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Investigation on the Reaction Between Polyhexamethylene Guanidine Hydrochloride Oligomer and Glycidyl Methacrylate

Dafu Wei,[1] Rihui Zhou,[2] Yong Guan,[1] Anna Zheng,[1] Youwei Zhang[2]

[1]Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

[2]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Chemical Fibers Research Institute, Donghua University, Shanghai 201620, People's Republic of China

Correspondence to: Y. Zhang (E-mail: zhyw@dhu.edu.cn)

ABSTRACT: Polyhexamethylene guanidine hydrochloride (PHMG) oligomer is attracting increasing attention for its highly efficient biocidal activity and nontoxicity. To make it bearing carbon-to-carbon double bonds and enlarge its application in production of antimicrobial materials via copolymerization, PHMG oligomer was modified via reaction with glycidyl methacrylate (GMA). The influence of reaction parameters on the conversion rate of GMA was investigated using ultraviolet absorption spectroscopy. The structures of PHMG oligomer before and after modification were characterized by Fourier transform infrared spectrometry, Raman spectrometry, nuclear magnetic resonance spectrometry, and electrospray ionization time-of-flight mass spectrometry. The results show that carbon-to-carbon double bond is successfully introduced into the modified PHMG oligomer. At a feeding molar ratio of GMA to PHMG of 1.0, the conversion rate of GMA reached up to 75% after 60 h of reaction at 60°C in dimethyl sulfoxide. Also, there is an activity difference in the different aminos of PHMG oligomer: the primary amino is ready to react with epoxy of GMA, while the guanidyl amino hardly reacts with GMA due to the p-π conjugation. Furthermore, the modified PHMG oligomer was used as comonomer to synthesize acrylonitrile copolymer, showing excellent antimicrobial activity against *Staphylococcus aureus*. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: polyhexamethylene guanidine hydrochloride; glycidyl methacrylate; UV–vis spectroscopy; modification; oligomers

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INTRODUCTION

Surface contamination by micro-organisms causes great attention in several areas that require a high level of hygiene. Particularly, infection control is of utmost importance in hospitals.[1,2] Various biocides, antimicrobials, and antimicrobial materials are developed and applied for this purpose. The cationic antimicrobials, such as commonly used quaternary ammonium compounds, bisbiguanides, and polymeric guanidines, are especially prominent in combating against bacterial nosocomial infections.[3] Among them, polymeric guanidines are water-soluble, odorless, colorless, and noncorrosive, and have a broad-spectrum activity against Gram-positive and Gram-negative bacteria, fungi, yeasts, and viruses.[1,4–6] They have a high binding affinity to the negatively charged cell walls and membranes of bacteria because of their own positive charges, and disruption is brought about by perturbation of these sites.[3] Furthermore, when compared with currently used disinfectants, they are significantly less toxic and harmless to humans and animals at concentrations below 1%.[1,4] Polyhexamethylene biguanide (PHMB), a member of the polymeric guanidines, has been widely used for many years as antiseptic and disinfectant in medicine, wound care, food industry, and water treatment.[7–10] Recently, polyhexamethylene guanidine hydrochloride (PHMG), another member of the polymeric guanidines, has received considerable attention as a novel disinfectant for hospital and household facilities.[1,2]

The usage of numerous disinfectants and antiseptics for treating materials in hospitals and community settings, as well as the adoption of medical devices impregnated with anti-infective agents were efficiently in combating infectious diseases. However, due to the leaching of antimicrobials, these approaches suffer from problems including short durability and useful life of the materials, adverse environmental impact, as well as the development of pathogen's resistance to antibiotics.[11] An ideal

approach is to develop permanently sterile, nonleaching materials via covalently functionalization of their surfaces[11,12] or matrixes[13–16] with antimicrobial compounds. Antimicrobial materials with nonleaching, permanent antibacterial surfaces have been becoming a new emerging field. For example, Klibanov and coworkers had covalently immobilized certain poly(4-vinyl *N*-alkylpyridine) and N-alkylated polyethylenimine onto the surfaces of a variety of diverse materials, thus rendering the surfaces permanently microbiocidal against waterborne and airborne bacteria, as well as fungi.[13,17–22] Homopolymer or copolymer of diallyl dimethylammonium chloride, quaternized copolymer of (2-dimethylamino ethyl) acrylate, quaternized poly(vinylpyridine), PHMG and N-halamine polymeric biocides were also covalently immobilized onto the surfaces of glass, paper, cellulose fibers, starch, poly(ethylene terephthalate) films, and synthetic fabrics to fabricate permanent sterile surfaces.[23–30]

(Graft) polymerization or copolymerization with monomers containing antimicrobial compound is a commonly used efficient route to produce antibacterial materials with permanent sterile surfaces or matrixes. As mentioned earlier, PHMG is a novel polymeric antimicrobial. However, due to lack of carbon-to-carbon double bonds, PHMG can not be directly used in the production of antibacterial materials via polymerization or copolymerization. The aim of this work is to endow PHMG with active carbon-to-carbon double bond by modification, thus expanding its application to the preparation of antibacterial fibers, fabrics, and plastics. Specifically, PHMG oligomer was modified via reaction with glycidyl methacrylate (GMA). The effects of reaction parameters, including solvent, time, temperature, and feeding molar ratio on the conversion rate of GMA, were discussed. The structures of PHMG oligomer before and after modification with GMA were characterized in details using FTIR, Raman spectrometry, NMR spectrometry, and electrospray ionization time-of-flight (ESI-TOF) mass spectrometry. Furthermore, the modified PHMG oligomer was used as the comonomer to synthesize antimicrobial acrylonitrile (AN) copolymer.

EXPERIMENTAL

Materials

Hexamethylenediamine, guanidine hydrochloride, nitric acid, and acetone were purchased from Sinopharm Chemical Reagents (Shanghai). PHMG oligomer was prepared according to the procedure reported in the literature.[31] According to the result of ESI-TOF mass spectrum, the $\overline{M_n}$, $\overline{M_w}$ and $\overline{M_w}/\overline{M_n}$ of the obtained PHMG oligomer were 771, 1008, and 1.31, respectively. GMA was purchased from Dow chemical company. Dimethyl sulfoxide (DMSO) was purchased from Shanghai Lingfeng chemical reagents company. AN was purchased from Zhangxing chemical reagent, and distilled before use. Sodium sulfite and sodium chlorate were purchased from Shanghai Shisihewei chemical industry, and purified via recrystallization in water. Deionized water was used in all the experiments.

