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Acrylonitrile Copolymers Containing Guanidine Oligomer: Synthesis and Use for the Preparation of Nonleaching Antimicrobial Acrylic Fibers

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ABSTRACT: Nonleaching acrylic fibers with permanent antibacterial activity were prepared via a combination of copolymerization and a wet-blend-spinning method. Specifically, poly[acrylonitrile-*co*-modified poly(hexamethylene guanidine hydrochloride)] [poly(AN-*co*-M-PHMG)] copolymers containing a covalently connected antibacterial guanidine oligomer were first synthesized via the precipitation copolymerization of acrylonitrile (AN) with a modified poly(hexamethylene guanidine hydrochloride) (M-PHMG) macromonomer in water. Then, modified acrylic fibers were prepared from a mixture of the copolymer and commercial fiber-grade AN terpolymer via a wet-spinning process with dimethyl sulfoxide as the solvent. The influences of the reaction time, temperature, pH value of the medium, and amount of initiator on the copolymerization and the effect of the copolymer content on the mechanical properties and antibacterial activity of the modified acrylic fibers were investigated in detail. The results show that the M-PHMG macromonomer exhibited a lower reactivity than AN. The poly(AN-*co*-M-PHMG) copolymer with a PHMG content of 5.49% and an intrinsic viscosity of 11.2 dL/g could be synthesized under optimized conditions. With increasing copolymer content, the tensile strength of the modified acrylic fibers decreased slightly, and the antibacterial activity increased. The modified acrylic fibers with a copolymer content of 50% (i.e., a PHMG content of 2.75%) exhibited both good mechanical properties and excellent antibacterial activity. The additional antibacterial function would surely enlarge the applications of the fiber. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 419–425, 2013

KEYWORDS: copolymers; fibers; functionalization of polymers; radical polymerization

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INTRODUCTION

With the growing awareness of public health, antimicrobial materials have found wide applications in various areas, including medical devices, water purification, hospital furniture, dental surgery equipment, food packaging and storage, and textiles.[1–6] Particularly, microorganisms can grow and survive on medically used textiles, such as hospital gowns, patient drapes, carpeting, and bedding materials, for at least days.[7] To prevent the cross-transmissions of diseases, antibacterial properties should be a necessary addition to textiles and polymers for medical and healthcare use.

The use of numerous disinfectants and antiseptics for treating materials in hospitals is efficient for combating infectious diseases. However, the approach suffers from problems caused by the leaching of antimicrobials: short durability, adverse environmental consequences, and the development of pathogenic resistance to antibiotics.[8] An ideal approach is the development of permanently sterile, nonleaching materials by a covalent connection with an antimicrobial compound.[9–13]

Acrylonitrile (AN) copolymer is one of the most important fiber-forming polymers, and it is used to prepare acrylic fiber. Acrylic fiber is the third largest consumable manmade fiber in the world. Because of the high elasticity, high voluminosity, high strength, good thermal stability, good weather and sunlight resistance, good mildew and insect resistance, and good chemical resistance; acrylic fiber is popular in apparel, upholstery, outdoor and industrial applications. Endowing acrylic fiber with antibacterial functions will further enlarge its applications. Also, polyacrylonitrile (PAN) fibrous membranes have been widely adopted in filtration.[14,15] Water and air filters, particularly, those that operate under dark and damp conditions, are constantly subjected to attacks from environmental

microorganisms. Endowing the filters with antimicrobial functions would not only extend their service life but also improve the quality of purified water and filtered air.[16]

Antimicrobial acrylic fibers can be fabricated by simple physical blend spinning with biocides[17] or silver-ion-loaded zeolites; however, they are subject to the aforementioned leaching-induced problems. Ko et al.[18] and Bahrami et al.[19] prepared antimicrobial acrylic fiber by the blend spinning of PAN and *N*-(2-hydroxyl)propyl-3-trimethylammonium chitosan chloride (HTCC) in sodium thiocyanate (NaSCN) aqueous solution and dimethyl sulfoxide (DMSO), respectively. The addition of only 0.5% HTCC caused a nearly 100% reduction in bacteria. However, because of the good water solubility of HTCC and the lack of a covalent bond connection between HTCC and PAN, HTCC is gradually lost during the spinning process and during use. Gu et al.[20] prepared modified acrylic fiber via the blend spinning of AN terpolymer and poly(acrylonitirle-*co*-3-allyl-5,5-dimethylhydantoin) in an NaSCN aqueous solution. Only when the hydantoin ring structures of the fiber were converted into *N*-halamine structures after chlorination did the fiber exhibit antibacterial activity. These *N*-halamine structures were reported to kill bacteria by transferring the oxidative halogen atoms from the polymer to the microbial cells.[21] Thus, its biocidal efficacy had to be restored by a chlorine bleaching treatment when the halogen atoms were lost. Also, when the coordination of Ag^+ ions with nitrile or amidoxime groups and the subsequent *in situ* reduction of Ag^+ ions to silver nanoparticles were taken advantage of, various antimicrobial PAN nanofibers or nanofibrous membranes were prepared.[16,22,23] However, silver nanoparticles were easily changed to a dark color in air with the presence of minute H_2S.

