

# Synthesis and Characterization of a Poly(acrylic acid)-*graft*-Methoxy Poly(ethylene oxide) Comblike Copolymer

Yanling Luo,<sup>1</sup> Qianping Ran,<sup>1,2</sup> Shishan Wu,<sup>1</sup> Jian Shen<sup>1,3</sup>

<sup>1</sup>School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

<sup>2</sup>Jiangsu Institute of Building Science, Nanjing 210008, People's Republic of China

<sup>3</sup>College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210097, People's Republic of China

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**ABSTRACT:** A methoxy poly(ethylene oxide) (MPEO) grafted poly(acrylic acid) (PAA) comblike copolymer was synthesized by the direct condensation of MPEO onto the PAA backbone in the presence of dicyclohexyl dimethylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Its chemical structure was characterized by Fourier transform infrared and <sup>1</sup>H-NMR spectroscopies. The effects of different catalysts, solvents, reaction temperatures, and reaction times on the grafting degree of the

PAA-g-MPEO comblike copolymer were investigated. Compared to *p*-toluene sulfonic acid, DMAP/DCC as a catalyst markedly increased the grafting degree. The optimum reaction conditions were a tetrahydrofuran/water mixture solvent, a reaction temperature of 50°C, and a reaction time of 168 h. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3286–3291, 2008

**Key words:** catalysts; esterification; synthesis

## INTRODUCTION

Polyelectrolyte polymers containing carboxylic acid or other ionizable groups are widely used as dispersants to increase the dispersion and electrosteric stabilization of colloidal suspensions and to decrease their viscosity. Poly(acrylic acid) (PAA) has carboxylic acid groups that dissociate to become ionized above a pKa of 5;<sup>1</sup> the dispersion of CaCO<sub>3</sub> suspensions with PAA relies on the electrostatically driven adsorption of the negatively charged PAA onto the cationic surface of the mineral.<sup>2–4</sup> The adsorption behavior of PAA on TiO<sub>2</sub> particle surfaces has been investigated in aqueous suspensions.<sup>5</sup> In addition to PAA, other polyelectrolytes containing sulfonic acid groups, such as lignosulfonic acid, melamine formaldehyde sulfonic acid, and naphthalene formaldehyde sulfonic acid, have been used to improve the fluidity and slump loss of Portland cement mortars. The steric layers of bishydrophilic diblock copolymers formed of poly(methacrylic acid) and poly(ethylene oxide) (PEO) have been investigated through the direct examination of repulsive forces.<sup>6</sup> It is believed that the electrolyte level affects the conformation of the stabilizing PEO chains. Increasing the electrolyte levels disrupts the hydrogen bonding between the polymer and solvent needed to create an extended

polymer conformation. Comblike copolymers with backbones and side chains have been designed to optimize the dispersion behavior and have shown great promise as colloid stabilizers.<sup>7–13</sup> The effects of a poly(methacrylic acid)-g-PEO comblike copolymer on the electrokinetic and rheological properties of concentrated Si<sub>3</sub>N<sub>4</sub> suspensions, and the effects of a PAA-g-PEO copolymer on the rheological properties and interparticle forces of aqueous silica suspensions have been reported.<sup>14,15</sup> Kirby and coworkers<sup>16,17</sup> studied the rheological behavior of concentrated cement suspensions and the stability of BaTiO<sub>3</sub> nanoparticle suspensions in the absence and presence of a PAA-g-PEO comblike copolymer. The concentrated cement/PAA-g-PEO copolymers suspensions exhibited complex rheological behavior ranging from a reversible gel-like response observed at short teeth lengths to a remarkable gel-to-fluid transition observed for systems comprised of longer PEO teeth; the presence of PEO teeth effectively shielded the underlying PAA backbone from ion interactions and, thereby, allowed the comblike copolymers to impart stability to BaTiO<sub>3</sub> nanoparticle suspensions. In general, comblike copolymers have been synthesized by the esterification reaction between poly(carboxylic acid) as a backbone and PEO as side chains at a reaction temperature of 120–180°C; their grafting degree has been low, and the product has been yellow or brown because of oxidization at high reaction temperatures. 4-Dimethylaminopyridine (DMAP) has been an effective catalyst and has been widely used

Correspondence to: S. Wu (shishanwu@yahoo.com.cn).

in the acylation reaction of alcohols with high conversion at room temperature and neutral conditions, even in the acylation reaction of impeditive and inert alcohols with acid anhydride.<sup>18–20</sup> In this study, a methoxy poly(ethylene oxide) (MPEO) grafted PAA comblike copolymer was synthesized with the grafting reaction of MPEO onto PAA chains in the presence of DMAP as an activator at a reaction temperature of 30–67°C. The effects of different catalytic systems, solvents, reaction temperatures, and reaction times on the grafting degree of the comblike copolymer were investigated.