Preparation of Modified PHMG Oligomer

A certain amount of PHMG oligomer solution in DMSO or water with a PHMG concentration of 38.0 wt % was first prepared in a round-bottomed flask equipped with a magnetic stirrer at room temperature. The system was then heated to and kept at a certain temperature (8, 25, 40, 60, 80, or 100°C) for 30 min, followed with swiftly injecting a certain volume of GMA (the feeding molar ratio of GMA to PHMG was 1.0, 1.5, or 2.0, and the moles of PHMG was calculated based on $\overline{M_n}$ obtained by EST-TOF mass spectrometry). The mixture was kept at the temperature under constant stirring for a certain period of time. At given intervals, small aliquots were withdrawn. To completely remove DMSO and unreacted GMA, the crude products were purified via repeated precipitation/dissolution in acetone/methanol at the assistance of sonication for three times. After drying in vacuum at room temperature for 12 h, the purified product was obtained for further analysis.

Synthesis of Poly(AN-*co*-M-PHMG) Copolymer

The modified PHMG oligomer obtained under the optimum reaction conditions, i.e., the feeding molar ratio of GMA to PHMG, reaction solvent, temperature and time are 1.0, DMSO, 60°C, and 60 h, respectively, was used in copolymerization. Typically, to a three-neck flask containing about 0.40 g of purified modified PHMG, 25 mL of deionized water and a certain amount of sodium chlorate were added to obtain a uniform aqueous solution, followed by adjusting pH value of the solution to 3.5 via addition of diluted nitric acid aqueous solution. Next, the system was kept at 25°C and purged with nitrogen under stirring to remove oxygen for 30 min, which was followed with injection of AN (3.0 mL) and sodium sulfite aqueous solution of pH 3.5. The copolymerization was occurred for 18 h. After the reaction, the unreacted AN monomers were removed under vacuum. The suspension was filtered. The precipitates were washed with a large amount of water for three times to remove free modified PHMG oligomer. Finally, the samples were obtained after drying under vacuum at 60°C for 24 h.

The yield (Y) of the copolymerization reaction was determined by weighing method and calculated as follows:

$$Y(\%) = \frac{W_p}{W_1 + W_2} \times 100\%$$

where W_p is the weight of the obtained copolymer. W_1 and W_2 are the feeding weights of AN and modified PHMG oligomer, respectively.

The content (C_{PHMG}) of PHMG in poly(AN-*co*-M-PHMG) copolymer was determined by element analysis.

Characterization

Ultraviolet (UV) absorption spectra were taken on a TU-1810 UV–visible spectrophotometer. FTIR spectra were recorded on a Nicolet 5700 Fourier transform infrared spectrometer using KBr pressed disks. Raman spectrum was recorded on a Jobin Yvon T64000 Raman system. The excitation was at 514.5 nm. The laser power was set to 35 mW. ^{1}H-NMR and ^{13}C-NMR spectra of samples in Deuterated DMSO were acquired on an AVANCE500 NMR spectrometer. Chemical shifts were reported in δ (ppm) units relative to tetramethylsilane. The C, H, N element contents of the samples were determined by a Elementar Vario EL III element analyzer. ESI-TOF mass spectra were acquired using a Micromass LCT time-of-flight mass

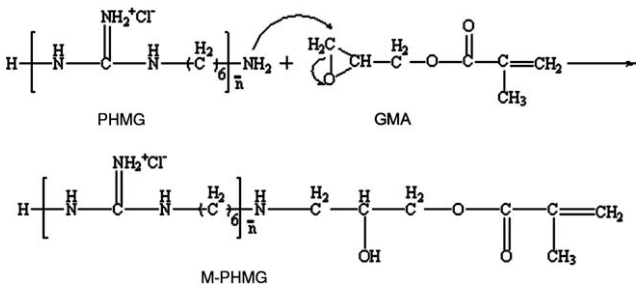
spectrometer equipped with electrospray ionization. Sample solutions were prepared using H_2O/CH_3OH (1 : 3) mixture as solvent. Ions were generated by electrospray ionization below 120°C. The results were analyzed with MASSLYNXTM 3.5 system. *m/z* values of the mono-isotopic peaks of any isotope distribution were reported. The intrinsic viscosity of the samples in dimethyl formamide (DMF) at 25°C was determined via dilution method using a Ubbelohde viscometer. Antibacterial activity of the copolymer was evaluated by Guangdong detection center of microbiology according to E 2149-01 standard test method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions (ASTM E 2149-01) using *Staphylococcus aureus* as the testing bacterium.

RESULTS AND DISCUSSION

The active epoxy group of GMA is easy to react with various functional groups such as hydroxyl, carboxyl, and amino via a S_N2 nucleophilic ring-opening substitution reaction. Here, the active terminal amino group of PHMG is expected to react with epoxy group of GMA, resulting in product (i.e., M-PHMG, Scheme 1) bearing carbon-to-carbon double bonds. The reaction begins with the attack of the lone electron pair of nitrogen atom of the terminal amino group of PHMG on the positively charged carbon atom of epoxy group of GMA, which is followed with the subsequent proton transfer from the amino group to oxygen atom of the GMA epoxy group. Also, in the presence of excess GMA, the hydroxyl [—CH(OH)—] end group in the M-PHMG oligomer is also reactive to epoxy group of GMA. However, due to the lower nucleophilic strength of hydroxyl groups as compared with amino groups, as well as the larger steric hindrance, the reaction of the hydroxyl end group with GMA is much slower. This was consistent with the fact that as the feeding GMA/PHMG molar ratio increased from 1.0 to 1.5, the molar ratio of GMA to PHMG in the modified PHMG only increased slightly from 0.75 to 0.80 (see Figure 4).

Determination of Conversion Rate of GMA via UV–Vis Absorption Spectrometry

The crude product of the reaction was a mixture composed of M-PHMG, unreacted PHMG, solvent (DMSO or water) and unreacted GMA. PHMG and M-PHMG are difficult to be separated from each other due to their similarities in the structures and properties. Therefore, even after careful purification treatments, only mixtures of M-PHMG and unreacted PHMG could be obtained. The conversion rate of GMA is very important for the further application of the product in the copolymerization



Scheme 1. Illustration of the main reaction between PHMG and GMA.

