 5, BP content of 10 wt% of AA), PLA+ AA without BP (initial AA/PLA weight ratio of 5), and BP+AA without PLA (BP content of 10 wt% of AA) after irradiated for 1 h under 254 nm UV.

were then characterized by ^1H -NMR, solid state ^{13}C -NMR, and DOSY NMR spectroscopies (Fig. 2). All the hydrogens and carbons in the proposed chemical structures can be clearly identified in the NMR spectra, especially the quaternary carbon of PLA-*g*-PAA in the solid state NMR spectrum (Fig. 2B). The ^1H -NMR signal at 1.0 ppm is also present in the spectrum of PLA raw material. The wide signal between 3 and 4 ppm cannot be identified, probably due to the photo-degradation product of PLA (more discussion on this later).

In DOSY NMR (Fig. 2C) spectrum, all the PLA and PAA signals are shown in one diffusion band, indicating that the PAA chains were chemically bound to the PLA chains and suggesting that the product was free from homopolymers of PAA. Therefore, the grafted PAA can be quantified in terms of PAA/PLA mass ratio by using the ^1H -NMR signals representing the methine hydrogens in the PAA chain (signal e at 2.5 ppm), the methylene hydrogens from PAA, and the methylene hydrogens from PLA (signals a, b, and d, 1.40–1.75 ppm):

$$\frac{\text{PAA}}{\text{PLA}} \text{ ratio} = \frac{A_e}{(A_{abd} - 2A_e)/3} \times \frac{\text{MW}_{\text{AA}}}{\text{MW}_{\text{LA}}}$$

where MW_{AA} and MW_{LA} are the formula weight of acrylic acid and lactic acid residues, respectively.

In addition to the grafting reaction, photo-degradation (both chain decomposition and crosslinking) of PLA under UV irradiation is also known in literature.^[16,17] For all the reaction conditions tested in this study, little amount of material was found insoluble in DMF, which is a common solvent for PLA and PAA, suggesting that crosslinking reaction was not significant. We then used GPC to characterize the apparent molecular weight of the PLA-*g*-PAA products after different irradiation times (Table 1). Compared with the PLA raw material, the apparent molecular weight and the molecular weight dis-

tribution (indicated by PDI in Table 1) of PLA-*g*-PAA products did not change much with irradiation. Considering that significant amount of PAA was grafted onto the PLA chains (Fig. 3a), the GPC results suggested that PLA chain decomposition did occur simultaneously with the grafting reaction. It also should be noted that what GPC actually characterized was the hydrodynamic size of polymer chains in the mobile phase solvent (*i.e.*, DMF), so PLA-*g*-PAA with different PAA/PLA ratios may have similar retention time even though their true molecular weights were different, and vice versa.

We then studied the effect of various reaction parameters on the graft ratio (Fig. 3). In principle, graft ratio is affected by the UV wavelength and intensity, the irradiation duration, the concentrations of photoinitiator, polymer, and monomer. Besides 254 nm UV, we also tested 365 nm UV irradiation, but no graft reaction took place in the latter condition. In addition to the 1-mm-deep system, we also conducted the experiments with a 3-mm-deep glass groove. Unlike the 1-mm setup, after UV irradiation, the reaction mixture in the 3-mm system showed layered structure: the top layer was opaque and solid-like, while the bottom layer remained liquid. Therefore, we considered that 3 mm would be too thick to achieve homogeneous reaction and conducted all the remaining experiments with 1-mm solutions. The graft ratio continuously increased with the irradiation time (Fig. 3a), while it initially increased with the photoinitiator concentration but levelled off after the BP/AA percentage reached 5% (Fig. 3b). Little amount of PAA was grafted onto PLA chains when the AA/PLA weight ratio in the initial mixture was 1/1, which had the highest viscosity among all the test groups. However, the graft ratio was much higher when the AA/PLA ratio increased to 2.5, and did not increase significantly with further addition of AA monomers. The reaction yield, which here is defined as