## EXPERIMENTAL

### Materials

Acrylic acid (AA) was produced by Tianjin Chemical Reagent Co. (Tianjin, China). Ammonium persulfate was produced by Shanghai Lingfeng Chemical Reagent Factory (Shanghai, China). MPEO (number-average molecular weight = 600) was produced by Takemoto Oil & Fat Co., Ltd. (Aichi, Japan). *p*-Toluene sulfonic acid (TsOH) was supplied by Shanghai Lingfeng Chemical Reagent Factory (Shanghai, China). Isopropyl alcohol was purchased from Shanghai Chemical Reagent Co. (Shanghai, China). Chloroform was supplied by Shanghai Lingfeng Chemical Reagent Factory. *N,N'*-dimethylformamide (DMF) was manufactured by Shanghai Chemical Reagent Co. Tetrahydrofuran (THF) was manufactured by Shanghai Shisihewei Chemical Co. (Shanghai, China). DMAP was produced by Fluka Co. (Buchs, Switzerland). Dicyclohexyl dimethylcarbodiimide (DCC) was manufactured by Huakang Technological Co. (Nanjing, China). Petroleum ether was supplied by Nanjing Chemical Reagent Factory (Nanjing, China).

### Synthesis of PAA

AA (3 g) and isopropyl alcohol (8.8 mL) were added to 60 mL of ammonium persulfate aqueous solution (1 wt %), and the mixture was heated to 60°C with stirring. AA (10 g) and an ammonium persulfate aqueous solution (10 mL, 2 wt %) were added dropwise into the previous mixture. Then the mixture was heated to 95°C and reacted for 4 h under stirring. After the reaction, the water inproducts was removed by reduced-pressure distillation. The products were then put into petroleum ether to precipitate PAA, filtered, and then thoroughly dried in a vacuum oven.

### Synthesis of the PAA-g-MPEO comblike copolymer

PAA, MPEO (PAA/MPEO molar ratio = 4 : 1), and THF were added to a flask. Under stirring, a homogeneous solution was formed. After DMAP and DCC were added, the mixture was reacted at 50°C for 168 h with stirring. The product was filtered to

remove dicyclohexyl urea (DCU) and put into  $\text{CHCl}_3$  to precipitate. Then, the deposition was washed with acetic ether to remove unreacted MPEO and dried in a vacuum oven; the PAA-g-MPEO comblike copolymer was obtained.

### Characterization

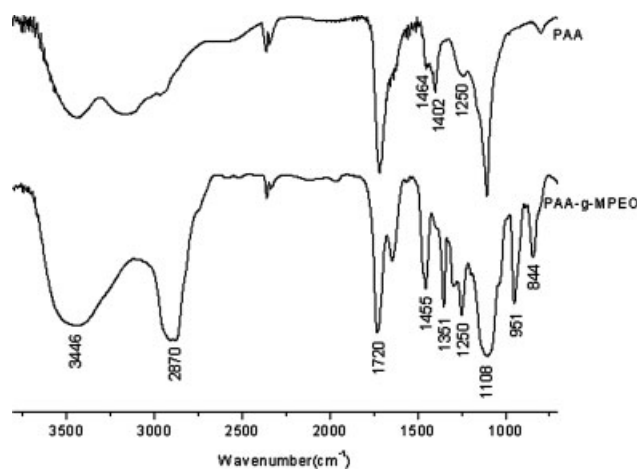
Fourier transform infrared (FTIR) analysis was carried out with an IFS-66 spectrometer (Bruker, Karlsruhe, Germany). The PAA or PAA-g-MPEO comblike copolymer was dissolved in THF, and the solution was coated on a KBr plate. After volatilization of the THF, the KBr plate was scanned from 4000 to 400  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$ .