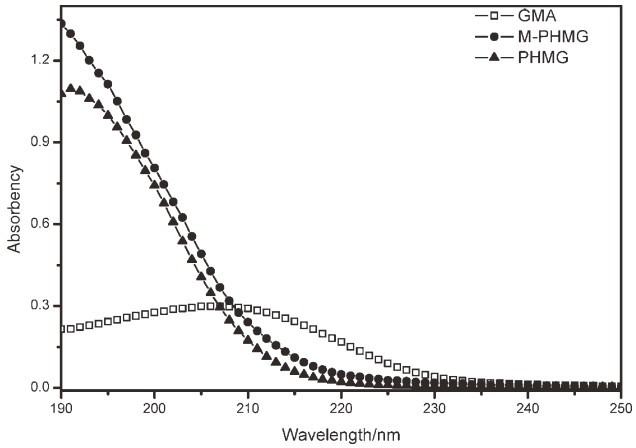


Figure 1. UV absorption spectra of GMA, PHMG, and M-PHMG.

modification. Because of the low volatility, the complete removal of DMSO and GMA can only be achieved by repeated cycles of dissolution/precipitation treatment at the assistance of sonication, which needs lots of organic solvents and complicated operations. Besides, both M-PHMG and PHMG are highly sensitive to the moisture. Consequently, it is not only of high cost but also of great difficulty to determine the conversion rate of GMA with proper accuracy using general weighing method.

Here, taking advantage of the characteristic ultraviolet absorptions of guanidyl carbon-to-nitrogen double bond of PHMG and carbon-to-carbon double bond of GMA at 192 nm and 207 nm, respectively, ultraviolet absorption spectrometry, which only needs very minute samples, was chosen to determine the conversion rate of GMA. The details are as follows:

The ultraviolet absorption spectra (190–250 nm) of a series of PHMG aqueous solutions or GMA aqueous solutions with known concentrations were first determined. The following calibration equations of the absorbance at 192 nm of PHMG and the absorbance at 207 nm of GMA were then obtained by linear fitting the plots of the absorbance vs. the concentration of PHMG or GMA solutions.

$$A_{192\text{nm}} = 0.0738 + 67.71005C_{\text{PHMG}} \ (R = 0.99544) \quad (1)$$

$$A_{207\text{nm}} = 0.0110 + 62.8821C_{\text{GMA}} \ (R = 0.99995) \quad (2)$$

where $A_{192\text{nm}}$ or $A_{207\text{nm}}$ denotes the absorbance at 192 or 207 nm, respectively; C_{PHMG} or C_{GMA} denotes the concentration of PHMG or GMA in μg/mL, respectively.

To eliminate the mutual absorption interference, the calibration equations of the absorbance at 207 nm of PHMG and the absorbance at 192 nm of GMA were also obtained in a similar way.

$$A_{207\text{nm}} = 0.0071 + 19.46046C_{\text{PHMG}} (R = 0.9996) \quad (3)$$

$$A_{192\text{nm}} = 0.0234 + 43.88646C_{\text{GMA}} (R = 0.99954) \quad (4)$$

From eqs. (1)–(4), the two following equations of the absorbance at 192 and 207 nm of the mixture of PHMG and GMA were obtained.

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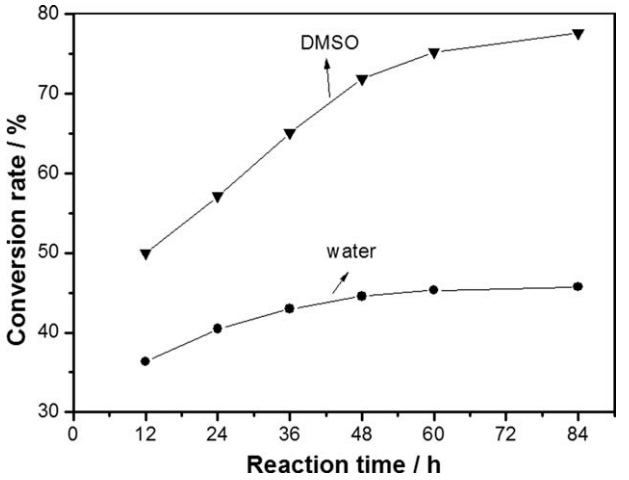


Figure 2. Change of the conversion rate of GMA with the reaction time in different solvents ($M_{GMA}/M_{PHMG} = 1.0$, 60°C).

$$A_{192nm} = 0.0972 + 67.71005C_{PHMG} + 43.88646C_{GMA} \quad (5)$$

$$A_{207nm} = 0.0181 + 19.46046C_{PHMG} + 62.88210C_{GMA} \quad (6)$$

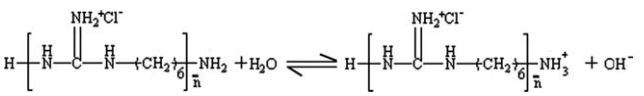
A certain amount of crude product of the reaction was subjected to purification, drying and dissolving in water to prepare aqueous solution with suitable concentration. According to eqs. (5) and (6), the concentrations of GMA and PHMG in the aqueous solution were determined via measuring its absorbance at 192 and 207 nm (Figure 1). The conversion rate of GMA (θ_{GMA}) was calculated as follows:

$$\theta_{GMA} = \frac{W_{PHMG}/W_{GMA}}{C_{PHMG}/C_{GMA}} \quad (7)$$

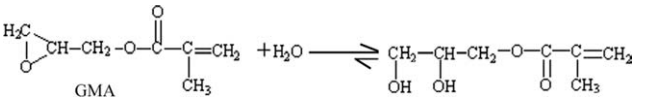
where W_{PHMG}/W_{GMA} is the feeding weight ratio of PHMG to GMA.

