Journal of Applied Polymer Science

Synthesis and Characterization of Polyaspartic Acid-Glutamic Acid Grafted Copolymers and Their Performances as Detergent Builder

Dongyu Zhu, Jianwei Guo, Ping Yang, Lihui Pan, Xing Zhong, Shaohua Chen
School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, People's Republic of China
Correspondence to: J. Guo (E-mail: guojw@gdut.edu.cn)

ABSTRACT: Polysuccinimide (PSI) was first synthesized via thermal polycondensation reaction using maleic anhydride and urea as the starting materials. Then, polyaspartic acid–glutamic acid (PASP–GLU) grafted copolymers were prepared from PSI and GLU. The structure of PASP–GLU was characterized by Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The molecular weight was measured by gel permeation chromatography, and the crystallinity was analyzed by X-ray diffraction spectra. The effects of grafting ratio on the builder performances were systematically studied, as well as on the thermal property and biodegradability. It is demonstrated that as the grafting ratio of GLU increases, the thermal stability and biodegradability decrease a little, but still maintain in high level. Most importantly, the incorporation of GLU into side chains significantly improves the builder performance of PASP–GLU. The maximum values for calcium ion chelating power, dispersion power of $CaCO_3$, and alkali-buffer ability reach 233.2 mg, 108.9 mg, and 1.70 mL, respectively, at the highest grafting ratio, in which the dispersion power of $CaCO_3$ and alkali-buffer ability are even better than that of sodium tripolyphosphate. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40282.

KEYWORDS: biodegradable; grafting; properties and characterization; copolymers

Received 18 November 2013; accepted 10 December 2013
DOI: 10.1002/app.40282

INTRODUCTION

Polyaspartic acid (PASP) is a kind of polyamino acids with carboxyl groups in the side chains, which possesses good biodegradability, as well as chelating ability and dispersability.[1,2] PASP molecule could easily adsorb or bind with metal ions because of its structural characteristics; however, its chelating and dispersion capacity is not as good as acrylic acid or maleic acid polymers which are widely used at present. Thus, to improve the chelating and dispersing capacity, some functional groups such as hydroxyl and sulfonic groups are introduced into the molecular structure of PASP, which has been previously reported.[3–6] The modified PASP is generally used for corrosion inhibition and water treatment[7–9]; however, to the best of our knowledge, neither PASP grafted with glutamic acid (GLU) nor PASP derivative used as detergent builder has been yet reported.

Therefore, the aim of this study is to improve the performance of PASP to extend its application in detergent builder field and, on the other hand, to develop new phosphorus-free biodegradable detergent builders based on the exploration of the already-existing properties of PASP. According to the emphasis on the requirements of detergent builder in an important review by Yu et al.,[10] the development of builders is not only to improve their washing power and capacity for sequestering all the hardness but also to require the obtained builders biodegradable and nonpolluting. Poly(glutamic acid) is a kind of ideal biodegradable high-molecular-weight polymer. Moreover, GLU molecule contains an amino group and two carboxylic acid groups that can enhance chelating ability and dispersability. Accordingly, GLU was introduced into the side chains of the PASP molecular structure so as to obtain the graft copolymeric detergent builder, which has nitrogen atoms in the backbone chain and carboxyl groups on the side chains.

The novel and biodegradable polyaspartic acid–glutamic acid (PASP–GLU) grafted copolymer was synthesized from polysuccinimide (PSI) and GLU by aminolysis reaction. The reaction mechanism was illustrated, and the effects of feed mole ratio on the grafting ratio were researched by using different raw ratios of GLU to PSI. Furthermore, the impacts of the grafting ratio on the molecular weight, crystallinity, thermal stability, biodegradability, and builder performances were systematically studied to optimize the combination properties of the synthesized grafted copolymer.