<sup>1</sup>H-NMR analysis was performed on a 1-Bay 300 NMR instrument (300MHz, Bruker, Karlsruhe, Germany) with deuterated dimethyl sulfoxide as the solvent.

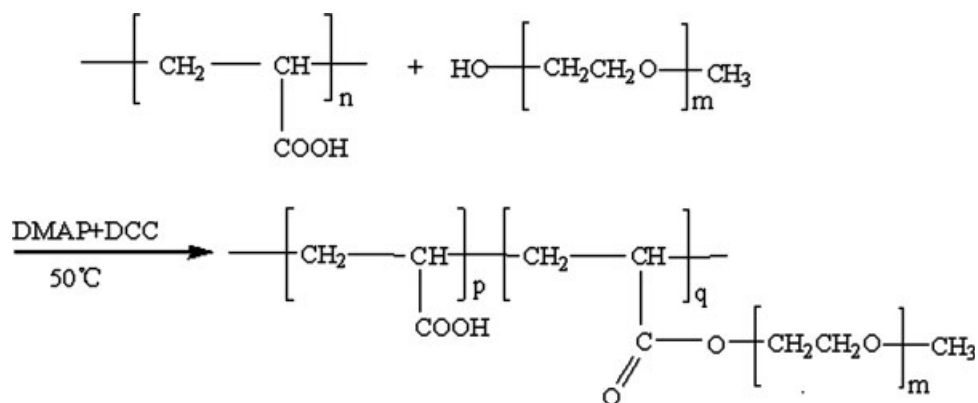
## RESULTS AND DISCUSSION

### FTIR analysis

The FTIR spectra of PAA and PAA-g-MPEO comblike copolymer are shown in Figure 1. From their spectra, it can be seen that the absorption peaks around 3446 and 2870  $\text{cm}^{-1}$  were ascribed to stretching vibrations of O—H and C—H, respectively. The absorption peak around 1720  $\text{cm}^{-1}$  was attributed to stretching vibrations of C=O. The absorption peak around 1464  $\text{cm}^{-1}$  was related to deformation vibrations of —CH<sub>2</sub>.<sup>21</sup> The absorption peaks at 1455 and 1351  $\text{cm}^{-1}$  were attributed to bending vibrations of —CH<sub>2</sub> adjacent to the O atom and scissoring in-plane vibrations of —CH<sub>2</sub> adjacent to the O atom,<sup>22</sup> respectively. The absorption peak at 1402  $\text{cm}^{-1}$  was related to stretching vibrations of COO<sup>−</sup>.<sup>22</sup> The absorption peaks around 1250 and 1108  $\text{cm}^{-1}$  were attributed to stretching vibrations of C—O in the ester group and stretching vibrations of C—O—C,