Influences of Reaction Parameters on the Conversion Rate of GMA

Figure 2 shows the changes of the conversion rate of GMA with the reaction time in DMSO and water. In DMSO, the conversion rate increased almost linearly until the reaction time reached 48 h. After that, the increase in the conversion rate slowed down. As compared with that in DMSO, the conversion rate in water was much lower under the similar reaction conditions. In water, the terminal primary amino groups in PHMG will react with water and produce quaternary ammonium ions (Scheme 2). When the primary amino groups are converted to be corresponding quaternary ammonium ions, their nucleophilic strengths decrease greatly, thus the reaction rate between PHMG and GMA decreases accordingly. Meanwhile, another product OH^- can catalyze the ring-open reaction of epoxy group with water, thus facilitating the hydrolysis of GMA with



Scheme 2. Reaction of PHMG with water.



Scheme 3. Hydrolysis of GMA with water.

water (Scheme 3). Both changes inhibit the reaction between PHMG and GMA. Consequently, the conversion rate of GMA became smaller as compared with the case of DMSO. Figure 3 shows the conversion rate of GMA at different reaction temperatures. The conversion rate of GMA increased with the rising of the temperature. It reached 75% at 60°C. Above 60°C, the increase in the conversion rate slowed down with the further rising of the temperature. Meanwhile, the appearance of the reaction solution turns from the starting colorless and transparent to light brown. The colors gradually darkened with the further rising of the temperature. The color change is probably caused by the oxidation of DMSO.

According to the typical structure of PHMG illustrated in Scheme 1, one PHMG molecule bears a guanidyl amino group and a primary amino group. To investigate the reaction of GMA with these two kinds of amino groups, we studied the conversion rates of GMA at different feeding molar ratios of GMA to PHMG (Figure 4). It could be seen that under the similar conditions, the conversion rate of GMA decreased substantially with the increasing feeding molar ratio of GMA to PHMG. However, increasing the feeding molar ratio of GMA to PHMG could shorten the reaction time. For example, to reach the level of ~ 0.75 mol GMA /mol PHMG in M-PHMG, the time needed was 60 h, 36 h, and 24 h at a feeding GMA/PHMG molar ratio of 1.0, 1.5, and 2.0, respectively (see the inset of Figure 4).

We determined the C, H, N element contents of PHMG, GMA, and M-PHMG, which was obtained under the conditions that the feeding molar ratio of GMA to PHMG, the concentration of PHMG, reaction solvent, temperature and time are 1.0, 38%, DMSO, 60°C, and 60 h, respectively (Table I). Based on the

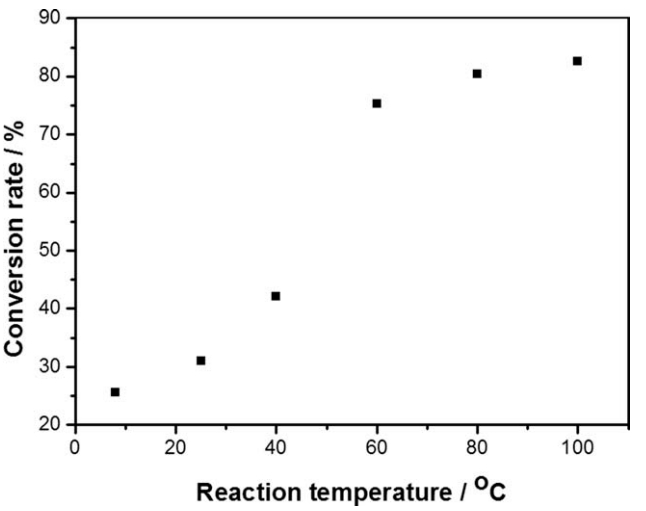


Figure 3. Change of the conversion rate of GMA with the reaction temperature (DMSO, $M_{GMA}/M_{PHMG} = 1.0$, 60 h).

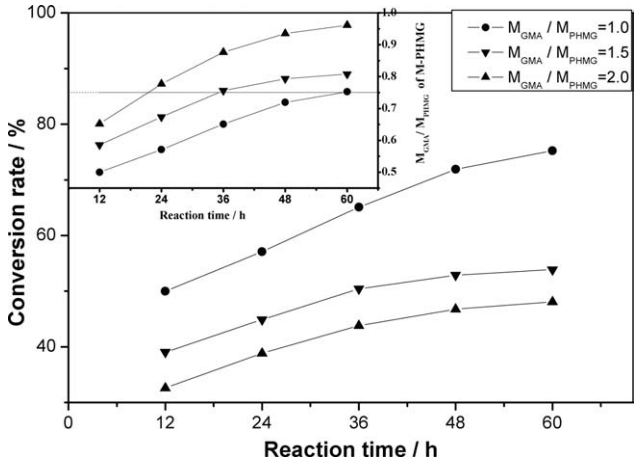


Figure 4. Dependence of the conversion rate of GMA on the reaction time at different feeding GMA/PHMG molar ratios (DMSO, 60°C).

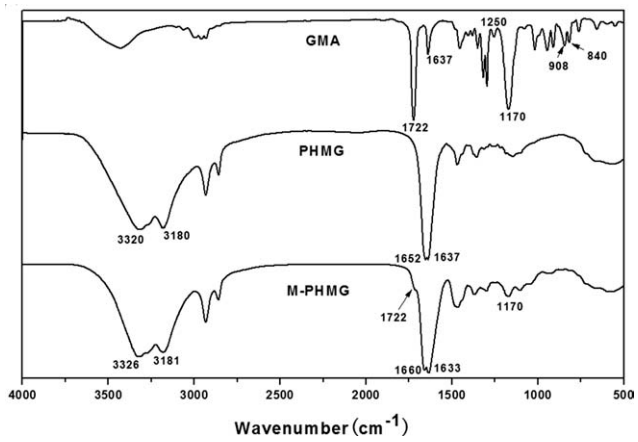


Figure 5. FTIR spectra of GMA, PHMG, and modified PHMG (M-PHMG).

data of C, H, or N element contents of PHMG, GMA, and M-PHMG, the calculated conversion rate of GMA was 74.1%, 69.6%, or 67.7%. The result was very close to that (75.2%) obtained by UV-absorption analysis, thus demonstrating the accuracy of the UV-absorption method for the determination of the conversion rate of GMA of the reaction.

Based on the balance between the cost and the GMA/PHMG molar ratio value of the product, as well as the above change trends of the conversion rate with various parameters, we consider the reaction between PHMG and GMA is optimum under the conditions that the feeding molar ratio of GMA to PHMG, reaction solvent, temperature and time are 1.0, DMSO, 60°C, and 60 h, respectively.