EXPERIMENTAL

Main Reagents

Maleic anhydride, urea, and *N*,*N*-dimethyl formamide were purchased from Tianjin Kermel Chemical Reagent. GLU was

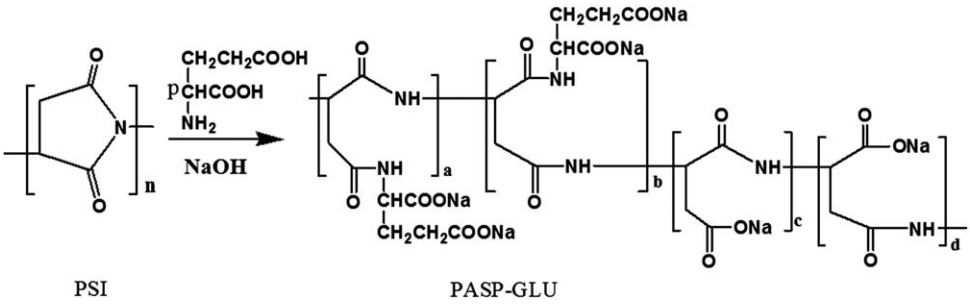

Figure 1. Synthesis route of graft copolymer.

purchased from Shanghai Juyuan Biological Technology. All the reagents were used as received and without further purification.

Synthesis of PSI

According to the method reported in the literature,[11] PSI was synthesized by amination followed with thermal polycondensation of maleic anhydride and urea. The product was purified by using *N*,*N*-dimethyl formamide as solvent to remove the unreacted reactants and then was dried.

Preparation of PASP–GLU

The grafted copolymers of PASP–GLU were prepared according to the route as shown in Figure 1. First, dried PSI was accurately weighed and added into an Erlenmeyer flask. After a certain amount of water was added, the mixture was stirred constantly at room temperature. Then, sodium glutamic acid solution was added slowly into the above suspension, and the pH of the system was kept at about 8–9 with sodium hydroxide solution (2 mol/L). After the reaction was carried out for 24 h, a reddish brown transparent liquid was obtained, and then the pH was adjusted to 3.0 with hydrochloric acid. The resultant solution was cooled down to 0–5°C to precipitate the unreacted glutamic acid. After filtration, the solution was concentrated and poured into a certain amount of ethanol. The product was obtained as reddish brown precipitate after dried in vacuum.

Characterization of PASP–GLU

Calculation of Grafting Rate. Based on the ninhydrin colorimetry method,[12] the residual GLU content was indirectly detected by absorbance data on a Shanghai Hengping UV-2000 UV/visible spectrophotometer.

The grafting ratio of PASP–GLU can be calculated by using the following equation:

$$GR = \frac{M_0 - M_1}{M_0} \times X \times 100\%, \quad (1)$$

where GR is the grafting ratio of the grafted copolymer, M_0 is the initial mass of amino acid (g), M_1 is the residual mass of amino acid (g), and X is the initial mole ratio of amino acid.

Structural Characterization. The structure of the grafted copolymer was characterized by Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (^{1}H-NMR) spectroscopy. The FTIR spectra were recorded in KBr pallets on a Nicolet 6700 FTIR spectrometer from 400 to 4000 cm^{-1}. The ^{1}H-NMR spectra were recorded on a Bruker AVANCE AV-500 NMR spectrometer with D_2O as the solvent. The average molecular weight and the molecular weight distribution of the copolymer were measured using gel permeation chromatography (GPC), with water as the eluent at a flow rate of 1.0 mL/min. The crystallinity was analyzed by X-ray diffraction (XRD) spectra, which was recorded on Giga D/max-2400 X-ray diffractometer, with the scanning angle in the range from 10° to 70° at a scanning rate of 4°/min.

Performance Tests of PASP–GLU

Thermal Properties. Thermal stability of the grafted copolymer was investigated by thermogravimetric analyzer (TGA; Metter-Toledo TGA) on heating from 30 to 620°C at a scanning rate of 10°C/min in nitrogen atmosphere flowing at 200 mL/min.

Biodegradability. The biodegradability of the copolymers was measured by shaking table test method.[13] The degree of biodegradability of the copolymers could be measured by potassium permanganate index [$\rho(COD_{Mn})$]. The potassium permanganate index would decrease with the degradation of the copolymers.

The microorganism was obtained from activated sludge from the Guangzhou Lijiao Wastewater Treatment Plant. The nutrient composition (g/L) contained in the microorganism is as follows: phosphate buffer: KH_2PO_4 (8.50), K_2HPO_4 (21.75), $Na_2HPO_4{\cdot}2H_2O$ (33.40), NH_4Cl (1.7); calcium chloride solution: $CaCl_2{\cdot}2H_2O$ (36.40 g); magnesium sulfate solution: $MgSO_4{\cdot}7H_2O$ (22.50 g); ferric chloride solution: $FeCl_3{\cdot}6H_2O$ (0.25 g); and ammonium sulfate solution: $(NH_4)_2SO_4$ (40 g).