**Figure 1** FTIR spectra of PAA and the PAA-g-MPEO comblike copolymer.



**Scheme 1** Synthesis of the PAA-g-MPEO comblike copolymer.

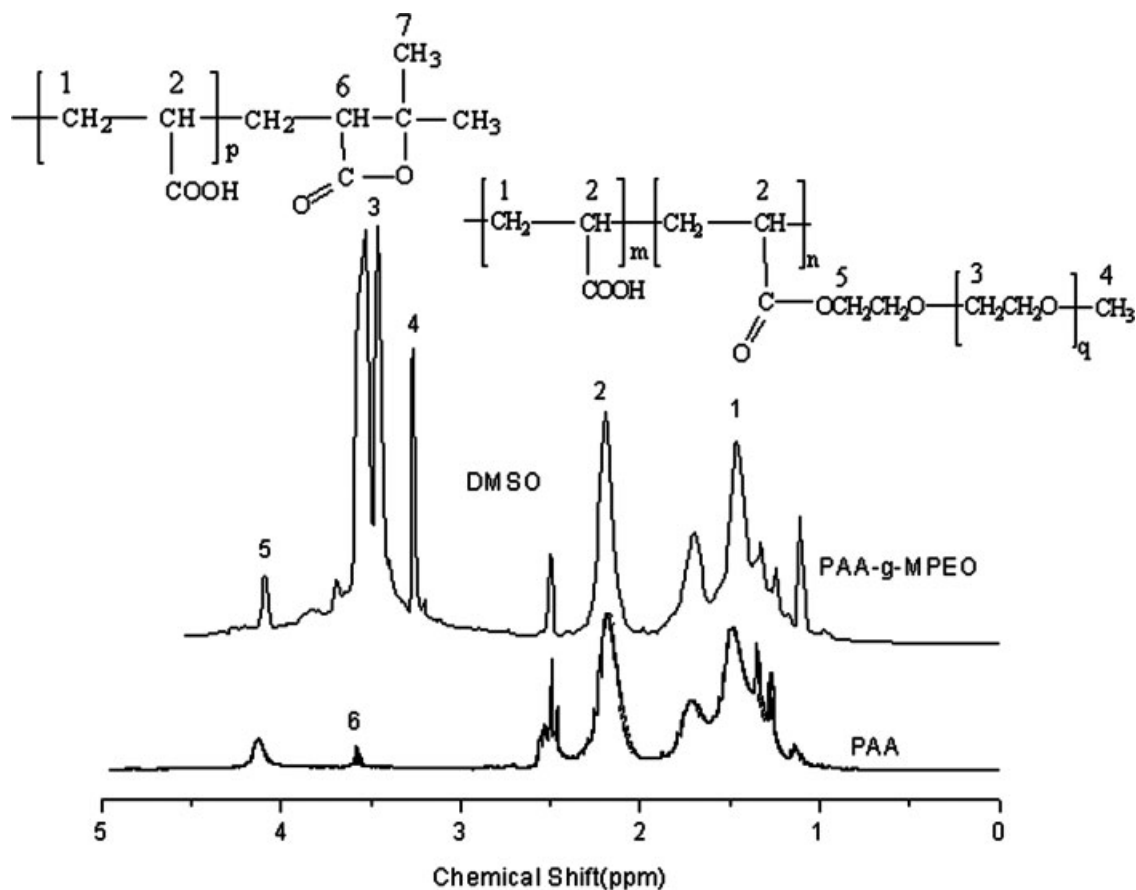
respectively. The absorption peaks around 951 and 844  $\text{cm}^{-1}$  were related to rocking in-plane vibrations of  $-\text{CH}_3$  adjacent to the C atom and the O atom,<sup>22</sup> respectively. The absorption bands of PAA at 3600–2500  $\text{cm}^{-1}$  was due to stretching vibrations of hydrogen bonds, and the absorption bands were defiladed by the stretching vibration peak of C–H.

Compared with the spectrum of PAA, the absorption intensity of MPEO-g-PAA at 2870 and 1250  $\text{cm}^{-1}$  increased, and there appeared some new

absorption peaks around 1455, 1351, 951, and 844  $\text{cm}^{-1}$ . These indicated that MPEO was grafted onto PAA chains by the esterifiable reaction between the PAA and MPEO in the presence of the catalyst. The reaction equation is shown in Scheme 1.

#### <sup>1</sup>H-NMR analysis

The <sup>1</sup>H-NMR spectra of PAA and the PAA-g-MPEO comblike copolymer are shown in Figure 2. The sig-