Polymeric guanidines are water-soluble polycationic disinfectants with a broad spectrum of activity against Gram-positive and Gram-negative bacteria, fungi, yeasts, and viruses.[24–27] Because of their odorlessness, colorlessness, noncorrosiveness, low mammalian toxicity, and good thermal stability,[28] they are not only widely used in medicine, wound care, the food industry, and water treatment[29–32] but also in fiber and plastics.[33–35] Their low fastness to laundering caused by their water solubility makes them unsuitable for direct application in industrial goods, such as fiber, plastics, and clothes. Various antimicrobial materials with covalently connected poly(hexamethylene guanidine hydrochloride) (PHMG), including polypropylene (PP) fiber, polyethylene, PP, polystyrene, and polyamide plastics and sulfite pulps and starch, were prepared via graft copolymerization[36] or a coupling reaction.[37]

In a previous study,[38] to make it bear carbon-to-carbon double bonds and enlarge its applications in the production of antimicrobial materials via copolymerization, we modified a PHMG oligomer (M-PHMG) via a reaction with glycidyl methacrylate (GMA) and investigated it in detail. We also reported the use of the M-PHMG as a comonomer to prepare an antibacterial AN copolymer. In this study, we examined further the influences of the reaction parameters on the copolymerization of AN with M-PHMG. Furthermore, the obtained poly[acrylonitrile-*co*-modified poly(hexamethylene guanidine hydrochloride)] [poly(AN-*co*-M-PHMG)] copolymer was used to prepare nonleaching modified acrylic fiber with permanent antibacterial activity via wet blend spinning with a commercial fiber-grade AN terpolymer with DMSO as the solvent. The effects of the copolymer content on the mechanical properties and antimicrobial activity of the modified acrylic fiber were also investigated.

EXPERIMENTAL

Materials

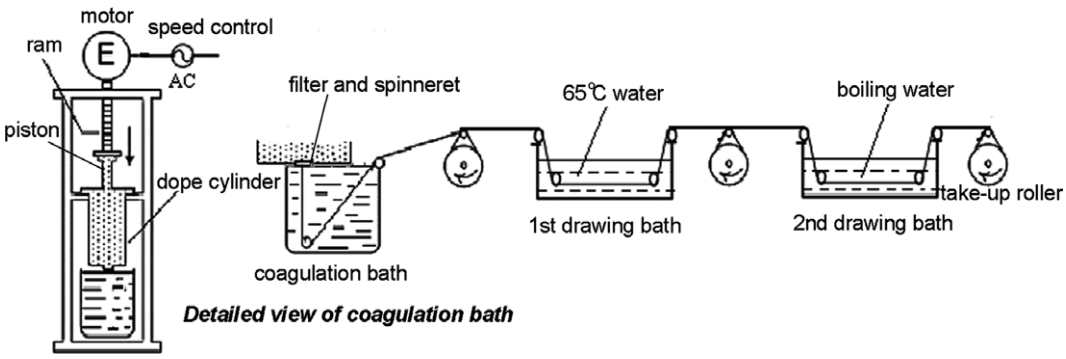
Hexamethylene diamine and guanidine hydrochloride were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). PHMG was prepared by the condensation polymerization of hexamethylene diamine and guanidine hydrochloride according to a procedure reported in the literature;[39] it's number-average molecular weight was 771 g/mol, and its weight-average molecular weight/number-average molecular weight was 1.31, as estimated by electrospray ionization time-of-flight mass spectrometry. GMA was purchased from Dow Chemical Co. (Shanghai, China) and was purified via vacuum distillation before use. AN terpolymer (AN–methyl acrylate–itaconic acid = 18 : 1 : 1) was purchased from Shanghai Petrochemical Acrylic Fibers Enterprise (China) with an intrinsic viscosity of 1.36 dL/L [25°C, in dimethylformamide (DMF)]. AN was purchased from Zhangxing Chemical Reagent Co., Ltd. (Shanghai, China), and was distilled before use. Sodium sulfite (Na_2SO_3) and sodium chlorate ($NaClO_3$) were purchased from Shanghai Shisihewei Chemical Industry Co., Ltd. (Shanghai, China), and was purified via recrystallization in water. DMSO was purchased from Shanghai Lingfeng Chemical Reagents Co. Nitric acid and acetone were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). Deionized water was used in all of the experiments.