The testing procedure was as follows: The sample was prepared with a concentration of 50 mg/L [$\rho(COD_{Mn})$ = 10–20 mg/L]. One liter of the above solution was added into the nutrient solution, which is obtained by mixing calcium chloride solution (2 mL), magnesium sulfate solution (2 mL), ammonium sulfate solution (2 mL), ferric chloride solution (4 mL), phosphate buffer (2 mL), and inoculums (20 mg). Besides, the same nutrient solution but without adding the sample was also prepared as a blank sample for control test.

The above sample and blank sample solution with the same amount (50 mL) were added to conical beakers, which were sealed by cotton plug and plastic paper. Then, the solutions were added to the shaking table to culture (30°C, 120 r/min), and the test time began.

A series of $\rho(COD_{Mn})$ values were measured according to the sample concentration after 1 day, 4 days, 8 days, 12 days, 16 days, 20 days, and 28 days.

The biodegradation rate of the sample was calculated by the following equation:

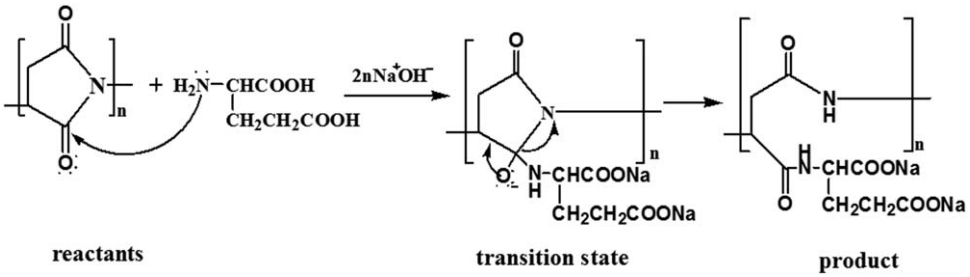

Figure 2. Schematic of the reaction mechanism for PASP–GLU.

$$\eta_n(\%)=[1-\rho(\mathrm{COD}_{\mathrm{Mn}}{}^n)/\rho(\mathrm{COD}_{\mathrm{Mn}}{}^0)]\times 100\%, \quad (2)$$

where η_n is biodegradation ratio, $\rho(\mathrm{COD}_{\mathrm{Mn}}{}^n)$ represents potassium permanganate index of the first n days, and $\rho(\mathrm{COD}_{\mathrm{Mn}}{}^0)$ is potassium permanganate index of initial solution.

Builder Performances. ***Calcium ion chelating power.*** The test procedure for calcium ion chelating power (CaCP) was as follows: in the first place, a sample (0.1500–0.2500 g) was accurately weighed and transferred to a 250-mL volumetric flask and then 100 mL of distilled water was added into the flask. After that, 25 mL of the $CaCl_2$ standard solution (0.05 mol/L) was pipetted into the volumetric flask and adjusted to volume by adding distilled water. After interrupted oscillation for 30 min, the above solution was dry filtered with qualitative filters. Subsequently, 25 mL of the filtrate was carefully pipetted into a 250-mL Erlenmeyer flask, and 25 mL of the ammonia–ammonium chloride buffer solution (pH = 10.5) was also added and mixed. In the last stage, the solution was titrated using EDTA standard solution (0.05 mol/L) with 4–5 drops of the chrome black T as indicator, which shows the titration end point based on the color change from wine red to deep blue in the titration process. Parallel determination experiments were done three times for each sample, and the results were also averaged.

The CaCP was calculated as mass ratio according to the following formula:

$$\mathrm{CaCP}\ (\mathrm{mg\ CaCO_3/g})=\frac{100.08\times(25C_0-10C_1V_1)}{m}, \quad (3)$$

where 100.08 is the molar mass of calcium carbonate ($CaCO_3$), in mg/mmol; C_0 is the molar concentrations of $CaCl_2$ standard solution, in mol/L; C_1 is the molar concentrations of EDTA standard solution, in mol/L; V_1 is the volume of EDTA standard solution consumed in the titration, in mL; and m is the mass of the sample taken for the test, in g.