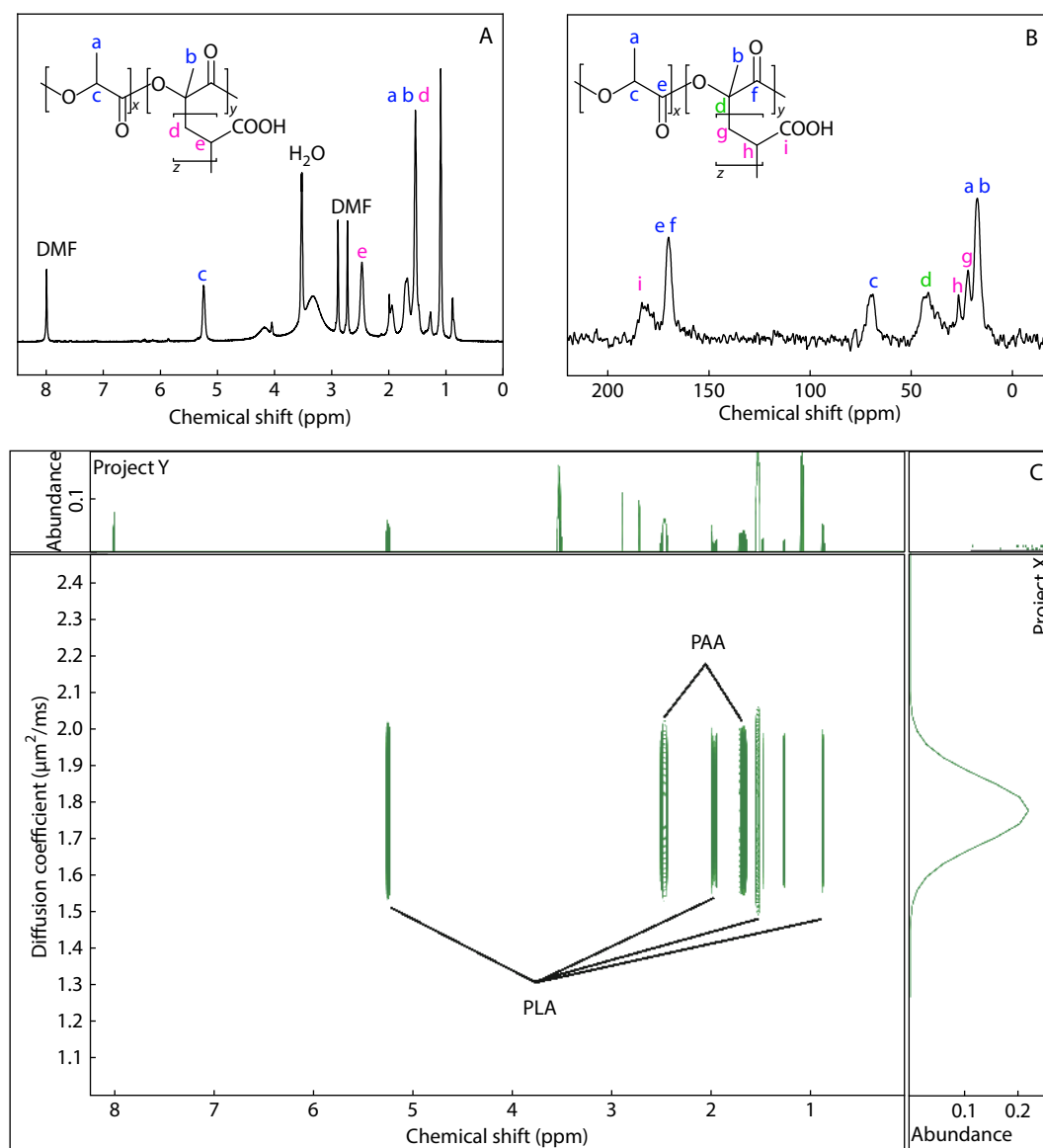


Fig. 2 (A) ^1H -NMR spectrum, (B) solid state ^{13}C -NMR spectrum, and (C) DOSY NMR spectrum of PLA-g-PAA. (Initial AA/PLA ratio of 5, BP content of 10%, after irradiated for 1 h under 254 nm UV.)