Preparation of the M-PHMG Macromonomer

The M-PHMG macromonomer was prepared via the reaction of a 38 wt % PHMG solution in DMSO with GMA at 60°C for 60 h at a molar ratio of GMA to PHMG of 1.5 according to ref. 38. The molar ratio of GMA to PHMG in the M-PHMG macromonomer was determined by ultraviolet spectrometry to be about 0.80.[38]

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

Typically, to a three-necked flask containing 1.0 g of crude product, which contained PHMG, modified PHMG, unreacted GMA, and DMSO, 15 mL of acetone was added to precipitate PHMG and modified PHMG. After 2 min of sonication, the upper liquid was removed. The treatment was repeated twice to remove DMSO and unreacted GMA completely. The remnant acetone was removed via evaporation in a ventilation cabinet at room temperature. After that, 25 mL of deionized water and a certain amount of $NaClO_3$ were added to obtain a uniform aqueous solution; this was followed by the adjustment of the pH value of the solution to 3.5 via the addition of diluted nitric acid aqueous solution. Next, the system was kept at a certain temperature and purged with nitrogen under stirring to remove oxygen for 30 min; this was followed by injections of AN (3 mL) and Na_2SO_3 aqueous solution of pH 3.5 (5 mL). The reaction was continued for 6 h. After that, the suspension was filtered and washed with a large amount of hot water to remove unreacted AN, unreacted M-PHMG, and PHMG. Finally, the



Scheme 1. Schematic diagram of the wet-spinning process. AC: alternating current; E: electric machinery.

precipitates of poly(AN-*co*-M-PHMG) copolymer were dried at 60°C for 24 h.

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

$$\text{Yield}\,(\%) = \frac{W_p}{W_1 + W_2} \times 100\%$$

where W_p is the weight of the obtained copolymer and W_1 and W_2 are the feeding weights of the AN and M-PHMG macromonomers, respectively.

Preparation of the Blend-Spinning Dopes of the AN Terpolymer and Poly(AN-*co*-M-PHMG) Copolymer

To obtain homogeneous solutions, mixtures of commercial fiber-grade AN terpolymer and poly(AN-*co*-M-PHMG) copolymer at weight ratios of 100 : 0, 80 : 20, 70 : 30, 60 : 40, 50 : 50, and 0 : 100 were first dispersed in DMSO and then subjected to successive swelling at 50°C for 2 h and dissolution at 60°C for 6 h under stirring. The spinning dopes were obtained after the solutions were deaerated overnight in a drying oven at 65°C. The solid content of all of the spinning dopes was fixed at 20 wt %.

Preparation of the Modified Acrylic Fibers Containing Poly(AN-*co*-M-PHMG) Copolymer

Various acrylic fibers were prepared via a wet-spinning process with a self-built experimental spinning apparatus (Scheme 1). The spinning dope at 65°C was first successively passed through a poplin (9.72 tex) filter layer and a spinneret with 30 holes with diameters of 0.08 mm and then entered into a coagulation bath containing a DMSO/water (50/50 v/v) mixture at 30°C. After coming out of the coagulation bath, the gel filaments were placed into the first drawing bath and prestretched in water at 65°C for 1.96 times; this was followed by stretching to 3.95 times in the second drawing bath composed of boiling water. After that, the filaments were collected on bobbins and were fully washed by water with the assistance of sonication to completely remove the residual DMSO. Finally, the filaments were heat-set at 110°C for 15 min and stored in a desiccator for further analysis.

Six acrylic fibers containing 0, 20, 30, 40, 50, and 100 wt % poly(AN-*co*-M-PHMG) copolymer, which were denoted as FPAN, F28, F37, F46, F55, and F100, respectively, were prepared.