Dispersion power. The sample (1.0000 g) was dissolved into 100 mL deionized water, and then 10 mL of 10 wt % Na_2CO_3 solution was added, followed by the addition of NaOH solution to adjust the pH to 11.0. Then, the above solution was titrated using calcium acetate solution (0.25 mol/L) until turbidity persists.

The dispersion power of $CaCO_3$ (CaDP) was calculated as mass ratio according to the following formula:

$$\mathrm{CaDP}\ (\mathrm{mg\ CaCO_3/g})=\frac{100.08CV}{m}, \quad (4)$$

where 100.08 is the molar mass of $CaCO_3$, in mg/mmol; C is the molar concentrations of calcium acetate solution, in mol/L; V is the volume of the calcium acetate solution used in the titration, in mL; and m is the mass of the sample taken for the test, in g.

Alkali-buffer ability. NaOH solution (0.1 mol/L) was added into 100 mL of the 0.1% sample solution to adjust the pH to 10.0. After that, hydrochloric acid was added dropwise to adjust the pH to 8.0. The alkali-buffer ability was the volume of the hydrochloric acid consumed in the titration.

RESULTS AND DISCUSSION

Synthesis of PASP–GLU

Reaction Mechanism. The mechanism of the reaction is shown in Figure 2. As shown in Figure 2, the carbonyl in the PSI is the electron-deficient center, which is vulnerable to be attacked by the nucleophilic reagent, whereas NH_2— in GLU has lone pairs of electrons. Thus, it is illustrated that the reaction takes place based on the nucleophilic substitution (addition–elimination) reaction and that PASP–GLU is obtained through a transition state under alkaline conditions.

Determination of Grafting Ratio. The grafting ratio of PASP–GLU was determined based on the standard curve constructed by investigating the relationship between the absorbance and the concentration of GLU as shown in Figure 3(a). It can be seen from Figure 3(b) that the grafting ratio increases monotonously with the feed mole ratio of GLU and PSI to a maximum value of 60% corresponding to the feed mole ratio of 1.8 : 1, and then the grafting ratio becomes almost constant or even slightly decreases with the feed mole ratio. This is due to the steric hindrance effect, that is, when the content of GLU increases to a certain extent, the GLU would prevent the proceeding of the reaction and make the grafting ratio to no longer increase.

Characterization of the Grafted Copolymer

FTIR and ^{1}H-NMR. The FTIR spectra of PASP and PASP–GLU are shown in Figure 4. The characteristic peaks at 3450 and 1601 cm^{-1} can be attributed to the stretching and bending vibration of N—H in amide, respectively. The peak at 1640 cm^{-1} was ascribed to C=O, whereas the peak at 1400 cm^{-1} corresponds to the strong signal of C—N. The above FTIR signals have indicated the structure of PASP in the two curves. Moreover, when comparing curve (b) with curve (a), it is shown that the absorption peak assigned to C=O of carboxyl groups becomes more obvious and that the signal belonging to C—O of carboxyl groups also exhibits much stronger signals, which demonstrates that the GLU part has been incorporated into the side chain of PASP.