Table 1 Number-average molecular weight and molecular weight distribution (PDI) of the initial PLA sample and PLA-g-PAA products with reaction time of 10, 30, and 60 min (200 mg PLA + 100 mg BP + 1 g AA under 254 nm UV).

Reaction time	M_n (Da)	PDI
0 (raw PLA)	21041	1.29
10 min	25047	1.21
30 min	21293	1.27
60 min	22103	1.22

the mass ratio between the purified PLA-g-PAA product and the initial PLA, was found increasing linearly with the graft ratio (Fig. 3d).

For all the reaction systems tested, the highest graft PAA/PLA ratio was found to be 1.8, i.e., the product polymer contained more PAA components than PLA. We then tested the water dispersibility of the PLA-g-PAA products with different

grafting ratios by adding concentrated polymer/DMF solution (100 mg/mL) into deionized water. For PLA-g-PAA products with PAA/PLA graft ratio below 1, the polymers formed large precipitate in the aqueous solution (data not shown). In contrast, those polymers with higher PAA/PLA ratios (1.1–1.8) formed homogeneous suspension (without apparent precipitating for at least 2 weeks at room temperature), and light scattering characterization showed the average radius of the suspension particles was 200–300 nm (Fig. 4). Random graft copolymers are known to self-assemble into various structures in selective solvents.^[18,19] We further characterized the particle size changes with the solution pH (Fig. 4). The self-assembled particles became smaller as the pH increased from 1 to 13, with a small plateau around pH 5–6, which is near the pK_a of the carboxylic acid groups in poly(acrylic acid). The observed particle size-pH relationship is similar to that of the well-defined polystyrene-*b*-poly(acrylic acid) block copoly-