Characterization

Fourier transform infrared (FTIR) spectra were taken on a Nicolet Nexus 670 FTIR spectrometer (USA) in the range 400–4000 cm^{-1} with polymer powders or scissored fibers. Taking advantage of the characteristic absorption of PHMG around 1638 cm^{-1} and the characteristic absorption of nitrile at 2244 cm^{-1}, we determined the content of PHMG in the poly(AN-*co*-M-PHMG) copolymer by infrared spectrometry. The FTIR spectra of the PAN homopolymer, which was synthesized under conditions of 0.039 g of $NaClO_3$, 0.128 g of Na_2SO_3, 3 mL of AN, a temperature of 35°C, a pH of 3.5, and a time of 6 h, PHMG and mixtures with known PHMG contents (W_{PHMG}) were determined. The calibration curve was obtained from the relationship between the intensity ratio of the absorption around 1638 cm^{-1} to that at 2244 cm^{-1} (I_{1638}/I_{2244}) and the W_{PHMG} values of the mixtures. The contribution of the neighboring absorption of PAN homopolymer at 1627 cm^{-1} to the I_{1638} of the mixtures was abstracted based on the I_{2244}/I_{1627} ratio of the PAN homopolymer. ^{1}H-NMR spectra of the PAN homopolymer, M-PHMG, and the copolymer were acquired by a Bruker Avance-400 NMR spectrometer (Switzerland) with DMSO-d_6 as the solvent. Chemical shifts were reported in δ units (parts per million) relative to tetramethyl silane. The intrinsic viscosities of the samples in DMF at 25°C were determined via a dilution method with an Ubbelohde viscometer. Thermogravimetric analysis was carried out on a PerkinElmer TGA 2050 analyzer (USA) in the temperature range 100–700°C at a heating rate of 10°C/min in nitrogen. The linear densities of acrylic fibers were determined via gravimetry. The single-filament tensile properties were determined with a XQ-1 tensile testing machine (Lanzhou Electron Instrument Co., Ltd., China) at a crosshead speed of 10 mm/min with a gauge length of 20 mm. For each sample, at least 10 filaments were tested. The antibacterial activities of the copolymer and modified acrylic fibers were evaluated at 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) with *Staphylococcus aureus* as the testing bacterium.

RESULTS AND DISCUSSION

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

Poly(AN-*co*-M-PHMG) copolymer was synthesized via the precipitation copolymerization of AN with modified PHMG in

Table I. Effect of the Reaction Time on the Precipitation Copolymerization of AN with M-PHMG in Water[a]

Reaction time (h)	Yield (%)	W_{PHMG} (%)	$[\eta]_{DMF,25°C}$ (dL/g)
6	73	3.56	1.47
9	77	3.83	1.43
12	80	3.95	1.46
18	83	4.02	1.42
24	90	3.98	1.44

[a]Other reaction conditions: $NaClO_3$ = 0.036 g; Na_2SO_3 = 0.125 g; pH = 2, temperature = 35°C.

water with a $NaClO_3$–Na_2SO_3 redox initiating system. As reported in our previous article, the successful copolymerization was confirmed by FTIR spectroscopy and ^{1}H-NMR.[38] To optimize the copolymerization, the influences of the reaction time, temperature, pH value of the medium, and amount of initiator on the yield, W_{PHMG}, and intrinsic viscosity of the obtained poly(AN-*co*-M-PHMG) copolymer were investigated.

Table I lists the data of the yield, W_{PHMG}, and intrinsic viscosity of the copolymers obtained after different reaction times. As shown, the copolymer yield reached above 70% after 6 h of reaction. As the reaction time was further prolonged, the yield continued to increase slowly. As the reaction time increased from 6 to 24 h, the intrinsic viscosity of the copolymer in DMF at 25°C ($[\eta]_{DMF,25°C}$), which was closely related to the molecular weight and spinnability, remained unchanged, whereas W_{PHMG} of the copolymer increased slightly. W_{PHMG} of the obtained copolymers varying from 3.56 to 4.02%, was much smaller than the feeding W_{PHMG} (ca. 7.2%), indicating the lower reactivity of M-PHMG macromonomer as compared with AN. This was also demonstrated by the fact that W_{PHMG} of the copolymer increased slightly as the reaction time was prolonged. The lower reactivity of M-PHMG caused an increasing ratio of M-PHMG to AN in the system with the extension of reaction time. Consequently, more M-PHMG macromonomers were incorporated into the copolymer chains in the later stages of copolymerization. The M-PHMG macromonomer bore an end group with a structure similar to methyl methacrylate, whose reactivity was higher than AN.[40] Thus, the lower reactivity of M-PHMG may have resulted from its large volume and positive charges due to the protonation of guanidyl and amine groups.