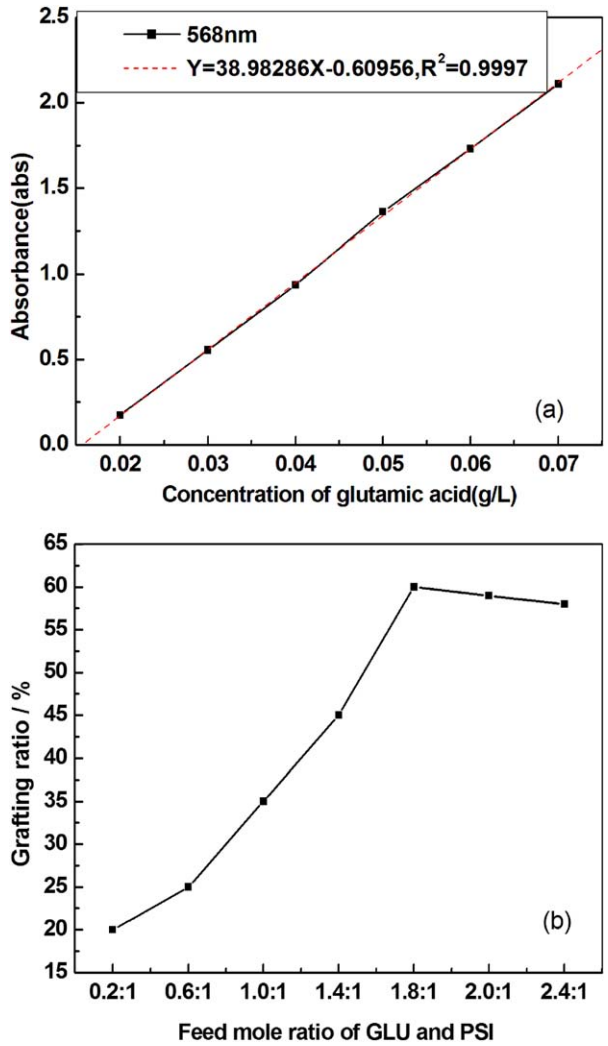

Figure 3. (a) The relationship between the absorbance and the concentration of glutamic acid. (b) The effect of feed mole ratio of GLU and PSI on the grafting ratio of PASP–GLU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To further confirm the structure of the grafted copolymer, the sample was also analyzed by ^{1}H-NMR, and the results are shown in Figure 5. As shown in Figure 5, the characteristic peaks for the ^{1}H-NMR spectrum of PASP appear at 2.47–2.83 ppm, which is assigned to the methylene protons of (—CH_2—), at 4.41 ppm for the methine proton of [t, —NH—C***H***(COOM)—CH_2CO—], and at 4.39 ppm for methine proton of [—NH—C***H***(CH_2COOM)—CO—]. In the grafted product, the peaks of [t, —NH—C*H*(COOM)—CH_2CO—] and [t, —NH—C*H*(CH_2COOM)—CO—] are having the chemical shifts at 4.45 and 4.58 ppm, and the peak of [t, —C*H*(CH_2CH_2COOM)—COOM] at 3.81 ppm, the peak of [m, —CH—CH_2—COOM, —CH—CH_2—CO—] at 2.61–2.68 ppm, the peaks of [m, —CH_2CH_2COONa] at 2.23–2.24 ppm, and the peaks of [m, —CH_2CH_2COONa] at $\delta = 1.95$–2.06. The above NMR signals of PASP and the grafted product indicate that the bonding between PASP and GLU has occurred.

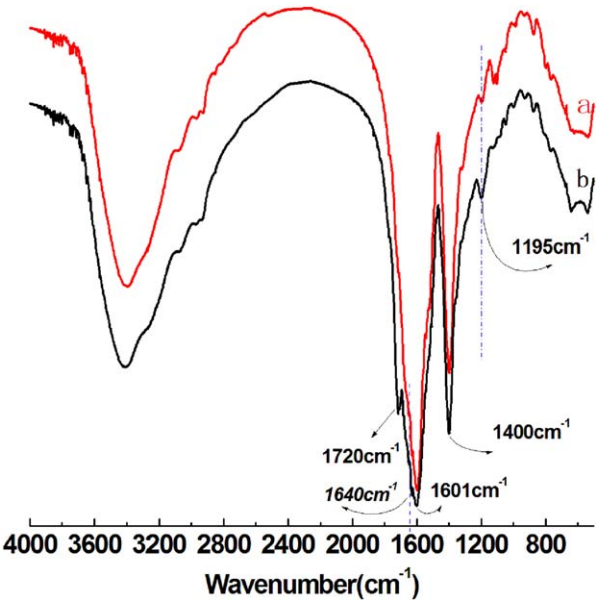

Figure 4. FTIR spectra of PASP and PASP–GLU graft copolymer: (a) PASP and (b) PASP–GLU graft copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thus, the results of ^{1}H-NMR spectra together with that from the FTIR spectra fully prove the structure of the designed grafted copolymer as PASP–GLU.