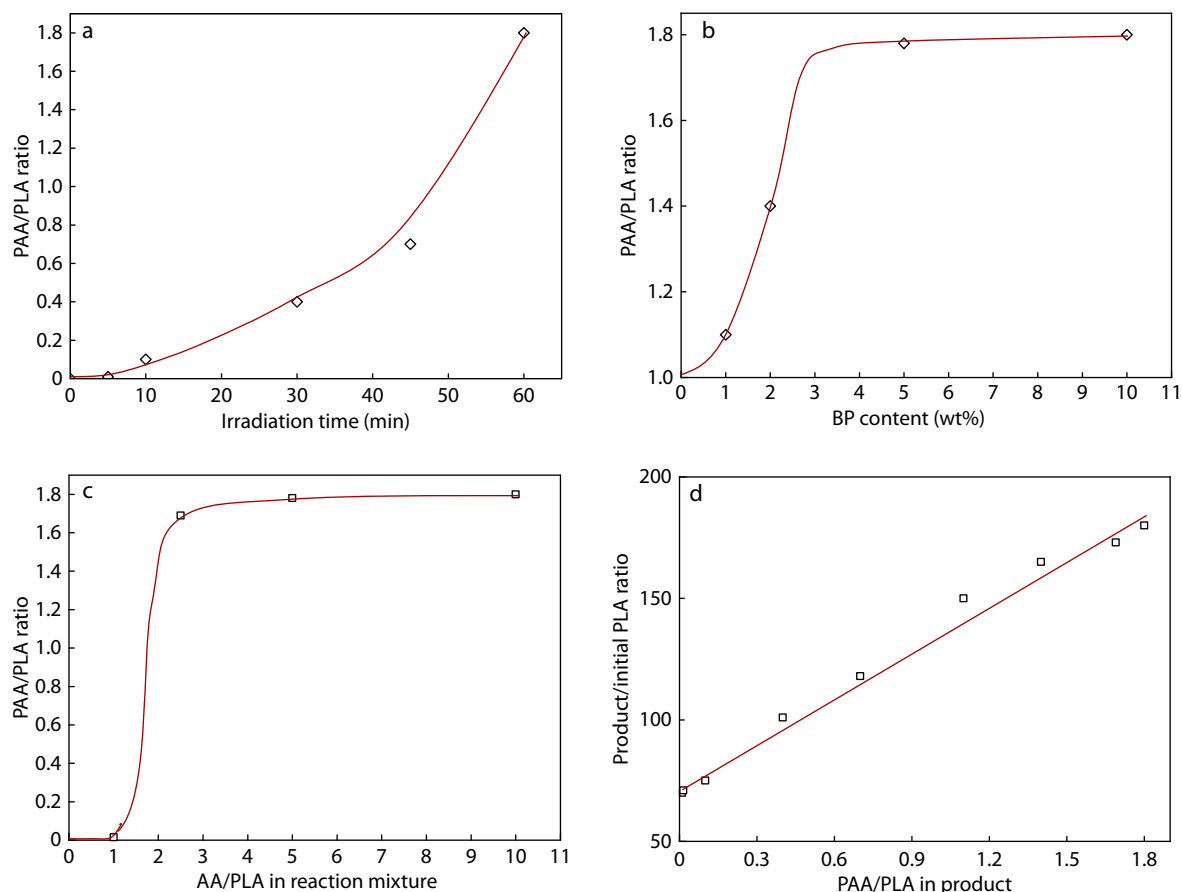


Fig. 3 (a) PAA/PLA graft ratios plotted as a function of reaction time (initial AA/PLA ratio of 5, BP content of 10%); (b) PAA/PLA graft ratios plotted as a function of BP content (initial AA/PLA ratio of 5, reaction time of 60 min); (c) PAA/PLA graft ratios as a function of AA/PLA ratios in the initial reaction mixture (BP content of 10%, reaction time of 60 min); (d) The reaction yield (purified product/initial PLA ratio) plotted as a function of PAA/PLA graft ratios in the PLA-g-PAA products.

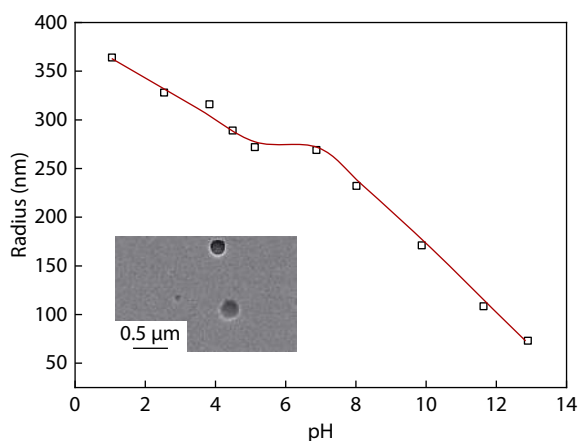


Fig. 4 Particle size of the PLA-g-PAA self-assembled structures in water at different pH (PAA/PLA graft ratio of 1.1).

mers,^[20] and may be similarly explained as follows: as pH increases, the ionization degree of PAA graft chains increases, and consequently the increased repulsion among the hydrophilic PAA chains decreases the aggregation number and the particle size.

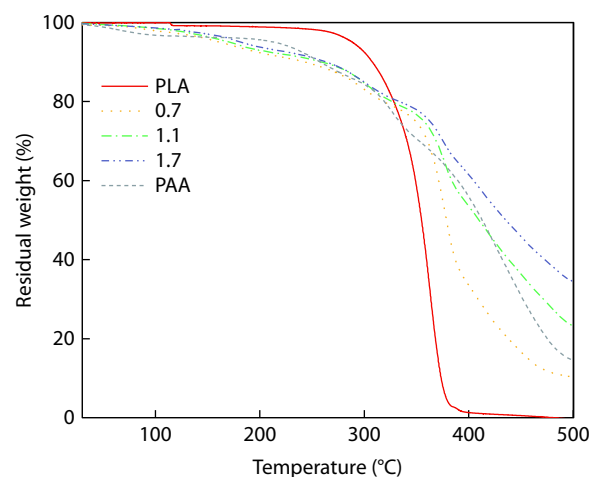


Fig. 5 TGA curves of PLA, PAA and PLA-g-PAA with PAA/PLA ratio of 0.7, 1.1, and 1.7.