The Structures of PHMG Before and After Modification with GMA

FTIR, NMR, Raman spectrometry, and EI-TOF-MS techniques were used to characterize the structure of modified PHMG obtained under the optimum conditions that the feeding molar ratio of GMA to PHMG, reaction solvent, temperature and time are 1.0, DMSO, 60°C, and 60 h, respectively. Figure 5 shows the FTIR spectra of GMA, PHMG and the modified PHMG. In the spectrum of GMA, the stretching vibrations of carbonyl and C—O of ester groups appeared at 1722 cm^{-1} and 1170 cm^{-1}, respectively. The band at 1637 cm^{-1} could be attributed to the stretching vibration of carbon-to-carbon double bonds. Also, the characteristic bands of epoxy appeared at 1250 cm^{-1}, 908 cm^{-1}, and 804 cm^{-1}.[32] For PHMG, the vibrations of ν (NH), δ (NH), and ν (C=N) appeared at 3320 cm^{-1} and 3180 cm^{-1}, 1637 cm^{-1}, and 1652 cm^{-1}, respectively.[31,33] In the spectrum of modified PHMG, the characteristic bands of PHMG remained and shift somewhat. Besides, there appeared the bands of the ester group of GMA. Meanwhile, the characteristic bands of epoxy disappeared. The ν (C=C) band at 1637 cm^{-1} might overlap with δ (NH) band of PHMG. The existence of C=C in the modified PHMG was confirmed by its Raman spectrum (Figure 6), which displayed a distinct characteristic C=C vibration at 1642 cm^{-1}.[32] Thus, the occurrence of ring opening reaction of the epoxy group of GMA by PHMG was verified.

Table I. The Elements C, H, N Contents of PHMG, GMA, and M-PHMG Determined by Element Analyzer

Sample	C (%)	H (%)	N (%)
PHMG	44.62	9.3	24.58
GMA	58.63	7.33	<0.05
M-PHMG	46.31	9.09	21.84

The ^{1}H-NMR spectra, ^{13}C-NMR spectra and the detailed attribution of various chemical shifts of PHMG, GMA, and modified PHMG are assembled in Figures 7 and 8. When compared with the ^{1}H-NMR spectrum of PHMG, there appeared new chemical shifts at δ = 1.84 (f), 5.70 (e), 6.06 (e') in the ^{1}H-NMR spectrum of modified PHMG (Figure 7). Also, when compared with the ^{13}C-NMR spectrum of PHMG, there appeared new chemical shifts at δ = 63 (e), 70 (f), 114 (g), 121 (h), and 172 (i) in the ^{13}C-NMR spectrum of modified PHMG (Figure 8). All these changes confirmed the chemical reaction between GMA and PHMG.

Figure 9 shows the ESI-TOF mass spectra of PHMG and modified PHMG. The analysis result for ESI-TOF mass spectrum of

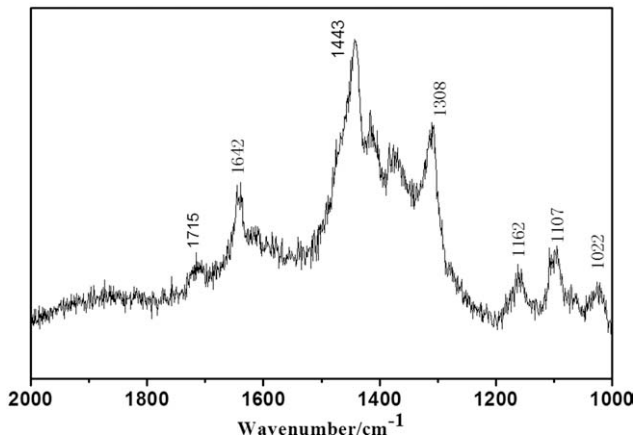


Figure 6. Raman spectrum of modified PHMG.

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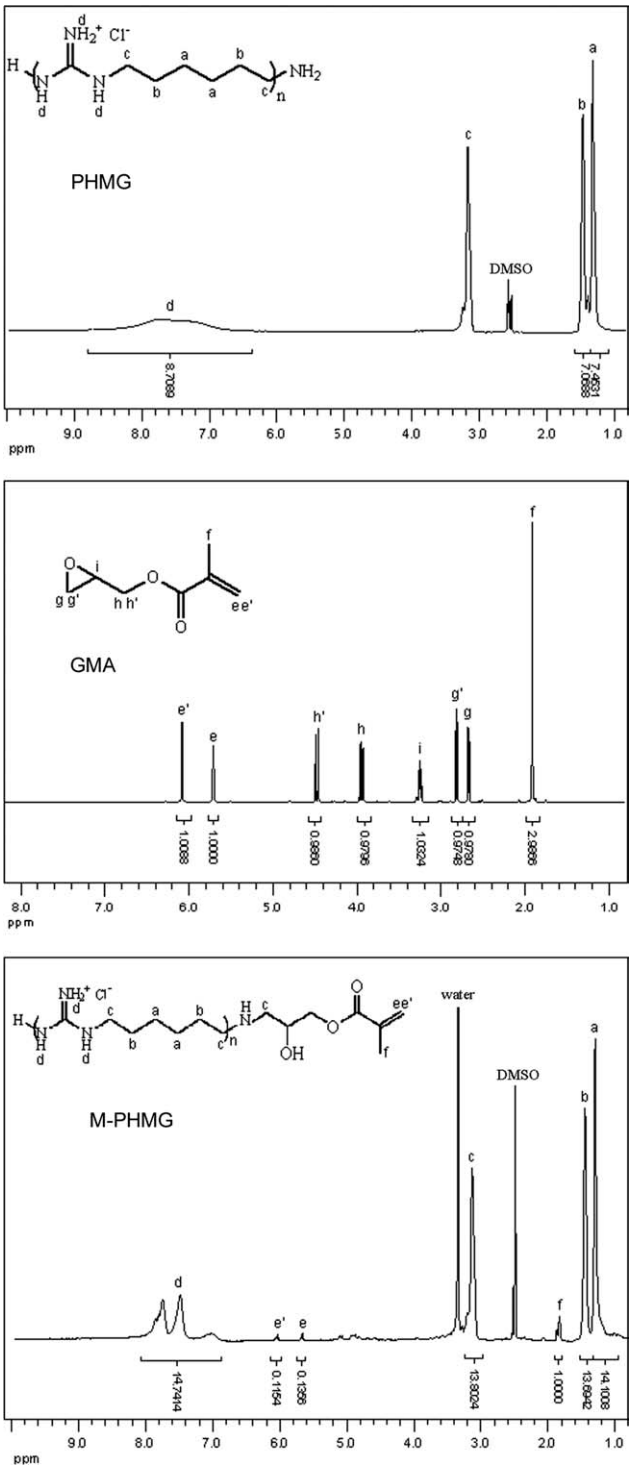


Figure 7. ^{1}H-NMR spectra of PHMG, GMA, and modified PHMG.