Average Molecular Weight. The average molecular weight (M_w) and its distribution (M_w/M_n) of the grafted copolymer measured by the GPC are shown in Table I. It can be seen that the M_w of PASP–GLU varies from 1.20 to 2.96 × 10^4 g/mol

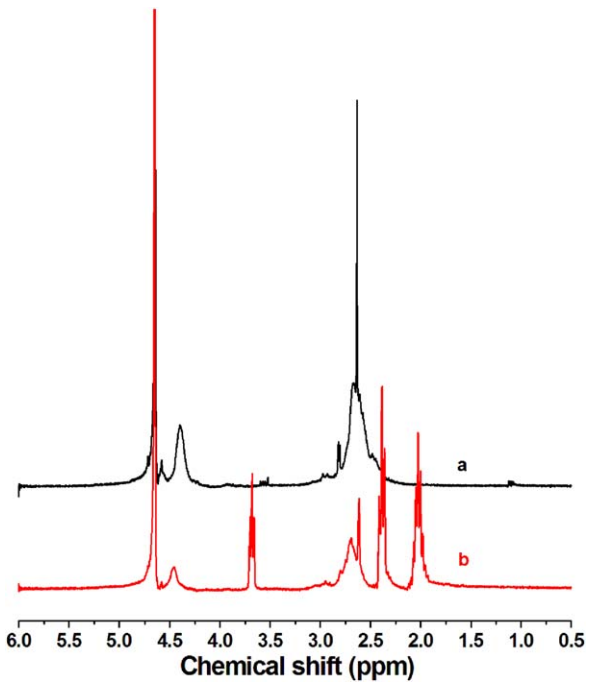

Figure 5. ^{1}H-NMR spectra of PASP and PASP–GLU graft copolymer: (a) PASP and (b) PASP–GLU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Physical Parameters and Builder Performances of PASP–GLU Grafted Copolymers

Code	Feed mole ratio of GLU and PSI	Grafting ratio (%)	M_w ($\times 10^4$)	M_w/M_n	CaCP (mg)	CaDP (mg)	Alkali-buffer ability (mL)
p-0	0	0	1.20	1.01	180.0	100.9	1.45
p-1	0.2 : 1	20	1.85	1.13	199.8	100.8	1.50
p-2	0.6 : 1	25	2.22	1.25	202.0	105.8	1.55
p-3	1.0 : 1	35	2.49	1.59	210.5	107.8	1.60
p-4	1.4 : 1	45	2.68	1.09	215.3	108.2	1.65
p-5	1.8 : 1	60	2.96	1.76	233.2	108.9	1.70
p-6	2.0 : 1	59	2.89	1.35	230.5	108.5	1.70
p-7	2.4 : 1	58	2.74	1.48	229.0	108.3	1.65
STPP	-	-	-	-	302.4	101.3	1.10

according to different grafting ratios. The corresponding polydispersity index M_w/M_n changes irregularly between 1.01 and 1.76. M_w increases with increasing grafting ratio due to the increase in the number of GLU groups on the side chain. As the grafting ratio has a limited value as discussed in the "Determination of Grafting Ratio" section, PASP–GLU has the largest molecular weight at the top point of grafting ratio.

X-ray diffraction. XRD was used to test the crystallinity of the grafted copolymer PASP–GLU. The wide-angle X-ray diffraction (WAXD) patterns of PASP (p-0) and PASP–GLU with the highest grafting ratio of 60% (p-5) are shown in Figure 6. The result shows that no sharp peak is observed in the diffraction curve of PASP (p-0), which indicates the amorphous structure of the PASP. The good biodegradability of PASP has been previously reported,[14] for the degradation of polymer always starts from amorphous region.[15] However, a weak peak in the diffraction curve of PASP–GLU (p-5) was observed at 19.8°C, from which it can be inferred that the biodegradability of PASP–GLU (p-5) would be slightly decreased when compared with PASP due to the incorporation of GLU in the side chains.

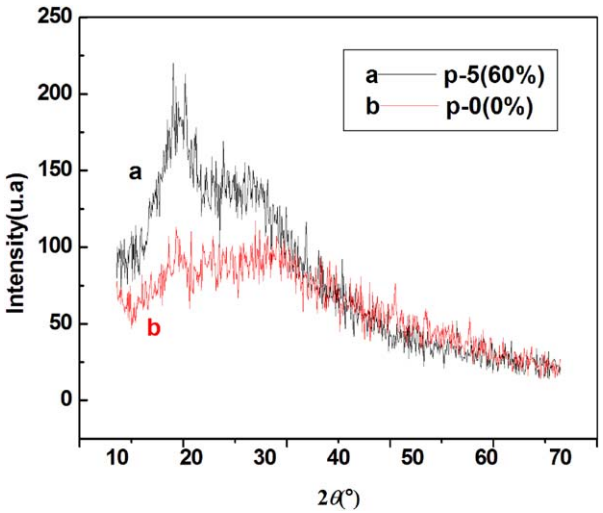

Figure 6. WAXD patterns of PASP and PASP–GLU with the highest grafting ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TGA of Grafted Copolymer