**Figure 2** <sup>1</sup>H-NMR spectra of PAA and the PAA-g-MPEO comblike copolymer.

**TABLE I**  
Effect of Different Catalytic Systems on the Grafting Degree of the PAA-g-MPEO Comblike Copolymer

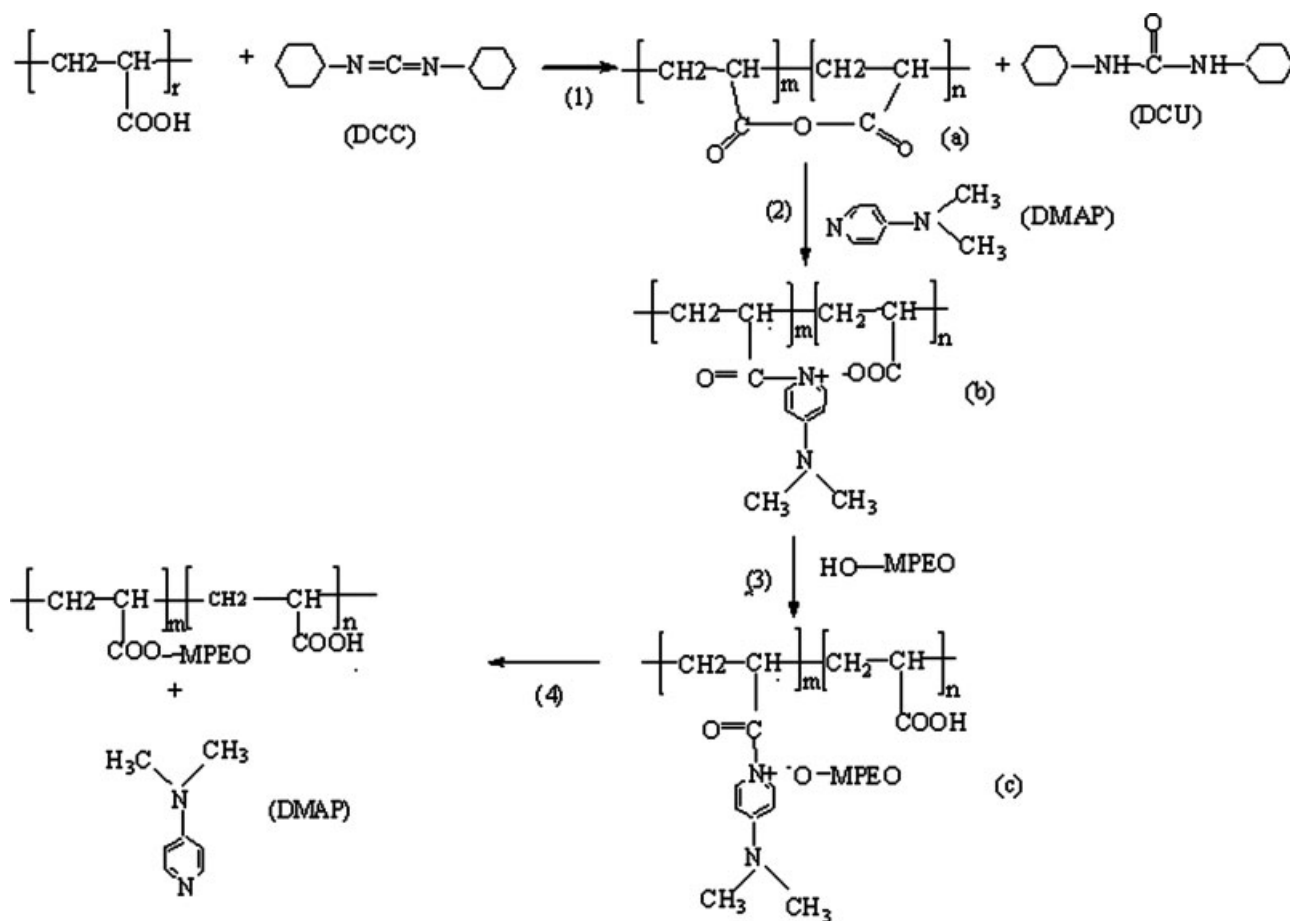
Catalytic system	<i>para</i> -Toluenesulfonic acid	DMAP/DCC
Graft degree (%)	13.5	23.0

nals at 1.15, 1.0–1.7, and 2.20 ppm were attributed to CH<sub>3</sub> protons (7), CH<sub>2</sub> protons (1), and the CHCOOR proton (2), respectively, in the PAA segments. The signal at 3.60 ppm was related to the CH proton (6) in the lactonic ring of PAA. The degree of polymerization of PAA was determined by the area ratio of the peaks at 2.20 and 3.60 ppm.<sup>23</sup> On the basis of the <sup>1</sup>H-NMR spectrum of PAA, the number-average molecular weight of PAA was calculated to be 3200.

Compared to those of PAA, there were some new peaks located at 3.24, 3.50, and 4.10 ppm in the PAA-g-MPEO copolymer, which were ascribed to —OCH<sub>3</sub> protons (4), —OCH<sub>2</sub> protons (3), and CH<sub>2</sub> protons (5), respectively.<sup>24</sup> Combined with FTIR analysis, these <sup>1</sup>H-NMR results showed that MPEO as a comb chain was successfully grafted onto the PAA backbone.