Table II lists the data of the yield, W_{PHMG}, and $[\eta]_{DMF,25°C}$ of the copolymers prepared at different temperatures. As the reaction temperature increased, the yield increased slightly, whereas W_{PHMG} decreased slightly. Meanwhile, there was also a substantial decrease in the intrinsic viscosity of the copolymer. At higher temperatures, the radical number increased; meanwhile, the molecules moved more quickly. The polymerization rate and the probability of both the chain transfer and chain termination reactions increased. Thus, the yield increased, and the molecular weight of the copolymer decreased. Furthermore, the water solubility of AN and the AN/M-PHMG ratio in the water phase increased with increasing temperature. The reactivity of AN also increased with rising temperature.[41] Consequently, fewer M-PHMG molecules were incorporated into the copolymer.

Table II. Effect of the Temperature on the Precipitation Copolymerization of AN with M-PHMG in Water[a]

Reaction temperature (°C)	Yield (%)	W_{PHMG} (%)	$[\eta]_{DMF,25°C}$ (dL/g)
25	70	4.54	1.71
35	75	3.88	1.59
45	74	3.46	1.24

[a]Other reaction conditions: $NaClO_3$ = 0.036 g, Na_2SO_3 = 0.125 g, pH = 3, time = 6 h.

Table III. Effect of the pH Value of the Reaction Medium on the Precipitation Copolymerization of AN with M-PHMG in Water[a]

pH value of the reaction medium	Yield (%)	W_{PHMG} (%)	$[\eta]_{DMF,25°C}$ (dL/g)
2.0	73	3.56	1.47
3.0	70	3.88	1.52
3.5	72	4.05	1.37
4.0	43	4.35	1.21
5.0	12	6.04	-

[a]Other reaction conditions: $NaClO_3$ = 0.036 g; Na_2SO_3 = 0.125 g, temperature = 35°C, time = 6 h.

Table III lists the data of the yield, W_{PHMG}, and $[\eta]_{DMF,25°C}$ of the copolymers prepared in media at different pH values. As shown, as the pH value of the medium increased from 2.0 to 3.5, the yield remained unchanged (ca. 70%). However, as the pH value increased further to 5.0, the yield decreased rapidly to 12%. The initiating activity of the $NaClO_3$–Na_2SO_3 redox system was closely related to the pH value of the medium, which determined the ionization equilibrium of H_2SO_3, that is, the relative concentrations of SO_3^{2-}, HSO_3^-, and H_2SO_3 (Scheme 2). H_2SO_3 was the key to the production of radicals. Meanwhile, HSO_3^- was very active in the chain-transfer reactions.[42] As the pH value of the medium increased, the relative concentrations of HSO_3^- and H_2SO_3 increased and decreased, respectively. Consequently, the polymerization rate decreased, and the probability of a chain-transfer reaction increased. The above change in the yield indicated that the initiating activity decreased substantially as the pH value of the medium increased above 4.0.

With increasing pH value of the medium, the weight content of PHMG increased; the intrinsic viscosity of the copolymer first increased slightly and then decreased slowly. The increase in W_{PHMG} may have been related to the decreasing positive charges of the M-PHMG macromonomer as the protonation of amine groups decreased with increasing pH value. The change in the intrinsic viscosity was codetermined by the initiating activity

$$ClO_3^- + H_2SO_3 \rightarrow ClO_2^- + HSO_3^{\bullet} + OH^{\bullet}$$

$$SO_3^{2-} \overset{+H^+}{\rightleftharpoons} HSO_3^- \overset{+H^+}{\rightleftharpoons} H_2SO_3$$

Scheme 2. Initiation mechanism of the $NaClO_3$–Na_2SO_3 redox system.

Table IV. Effect of the Initiator Amount on the Precipitation Copolymerization of AN with M-PHMG in Water[a]

$NaClO_3$ (g)	Na_2SO_3 (g)	Yield (%)	W_{PHMG} (%)	$[\eta]_{DMF,25°C}$ (dL/g)
0.036	0.125	80	4.84	1.66
0.072	0.250	85	5.49	1.22
0.108	0.375	91	5.87	1.08

[a]Other reaction conditions: pH = 3.5, temperature = 25°C, time = 18 h.

and the chain-transfer reaction. As the pH value of the medium increased, the initiating activity decreased, and fewer radicals were produced; this led to a higher molecular weight. Meanwhile, more HSO_3^- ions were present in the system; this caused an increasing probability of chain-transfer reaction and a lower molecular weight.