The TG curves of PASP and PASP–GLU are shown in Figure 7. For the sample of p-0 (PASP), before 250°C, the slow weight loss stage corresponds to the loss of bound water in PASP molecular. Within the range of 250–425°C, the rapid weight loss may be attributed to the thermal decomposition of PASP. As to grafted copolymers p-1 and p-5, there are two rapid weight loss stages. The first sharp weight loss stage begins around 200°C, which may be attributed to the disintegration of GLU moieties of the side chains, whereas the second fast weight loss follows at 250–350°C, which corresponds to the decomposition of PASP parts. When comparing p-1 and p-5, it can be found that the original thermal decomposition temperature of PASP–GLU hardly decreases with the increase of grafting ratio, but the loss ratio in the first rapid weight loss stage increases, which is consistent with the increase of grafting ratio of GLU. Altogether, the thermal stability of PASP–GLU grafted copolymers still keeps well below 200°C, which can meet the requirements of detergent builder in application.

Biodegradability

The biodegradation of the grafted copolymers under different test times is shown in Figure 8. On one hand, the ratio of

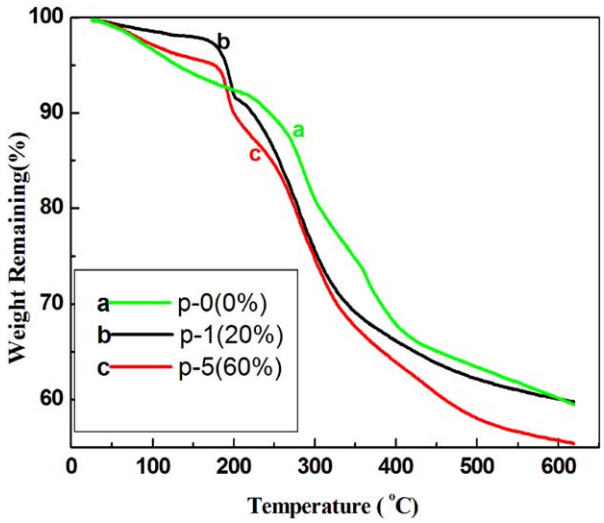

Figure 7. TG of PASP and PASP–GLU graft copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

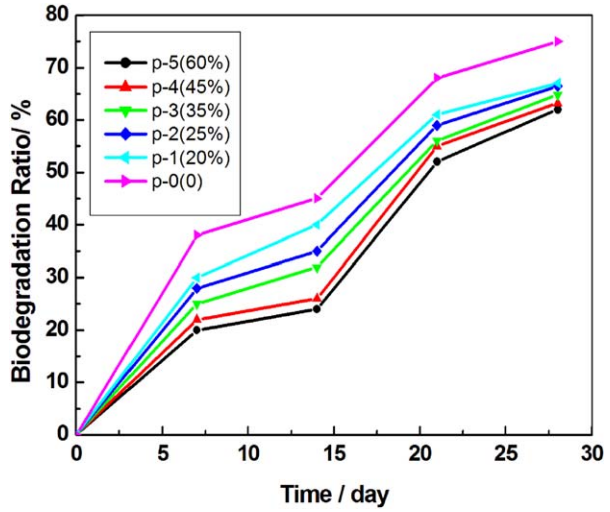

Figure 8. Biodegradation of PASP–GLU with different grafting ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

biodegradation for all the samples increases with time. On the other hand, the biodegradation ratio decreases slowly with the grafting ratio increasing, which may be attributed to the increase of irregular side groups.[16] At each test time, the biodegradation ratio of PASP is higher than that of the grafted copolymers, which is consistent with the XRD results. After 28 days, 75% of the biodegradation has been finished for PASP, and biodegradation degree of the grafted copolymers varies in the range of 62–67% depending on different grafting ratios. Overall, the grafted copolymer PASP–GLU still has good biodegradability.

Builder Performances

The builder performances of PASP–GLU were evaluated for usage as a detergent builder in aspects of CaCP, CaDP, and alkali-buffer ability. The results for a series of the synthesized PASP–GLU with different grafting ratios are summarized in Table I.