### Effect of different catalytic systems on the grafting degree of the PAA-g-MPEO comblike copolymer

The grafting degree of the PAA-g-MPEO comblike copolymer was determined by the ratio of the peak area of —OCH<sub>3</sub> protons in the MPEO side chains (at  $\delta = 3.24$  ppm) to the peak area of —CHCOOR protons in the PAA main chains (at  $\delta = 2.2$  ppm).<sup>24</sup> The grafting degrees of the PAA-g-MPEO comblike copolymer synthesized with TsOH and DMAP/DCC as catalysts are listed in Table I. Obviously, the grafting degree of the polymer catalyzed by DMAP/DCC was 23.0%, higher than that by TsOH (13.5%). It was because the esterification reaction between PAA and MPEO was a typical reversible reaction in the presence of TsOH as a catalyst for the water produced during the reaction, which led to low the grafting degree. However, when DMAP/DCC was used as a catalyst, the polymerization process of the PAA-g-MPEO comblike copolymer could be illustrated as shown in Scheme 2.<sup>18,20,25</sup> First, the carboxylic acid was converted to acid anhydride (a) by the reaction with DCC (1);<sup>26</sup> then, the nucleophilic DMAP attacked the carbonyl group in the acid anhydride (2) to form the intermediate (b). The intermediate (b) reacted with MPEO (3) to form the intermediate (c).



**Scheme 2** Polymerization process of the PAA-g-MPEO comblike copolymer.

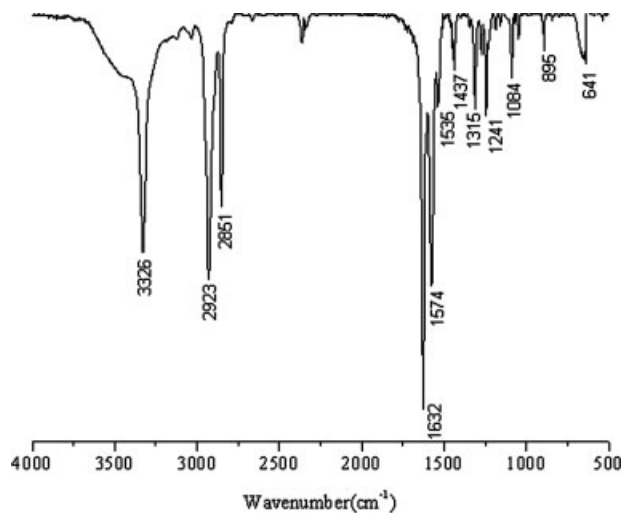


Figure 3 FTIR spectrum of DCU.

Finally, the PAA-g-MPEO comblike copolymer and regenerated DMAP were received by the decomposition of the intermediate (c). Obviously, no water was produced in the esterification reaction between PAA and MPEO, which led to an irreversible esterification reaction and a high grafting degree.

The white solid deposit formed during the esterification reaction was analyzed by FTIR spectroscopy (Fig. 3). The absorption peaks at 3326 and 1535  $\text{cm}^{-1}$  were related to stretching vibrations and bending vibrations of N—H,<sup>27,28</sup> the peaks at 2933 and 2857  $\text{cm}^{-1}$  were attributed to asymmetric and symmetric stretching vibrations of C—H,<sup>29</sup> the strong absorption peak at 1625  $\text{cm}^{-1}$  corresponded to stretching vibrations of C=O in amide,<sup>30</sup> the peaks at 1574 and 1241  $\text{cm}^{-1}$  were stretching vibrations of C—N in O=C—N,<sup>31</sup> the peaks at 1437 and 1311  $\text{cm}^{-1}$  were attributed to bending vibrations of the methylene group,<sup>21,32</sup> the peaks at 1084 and 895  $\text{cm}^{-1}$  were related to stretching vibrations of C—N in  $\text{C}_6\text{H}_4\text{NH}$  and C—C intra-annular stretching vibrations,<sup>33</sup> and the peak at 641  $\text{cm}^{-1}$  was attributed to variable-angle vibrations of O=C—N. So these results indicate that the white solid was DCU. In other words, DCU was formed from the transition of DCC during the previous esterification reaction.