Table IV lists the data of the yield, W_{PHMG}, and $[\eta]_{DMF,25°C}$ of the copolymers prepared with different amounts of initiator. As shown, as the initiator amount increased, the yield and W_{PHMG} increased, and the intrinsic viscosity of the copolymer decreased. These changes could be reasonably explained by the increase in the radical number in the reaction system.

On the basis of the above results and the balance between the antibacterial activity, which was determined by W_{PHMG}, and the spinnability, which was determined by the intrinsic viscosity of the copolymer, the optimal reaction conditions for the preparation of the poly(AN-*co*-M-PHMG) copolymer were as follows: $NaClO_3 = 0.072$ g, $Na_2SO_3 = 0.250$ g, temperature = 25°C, time = 18 h, and pH = 3.5. Under these conditions, W_{PHMG} and the intrinsic viscosity of the obtained copolymer were 5.49% and 1.22 dL/g, respectively. The resulting copolymer exhibited excellent antibacterial activity: the reduction rate of the bacteria was larger than 99.99% after the copolymer was contacted with the suspension of *S. aureus* for 24 h.

Structure and Properties of the Modified Acrylic Fibers

The poly(AN-*co*-M-PHMG) copolymer obtained under optimal conditions was mixed with commercial fiber-grade AN terpolymer at different ratios to prepare blend-spinning dopes composed of poly(AN-*co*-M-PHMG) copolymer and AN terpolymer, from which a series of modified acrylic fibers were prepared via a wet-spinning process. Figure 1 shows the FTIR spectra of the modified acrylic fibers spun from pure AN terpolymer (FPAN), pure poly(AN-*co*-M-PHMG) copolymer (F100), and mixtures of the two copolymers at a weight ratio of 70 : 30 (F37). From the spectrum of FPAN, the absorption at 1733 cm^{-1}, which corresponded to the stretch vibration of the carbonyl groups from methacrylate and itaconic acid units, was slightly stronger than that of the stretching vibration of nitrile groups at 2244 cm^{-1}. The absorption at 1635 cm^{-1}, which may have corresponded to the bending vibration of water molecules, was much weaker compared with that at 2244 cm^{-1}. In the spectrum of modified acrylic fiber F37, the absorption at 1635 cm^{-1} became stronger than that of FPAN. The enhancement in the absorption demonstrated the presence of PHMG, which displayed characteristic vibrations of imide and amine groups at 1638 cm^{-1}, in the acrylic fiber F100.

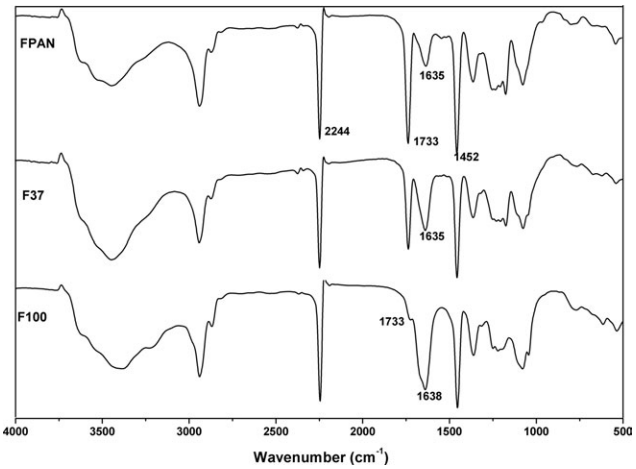


Figure 1. FTIR spectra of acrylic fibers containing 0 wt % (FPAN), 30 wt % (F37), and 100 wt % (F100) of the poly(AN-*co*-M-PHMG) copolymer.

The thermal properties of FPAN, F37, and F100 acrylic fibers and PHMG were also studied. As shown in Figure 2, the PHMG oligomer and modified acrylic fibers F37 and F100 displayed better thermostability than the acrylic fiber FPAN. The starting decomposition temperatures (i.e., the temperature at 5% weight loss) of FPAN, F37, F100, and PHMG were 278, 299, 299, and 322°C, respectively. FPAN displayed a large weight loss of about 25% at a temperature range of 280–380°C with a maximum decomposition rate at 294°C; this corresponded to the cyclization, oxidization, and dehydrogenation of PAN. The small decomposition peak around 418°C may have corresponded to the oxidative composition of PAN. PHMG displayed a two-stage mass loss with maximum decomposition rates around 375 and 485°C, respectively. The first stage of the mass loss may have been caused by the breakage of C—N bonds and the removal of the amine and guanidine groups of PHMG; the second one may have been caused by the extensive degradation of the residual polymer.