As shown in Table I, we can find that the CaCP, CaDP, and alkali-buffer ability are all increasing gradually with the grafting ratio of PASP–GLU. It is because that the higher the grafting ratio, the higher are the weight–average molecular weight and the density of carboxylic radicals so as to result in higher CaCP and CaDP. In addition, as the grafting ratio increases, the higher concentration of conjugate acid–base pairs of COOH/COONa in solution determines that the copolymers possess better alkali-buffer ability.[17] Thus, we can obtain the maximum CaCP, CaDP, and alkali-buffer ability of 233.2 mg, 108.9 mg, and 1.70 mL, respectively, at the highest grafting ratio of 60% corresponding to the best feed mole ratio of 1.8 : 1. The builder performance of the synthesized PASP–GLU grafted copolymer is much better than that of PASP. When compared with sodium tripolyphosphate (STPP), it is found that the CaDP and alkali-buffer ability are even better than that of STPP and that the CaCP is close to the level of STPP, and thus, PASP–GLU can be a promising substitute of STPP as detergent builder.

CONCLUSIONS

PASP–GLU grafted copolymer containing GLU in the side chain was successfully synthesized. The effect of grafting ratio on the properties of PASP–GLU was systematically investigated. It is found that the incorporation of GLU slightly decreases the thermal stability and biodegradability of PASP–GLU, but they still remain in high level. PASP–GLU can be kept stable below 200°C, and the biodegradation ratio of 28 days is above 62%. The introduction of GLU obviously improves the builder performances, including increased CaCP, CaDP, and alkali-buffer ability with the maximum values as 233.2 mg, 108.9 mg, and 1.70 mL, respectively, which is even better than that of STPP, except for CaCP a little inferior. In other words, the GLU-modified PASP–GLU grafted copolymer significantly enhances the builder performances without substantially impairing the thermal stability and biodegradability of PASP. Therefore, PASP–GLU can be used as an environmentally friendly detergent builder with high performances.

ACKNOWLEDGMENTS

This work was financially supported by the Key Program for Scientific and Technological Innovations of Higher Education Institutes in Guangdong Province (No. CXZD1022).

REFERENCES

1. Li, F.; Tan, T. *Dev. Appl. Chem. Ind.* **2001**, *3*, 24.
2. Zhang, R.; Tan, T. W. *J. Appl. Polym. Sci.* **2006**, *100*, 3626.
3. Arimura, H.; Ohya, Y.; Ouchi, T. *Biomacromolecules* **2005**, *6*, 720.
4. Tang, J. S.; Fu, S. L. U.S. Patent 6,022,401 (**2000**).
5. Huang, Y. S.; Cui, F. Z. *Curr. Appl. Phys.* **2005**, *5*, 546.
6. Tang, G. P.; He, B. B. *J. Appl. Polym. Sci.* **2006**, *102*, 46.
7. Oda, Y. Jpn. Pat. 081188 (**2001**).
8. Oda, Y. Jpn. Pat. 344,887 (**2000**).
9. Nakato, T.; Tomida, M.; Suwa, M.; Morishima, Y.; Kusuno, A.; Kakuchi, T. *Polym. Bull.* **2000**, *44*, 385.
10. Yu, Y. X.; Zhao, J.; Bayly, A. E. *Chin. J. Chem. Eng.* **2008**, *16*, 517.
11. Xu, Y.; Zhao, L. L.; Wang, L. N.; Xu, S. Y.; Cui, Y. C. *Desalination* **2012**, *286*, 285.
12. Chen, J. Y. Master's Thesis, Jiangnan University, Jiangsu, China, **2008**.
13. Huang, Y. X.; Lei, Z. F. *J. Fudan. Univ.* **2003**, *42*, 1053.
14. Ma, Z. S. Non-Phosphorous Detergent Builders; Chemical Industry Press: Beijing, **2005**; p 339.
15. Xu, Y. P.; Li, J. H.; Chen, M. Q.; Ren, J. J.; Ni, Z. B. *Acta. Polym. Sin.* **2010**, *3*, 300.
16. Hiraishi, T.; Tabata, K.; Doi, Y. *Riken. Rev.* **2001**, *12*, 81.
17. Ma, Z. S. Non-Phosphorous Detergent Builders; Chemical Industry Press: Beijing, **2005**; p 180.