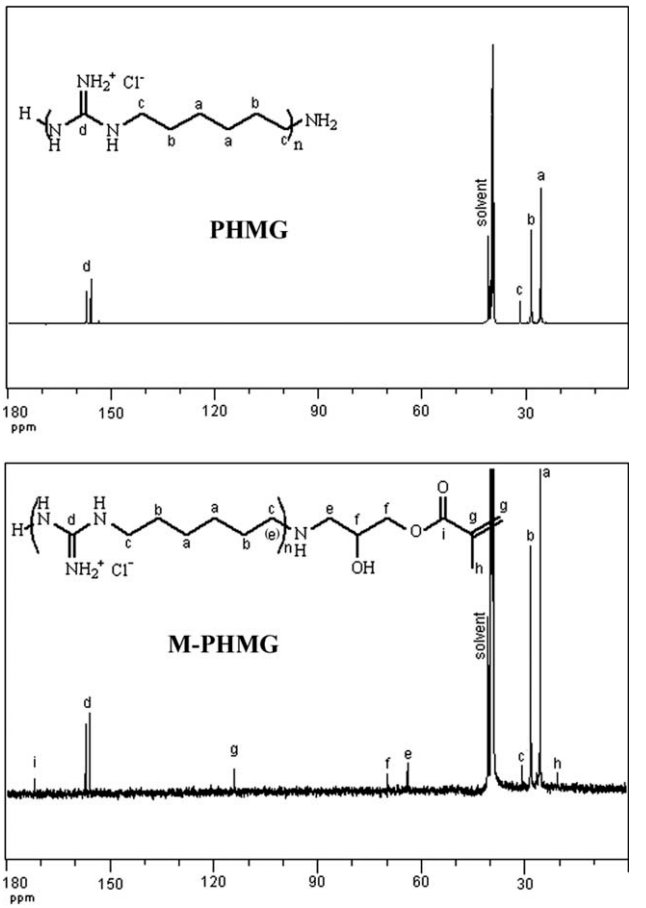


Figure 8. ^{13}C-NMR spectra of PHMG and modified PHMG.

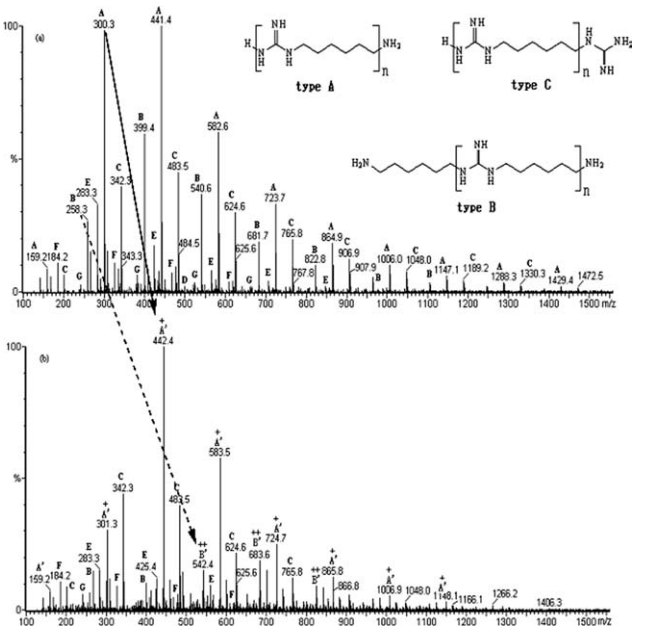
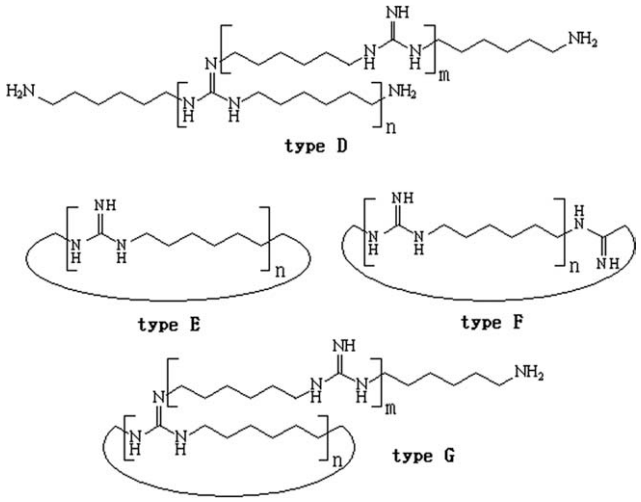


Figure 9. ESI-TOF mass spectra of PHMG (a) and M-PHMG (b) ("+" represent the products from one PHMG molecule and one GMA molecule; "++" represent the products from one PHMG molecule and two GMA molecules).

PHMG was similar to that reported by our previous study[31]: it contains seven types of chemical structures including three linear (A, B, C, see Figure 9) and four branched or cyclic ones (D, E, F, G, see Scheme 4). The molar contents of structure A-G in PHMG are 34.4%, 19.5%, 16.9%, 5.2%, 12.1%, 7.7%, and 4.3%, respectively. The nominal masses of their species series in the ESI-TOF mass spectrum are [1+(141 × *n*) +16 + 1] Da (A),



Scheme 4. The detailed chemical structure of types D–G in PHMG.