Finally, we characterized the thermal stability of the PLA-g-PAA polymers with TGA (Fig. 5). Unlike PLA, which remained stable until 280 °C and almost completely decomposed at 400 °C, PAA went through continuous decomposition (e.g.,

dehydration/anhydride formation and decarboxylation) with heating, especially above its glass transition temperature around 100 °C.^[21] However, at 500 °C, there were more residual solids from PAA than PLA. PLA-g-PAA products with various graft ratios behaved more like PAA than PLA.

CONCLUSIONS

This study proved that acrylic acid could be efficiently graft polymerized onto poly(lactic acid) chains via a photo-grafting reaction in solution. Similar surface photo-grafting reactions on the PLA films are widely studied in literature, but the bulk solution reaction has not been reported before, which was made possible only after we realized that poly(lactic acid) can be readily dissolved in the AA monomer at room temperature.

PAA/PLA graft ratio in the PLA-g-PAA products can be adjusted by varying the reaction parameters, and high graft ratios such as 1.8 could be achieved. Compared with the known thermally-initiated graft reaction, the current photo-grafting reaction was fast, took place at room temperature, and more importantly, resulted in little homo-polymerization of acrylic acid. On the other hand, as for all photo-chemical reactions, the light penetration depth limited the scale-up potential of this photo-grafting reaction, unless continuous operation is achieved through specially designed reactors.

The resulting PLA-g-PAA polymers with enough high-graft ratios were found water dispersible, which potentially enables the aqueous processing of PLA-based materials. Moreover, PLA-g-PAA may be used as a compatibilizer for blending PLA with other polymers and inorganic materials.^[22,23]

It is tempting to expand the photo-grafting reaction to other vinyl monomer systems. For the photo-grafting reaction to be effective, there are at least two requirements for the vinyl monomer: one is that PLA has to be soluble in the monomer without significant heating, and the other is that there are no hydrogen atoms in the monomer structure which are easier to be abstracted than those in the PLA chains. Other vinyl monomers will be screened in the next step.

ACKNOWLEDGMENTS

The work was financially supported by the National Natural Science Foundation of China (No. 21434008). We thank Professor Lei Tao and his laboratory for the GPC characterization.