On the differential thermogravimetry curve of the modified acrylic fibers F37 and F100, there only appeared two peaks. The maximum decomposition peaks of PAN and PHMG were merged. This may have indicated strong interactions between the nitrile groups of PAN and the amine and guanidine groups of PHMG. As the weight content of poly(AN-*co*-M-PHMG) in the modified acrylic fibers increased, both decomposition peaks appeared at higher temperatures.

The mechanical properties of the various acrylic fibers are summarized in Table V. When the weight content of poly(AN-*co*-M-PHMG) copolymer was below 30%, the spinnability of the dopes was excellent, and the fibers could be smoothly stretched in a boiling water bath to 3.95 times. The titer and breaking elongation of the fibers remained unchanged, and the tensile strength of the fibers decreased slightly from 4.55 cN/dtex (acrylic fiber) to 4.24 cN/dtex. When the content of poly(AN-

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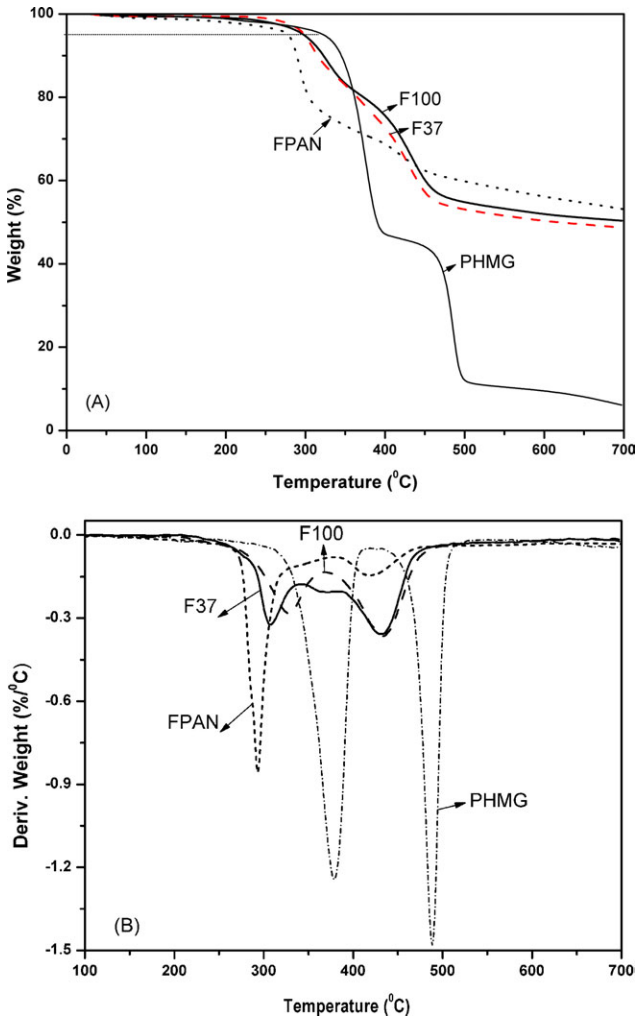

Figure 2. Thermograph of acrylic fibers containing 0 wt % (FPAN), 30 wt % (F37), 100 wt % (F100) of poly(AN-*co*-M-PHMG) copolymer, and PHMG: (A) thermogravimetry curve and (B) differential thermogravimetry curve. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

co-M-PHMG) copolymer was increased further, the spinnability of the dopes deteriorated somewhat. The maximum stretching ratio of the modified acrylic fibers in boiling water decreased. As the copolymer weight increased from 40 to 100%, the stretching ratio decreased from 3.83 to 2.75. Consequently, the titer of the fiber increased, the tensile strength and the breaking elongation, respectively, decreased and increased substantially. As far as the mechanical properties were considered, though the tensile strengths of the modified acrylic fiber were lower than that of the acrylic fiber, they still met the requirement for garment production except for F100.

The antibacterial activities of various modified acrylic fibers against *S. aureus* were determined. As shown in Figure 3, when the poly(AN-*co*-M-PHMG) copolymer content increased, the antibacterial activity of the fiber increased and reached above 99% at a poly(AN-*co*-M-PHMG) content of 50% (i.e., $W_{PHMG} = 2.75\%$). Thus, F55 exhibited both excellent antibacterial activity and acceptable mechanical properties.