[100 + (141 × *n*) + 16 + 1] Da (B), and [1 + (141 × *n*) + 58 + 1] Da (C), [100 + (141 × (*n* + *m*)) −1 + 100 + 16 + 1] Da (D), [(141 × *n*)+1] Da (E), [(141 × *n*) + 42 + 1] Da (F), and [(141×(*n* + *m*)) −1 + 100 + 1] Da (G), respectively (*n* is the number of the repeat unit). In these seven species, there are two types of functional groups that may react with epoxy group of GMA, that is, the terminal amino-group and the terminal amino-group of guanidine. Because of the resonance between the lone pair of electrons on terminal amino-group and imido-group of guanidine, the nucleophilic strength of the terminal amino-group of guanidine decreases as compared with the terminal amino-group. Thus, the reactivity of the terminal amino-group with GMA is higher.

The nominal mass of the repeat unit of all the types of structures in PHMG is 141 Da. The molecular mass of GMA is 142 Da. Thus, the reaction of one or two GMA molecules with one PHMG will result in a mass increase of 142 or 284 Da in the product as compared with that of PHMG. The difference of 1 or 2 Da can be used to differentiate the product species from PHMG species with larger *n*, and thus can be used to analyze the reaction behavior between PHMG and GMA. For example, in the mass spectrum of modified PHMG (Figure 9), one can find the specie series (type A') with nominal mass of 301.3 (A'1, $n = 1$), 442.4 (A'2), 583.5 (A'3), 724.7 (A'4), and 865.8 (A'5). Their mass is 1 Da larger than that of the type A series with higher *n* [i.e., 300.3 (A2, $n = 2$), 441.4 (A3), 582.6 (A4), 723.7 (A5), and 864.9 (A6)] found in the mass spectrum of PHMG. This indicates the reaction of type A specie with GMA occurs in a molar ratio of 1 : 1.

We further analyzed the reactions of the three main types of structures in PHMG with GMA by comparing the relative intensity changes of the specie series in mass spectrum of PHMG before and after modification. The results are assembled in Table II. After modification, the relative intensity of specie series (An) with mass of A_n ($A_n = 141 \times n + 18$) decreased, while that of specie series with mass of A_{n+1}+1 (i.e., specie A'n) and A_{n+2}+2 (i.e., specie A"n) increased. Also, the increase magnitude of specie series with mass of A_{n+1}+1 is much larger. This suggests that 1 mol of specie A can react with 1 or 2 mol of GMA, and the possibility of the reaction occurring in a molar ratio of 1 : 1 is much larger. Similarly, one can also find that after modification the relative intensity of specie series with mass of B_n ($B_n = 141 \times n + 117$) (i.e., specie Bn) and B_{n+1}+1 (i.e., specie B'n) decreased, while that of specie series (B"n) with mass of B_{n+2}+2 increased. This suggests the reaction of specie B with GMA occurs in a molar ratio of 1 : 2. Naturally, the reaction of specie B with GMA in a molar ratio of 1 : 1 can not be excluded. For specie C, after modification, the relative intensity of specie series with mass of C_n ($C_n = 141 \times n + 60$) (i.e., specie Cn) and $C_{n+1} + 1$ (i.e., specie C'n) displayed similar changes: both became larger at $n = 1$ and 2 or smaller at $n = 3$, 4, and 5. This might suggest no reaction occurs between specie C and GMA.

Table II. Relative Intensity Changes in the Series Species of Three Main Structures (A1-A5, A'1-A'4, A"1-A"3, B1-B5, B'1-B'4, B"1-B"3, C1-C5, C'1-C'4, C"1-C"3) of PHMG Before and After Modification with GMA

	Mass	PHMG (%)	M-PHMG (%)		Mass	PHMG (%)	M-PHMG (%)		Mass	PHMG (%)	M-PHMG (%)
A1	159.2	8.5	7.2	B1	258.3	8.5	7.2	C1	201.2	6.1	8.7
	160.2	0.9	0.8		259.3	0.9	0.8		202.2	0.8	1.3
A2	300.3	98.2	11.1	B2	399.4	59.3	2.1	C2	342.3	39.6	44.1
A'1	301.3	18.0	30.3	B'1	400.4	15.4	10.2	C'1	343.3	8.7	10.9
	302.3	2.1	5.3		401.4	2.4	2.8		344.3	1.1	2.0
A3	441.4	100	8.3	B3	540.6	36.7	0.9	C3	483.5	44.9	39.8
A'2	442.5	26.1	100	B'2	541.6	12.8	7.5	C'2	484.5	13.7	13.1
A"1	443.5	4.3	25.3	B"1	542.4	2.5	15.1	C"1	485.5	2.4	3.6
A4	582.6	60.0	4.0	B4	681.7	18.8	0.4	C4	624.6	29.7	21.5
A'3	583.6	21.8	57.6	B'3	682.7	8.3	4.5	C'3	625.6	11.5	9.6
A"2	584.6	4.5	21.1	B"2	683.7	2.2	18.9	C"2	626.6	2.6	4.0
A5	723.7	32.9	1.9	B5	822.8	9.8	0.9	C5	765.8	19.6	12.1
A'4	724.7	14.6	24.9	B'4	823.8	5.2	2.3	C'4	766.8	9.1	6.3
A"3	725.7	3.7	11.7	B"3	824.8	1.6	9.1	C"3	767.8	2.5	3.1

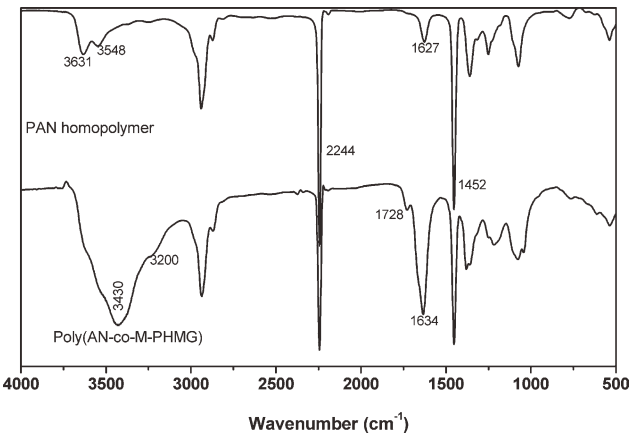


Figure 10. FTIR spectra of PAN homopolymer and poly(AN-*co*-M-PHMG) copolymer.