REFERENCES

- Di Lorenzo, M. L.; Androsch, R. (eds.) *Synthesis, structure and properties of poly(lactic acid)*. Springer, Switzerland, **2018**, p. 1.
- Aurus, R.; Lim, L.; Selke, S. E. M.; Tsuji, H. (eds.) *Poly(lactic acid): synthesis, structures, properties, processing, and applications*. Wiley, Canada, **2010**, p. 141.
- Krishnan, S.; Pandey, P.; Mohanty, S.; Nayak, S. K. Toughening of poly(lactic acid): an overview of research progress. *Polym. Plastic. Tech. Eng.* **2016**, *55*, 1623–1652.
- Ramot, Y.; Haim-Zada, M.; Domb, A. J.; Nyska, A. Biocompatibility and safety of PLA and its copolymers. *Adv. Drug Deliver. Rev.* **2016**, *107*, 153–159.
- Tyler, B.; Gullotti, D.; Mangraviti, A.; Utsuki, T.; Brem, H. Poly(lactic acid) (PLA) controlled delivery carriers for biomedical applications. *Adv. Drug Deliver. Rev.* **2016**, *107*, 163–168.
- Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. Poly(lactic acid) modifications. *Prog. Polym. Sci.* **2010**, *35*, 338–356.
- Critchfield, F. E.; Koleske, J. V. US Patent 3,760,034, 1973.
- Wu, C. Improving polylactide/starch biocomposites by grafting polylactide with acrylic acid—characterization and biodegradability assessment. *Macromol. Biosci.* **2005**, *5*, 352–361.
- Dorman, G.; Nakamura, H.; Pulsipher, A.; Prestwich, G. D. The life of pi star: exploring the exciting and forbidden worlds of the benzophenone photophore. *Chem. Rev.* **2016**, *116*, 15284–15398.
- Yang, W. T.; Ranby, B. Bulk surface photografting process and its applications. I. Reactions and kinetics. *J. Appl. Polym. Sci.* **1996**, *62*, 533–543.
- Li, Y.; DeSimone, J. M.; Poon, C.; Samulski, E. T. Photoinduced graft polymerization of styrene onto polypropylene substrates. *J. Appl. Polym. Sci.* **1997**, *64*, 883–889.
- Ranby, B.; Yang, W. T.; Tretinnikov, V.; Tokarev, V.; Xu, Y. H. Lamination of polymer films by bulk surface photografting process and properties. *Chinese J. Polym. Sci.* **2001**, *19*, 123–127.
- Yang, W. T.; Ranby, B. Bulk surface photografting process and its applications. II. Principal factors affecting surface photografting. *J. Appl. Polym. Sci.* **1996**, *62*, 545–555.
- Ma, H.; Davis, R. H.; Bowman, C. N. A novel sequential photoinduced living graft polymerization. *Macromolecules* **2000**, *33*, 331–335.
- Janorkar, A. V.; Metters, A. T.; Hirt, D. E. Modification of poly(lactic acid) films: enhanced wettability from surface-confined photografting and increased degradation rate due to an artifact of the photografting process. *Macromolecules* **2004**, *37*, 9151–9159.
- Ikada, E. Photo- and bio-degradable polyesters, photodegradation behaviours of aliphatic polyesters. *J. Photopolym. Sci. Tech.* **1997**, *10*, 265–269.
- Tsuji, H.; Echizen, Y.; Nishimura, Y. Photodegradation of biodegradable polyesters: a comprehensive study on poly(L-lactide) and poly(ε-caprolactone). *Polym. Degrad. Stab.* **2006**, *91*, 1128–1137.
- Li, L.; Raghupathi, K.; Song, C.; Prasad, P.; Thayumanavan, S. Self-assembly of random copolymers. *Chem. Commun.* **2014**, *50*, 13417–13432.
- Zhou, Y.; Liu, B.; Wang, X. Self-assembly of homopolymers through strong dipole-dipole interaction in their aqueous solutions. *Polymer* **2016**, *97*, 1–10.
- Choucair, A.; Lavigueur, C.; Eisenberg, A. Polystyrene-b-poly(acrylic acid) vesicle size control using solution properties and hydrophilic block length. *Langmuir* **2004**, *20*, 3894–3900.
- McNeill, I. C.; Sadeghi, S. M. T. Thermal-stability and degradation mechanisms of poly(acrylic acid) and its salts. I. Poly(acrylic acid). *Polym. Degrad. Stab.* **1990**, *29*, 233.
- Chen, L.; Hu, K.; Sun, S.; Jiang, H.; Huang, D.; Zhang, K.; Pan, L.; Li, Y. Toughening poly(lactic acid) with imidazolium-based elastomeric ionomers. *Chinese J. Polym. Sci.* **2018**, *36*, 1342–1352.
- Zhang, J.; Jia, J.; Kim, J. P.; Shen, H.; Yang, F.; Zhang, Q.; Xu, M.; Bi, W.; Wang, X.; Yang, J.; Wu, D. Ionic colloidal molding as a biomimetic scaffolding strategy for uniform bone tissue regeneration. *Adv. Mater.* **2017**, *29*, 1605546–1605554.