Table V. Mechanical Properties of Various Acrylic Fibers Wet-Spun from Blends of Commercial Fiber-Grade AN Terpolymer and Poly(AN-*co*-M-PHMG) Copolymer[a]

Sample	Content of poly(AN-*co*-M-PHMG) (wt %)	Titer (dtex)	Tensile strength (cN/dtex)	Breaking elongation (%)
FPAN	0	1.18	4.55	11.5
F28	20	1.19	4.35	11.7
F37	30	1.17	4.24	11.7
F46	40	1.23	4.01	11.9
F55	50	1.31	3.67	12.6
F100	100	1.73	1.83	16.8

[a]The drawing ratios in the boiling water of FPAN, F28, F37, F46, F55, and F100 were 3.95, 3.95, 3.95, 3.83, 3.55 and 2.75, respectively.

Here, to exhibit excellent antibacterial activity, the minimum W_{PHMG} in the blend fiber was 2.75 wt %, which was much larger than that in other reported PHMG-modified systems. For example, PHMG-modified cellulose fiber displayed an antibacterial activity above 99% at a W_{PHMG} of 1.0 wt %; PHMG-modified starch displayed an antibacterial activity of 100% at a W_{PHMG} of 1.0 wt %. The PHMG-modified PP fiber, which was prepared by the blend spinning of pure PP and PP-*g*-PHMG, also exhibited an antibacterial activity of 100% at a W_{PHMG} of 1.0 wt %. The above difference may have resulted from the different distributions of PHMG in the material as only the PHMG distributed on the surface could display bactericidal action. PHMG oligomers were grafted to the surfaces of the starch and the cellulose. As to the PHMG-modified PP fibers, the poor miscibility between the strong polar PHMG and nonpolar PP matrix led to an enrichment of PHMG on their surfaces. In our system, the interactions between polar nitrile and polar PHMG may have suppressed the enrichment of PHMG on the surface of the modified acrylic fiber. Thus, more

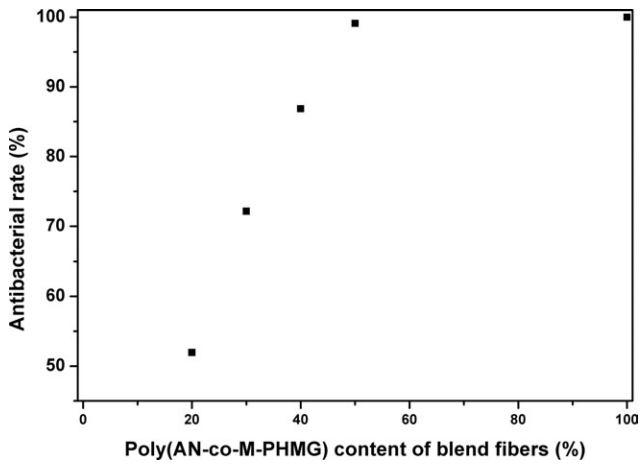

Figure 3. Effect of the poly(AN-*co*-M-PHMG) content on the antibacterial activity of the modified acrylic fibers wet-spun from blends of commercial fiber-grade AN terpolymer and poly(AN-*co*-M-PHMG) copolymer.

PHMG was needed to incorporate into the acrylic fiber to endow it with antibacterial function.

CONCLUSIONS

Various poly(AN-*co*-M-PHMG) copolymers containing covalently connected antibacterial guanidine oligomer were synthesized via the precipitation copolymerization of AN with an M-PHMG macromonomer in water. Because of the lower reactivity of M-PHMG, the W_{PHMG} of the copolymer was significantly lower than the feeding one. With decreasing temperature, increasing reaction time, increasing amount of initiator, and increasing pH value of the medium, the W_{PHMG} value of the copolymer increased. An increase in the temperature, pH value of the medium, or the amount of initiator caused a decrease in the molecular weight of the copolymer. Taking into consideration of the balance of antibacterial properties and spinnability, we used a copolymer with a W_{PHMG} of 5.49% and an intrinsic viscosity of 1.22 dL/g to mix with a commercial fiber-grade AN terpolymer to prepare modified acrylic fibers via a wet-spinning process using DMSO as the solvent. The tensile strength of the modified acrylic fiber decreased slightly, whereas the antibacterial activity increased with increasing copolymer content. At a copolymer content of 50% (i.e., $W_{PHMG} = 2.75\%$), the modified acrylic fiber exhibited both good mechanical properties and excellent antibacterial activity. This would surely enlarge the applications of this fiber.

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