As shown in Figure 9, type A is terminated with a guanidyl amino group and a primary amino group; type B is terminated with two primary amino groups; while type C is terminated with two guanidyl amino groups. The above results indicate that epoxy groups of GMA can react with both primary amino and guanidyl amino. Also, the reaction activity of primary amino is much higher than that of guanidyl amino. This is understandable as the electrons are delocalized between the guanidyl amino and imido-groups through resonance, the nucleophilic strength and thus the reactivity of the terminal guanidyl amino-groups decrease greatly as compared with the terminal amino-groups. This result was also consistent with that reported in literature.[31]

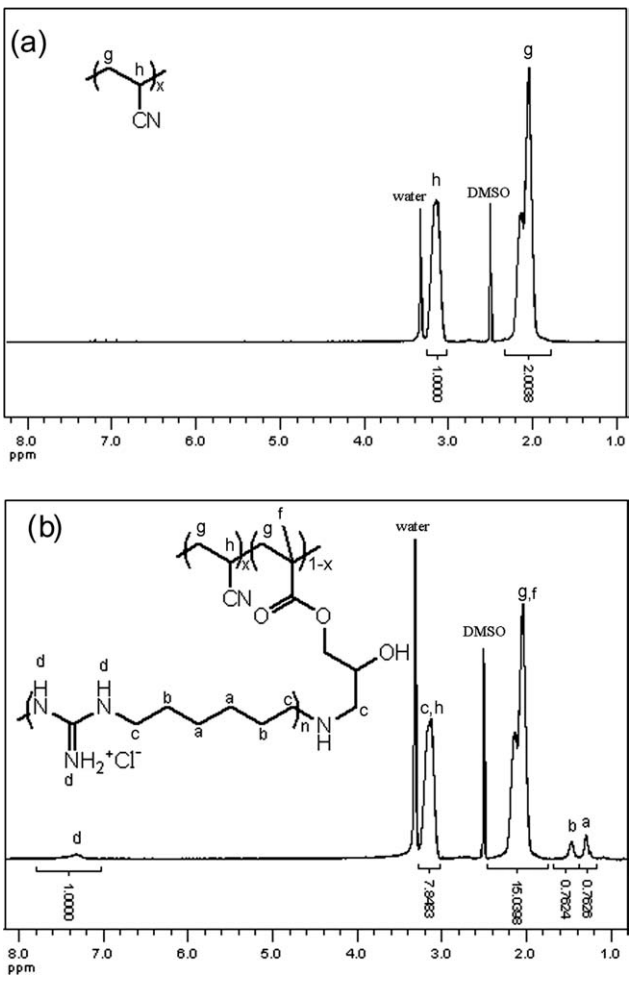


Figure 11. ^{1}H-NMR spectra of PAN (a) and poly(AN-*co*-M-PHMG) copolymer (b).

Table III. Synthesis of Poly(AN-*co*-M-PHMG) Copolymer and PAN Homopolymer as Well as Related Parameters

Sample	M-PHMG (mg/mL)	AN (mg/mL)	Yield (%)	[η] (L/g)	C_{PHMG} (wt %)
Poly(AN-*co*-M-PHMG)	12	80	91	0.112	4.55
PAN	0	80	95	0.104	-

The Structure and Antimicrobial Activity of Poly(AN-*co*-M-PHMG) Copolymer

Poly(AN-*co*-M-PHMG) copolymer was synthesized via precipitation copolymerization of AN and modified PHMG in water initiated by $NaClO_3$ —Na_2SO_3 redox system. The copolymerization was confirmed by FTIR and ^{1}H-NMR techniques. Figure 10 shows FTIR spectra of PAN homopolymer and poly(AN-*co*-M-PHMG) copolymer. In FTIR spectrum of PAN homopolymer, the characteristic absorption peaks appeared at 2244 cm^{-1} and 1452 cm^{-1}, corresponding to the stretching vibration of nitrile groups and scissoring vibration of methyl groups, respectively. Both the characteristic absorption peaks of PAN homopolymer (2244 cm^{-1}, 1452 cm^{-1}) and those of M-PHGM (3200 cm^{-1}, 1728 cm^{-1}, and 1634 cm^{-1}, see Figure 5) appeared in the FTIR spectrum of poly(AN-*co*-M-PHMG) copolymer, indicating the successful introduction of PHMG to the copolymer.

The ^{1}H-NMR spectra and the detailed attribution of various chemical shifts of PAN homopolymer and poly(AN-*co*-M-PHMG) copolymer are assembled in Figure 11. When compared with the ^{1}H-NMR spectrum of PAN homopolymer, the appearance of new chemical shifts at δ = 1.24–1.29 (a), 1.46 (b), 7.04–8.82 (d), which are the characteristic chemical shifts of PHMG (see Figure 7), in the ^{1}H-NMR spectrum of poly(AN-*co*-M-PHMG) copolymer suggests the successful copolymerization of AN and M-PHMG.

Table III listed the parameters for the synthesis of poly(AN-*co*-M-PHMG) copolymer and PAN homopolymer. It could be seen that the addition of M-PHMG produced little influence on the polymerization of AN: a copolymer with a intrinsic viscosity, which is closely related to the molecular weight of the polymer as well as the spinnability, slightly larger than that of PAN homopolymer was obtained; the copolymerization only lead to a minor decrease in the yield. However, the content of PHMG (C_{PHMG}) in the copolymer was much less than that of the feeding one. This may suggest the lower activity of M-PHMG as compared with AN. The obtained copolymer powder showed an antibacterial rate lager than 99.99% after contacting the suspension of *Pseudomonas aeruginosa* for 24 h, demonstrating the excellent antimicrobial activity of the copolymer.

CONCLUSIONS

The reaction between GMA and PHMG was investigated. The analysis results of UV absorption show that when the reaction occurred in DMSO at a feeding molar ratio of GMA to PHMG of 1.0, 60°C for 60 h, the conversion rate of GMA reached 75%. The results of FTIR, Raman spectrometry, ^{1}H-NMR confirm the reaction between epoxy of GMA and amino of PHMG, as well as the successful introduction of carbon-to-carbon bonds to the modified PHMG. The results of mass spectra disclose the activity difference in the different aminos of PHMG: the primary amino group is ready to react with epoxy of GMA, whereas the guanidyl amino hardly reacts with GMA because of the formation of p-π conjugate with imido-groups. The modified PHMG can be used as a comonomer to copolymerize with vinyl monomer such as AN to prepare copolymers with excellent antimicrobial activity.

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