#### Effect of the DMAP content on the grafting degree of the PAA-g-MPEO comblike copolymer

Table II shows the effect of the content of DMAP in the catalyst system on the grafting degree of the

TABLE II  
Effect of the DMAP Content on the Grafting Degree of the PAA-g-MPEO Comblike Copolymer

DMAP/MPEO (molar ratio)	0.1	0.2	0.3	0.4
Grafting degree (%)	15.7	17.6	23.0	23.0

TABLE III  
Effect of Different Solvents on the Grafting Degree of the PAA-g-MPEO Comblike Copolymer

Solvent	DMF	THF	THF/H <sub>2</sub> O
Grafting degree (%)	0.9	23.0	23.0

PAA-g-MPEO comblike copolymer. The grafting degree increased with increasing DMAP content and reached a constant value (23.0%) when the molar ratio of DMAP to MPEO was 0.3. In other words, a 0.3 DMAP/MPEO molar ratio was enough for the esterification reaction between PAA and MPEO.

#### Effect of different solvents on the grafting degree of the PAA-g-MPEO comblike copolymer

The grafting degrees of the PAA-g-MPEO comblike copolymers synthesized in DMF, THF, and THF/H<sub>2</sub>O (3/2, v/v) solvents are shown in Table III. The grafting degree with DMF as a solvent was very low, about 0.9%. This was because DMF had an inhibition effect on the esterification reaction.<sup>34</sup> However, the grafting degrees with THF and THF/H<sub>2</sub>O as solvents were 23.0%. However, the viscosity of the reaction system was high in the last period of the esterification reaction when THF was used as a solvent, some products easily adhered on the wall of the reaction flask, and the productive yield of the PAA-g-MPEO comblike copolymer was low. When THF was replaced by THF/H<sub>2</sub>O, the viscosity of the reaction system decreased, the adherence behavior of the PAA-g-MPEO comblike copolymer was efficiently controlled, and thereby, the productive yield increased remarkably. The grafting degree in the THF/H<sub>2</sub>O mixed solvent was not affected by the presence of water because the esterification reaction between PAA and MPEO was irreversible in the presence of DCC/DMAP as a catalyst.<sup>18</sup>

#### Effect of the reaction temperature and reaction time on the grafting degree of the PAA-g-MPEO comblike copolymer

The influence of the reaction temperature on the grafting degree of the PAA-g-MPEO comblike copolymer in the THF/H<sub>2</sub>O mixed solvent is shown Table IV. Obviously, the grafting degree of the copolymer synthesized at 30°C was very low, about 3.6%. This was because the solubility of the intermediate (c) in Scheme 2 was limited by the temperature, and there

TABLE IV  
Effect of the Reaction Temperature on the Grafting Degree of the PAA-g-MPEO Comblike Copolymer

Reaction temperature (°C)	30	50	67
Grafting degree (%)	3.6	23.0	23.0

**TABLE V**  
**Effect of the Reaction Time on the Grafting Degree of the PAA-g-MPEO Comblike Copolymer**

Reaction time (h)	24	48	72	120	144	168	182
Grafting degree (%)	10.6	13.6	17.0	19.5	21.0	23.0	23.2

were some white flocculent matter in the reaction system, which led to low grafting degree. However, when the temperature was increased to 50°C, the reaction system became milky because of the poor solubility of DCU in the early reaction stage; then, the solution slowly became transparent, and some white solids formed at the bottom of flask. Thereby, the grafting degree increased to 23.0%. If the reaction temperature was further increased to 67°C (the reflux temperature of THF), the grafting degree did not increase further.

The influence of the reaction time on the grafting degree of the PAA-g-MPEO comblike copolymer in the THF/H<sub>2</sub>O mixed solvent is shown Table V. The grafting degree increased with increasing reaction time. However, the grafting degree did not increase further when the reaction time was over 168 h.

## CONCLUSIONS

A PAA-g-MPEO comblike copolymer containing a PAA backbone and an MPEO tooth was successfully synthesized by an esterification reaction between the carboxylic groups in PAA and the hydroxyl groups in MPEO. Compared to TsOH, DMAP/DCC as a catalyst markedly increased the grafting degree of the PAA-g-MPEO comblike copolymer. The optimum reaction conditions were the use of a THF/water mixture as a solvent, a reaction temperature of 50°C, and a reaction time of 168 h.

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