

Amphiphilic Graft Copolymers of Hydroxypropyl Cellulose Backbone with Nonpolar Polyisobutylene Branches

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Electronic Supplementary Information

Abstract The novel amphiphilic graft copolymers with hydrophilic hard polar hydroxypropyl cellulose (HPC) backbone and hydrophobic soft nonpolar polyisobutylene (PIB) branches have been successfully synthesized through nucleophilic substitution reaction of living PIB chains carrying oxonium ions with the –OH groups along HPC backbone. The PIB branch length in the graft copolymers could be designed by living cationic polymerization and the grafting density could be adjusted by PIB⁺/–OH molar ratio. The living PIB chains carrying oxonium ion were prepared by transformation of allyl bromide end groups in the presence of AgClO₄ and silver nanoparticles (3.2±0.3 nm, 0.7 wt%–1.8 wt%) generated *in situ* from AgBr. The phase-separation morphology was formed in the graft copolymers due to their incompatibility between backbone and branches. The hydrophilicity on the surface of graft copolymer films could be turned to hydrophobicity by increasing grafting density or/and length of PIB branches. The soft PIB segments in graft copolymers provided a unique surface *via* self-assembly for anti-protein adsorption against bovine serum albumin. A small amount of Ag nanoparticles in the copolymers contributed to good antibacterial activities against *Staphylococcus aureus* or *Escherichia coli*.

Keywords Hydroxypropyl cellulose; Polyisobutylene; Graft copolymer; Cationic polymerization

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INTRODUCTION

Cellulose as a safe, biorenewable and biodegradable natural resource on earth has drawn more and more attention in recent decades. Cellulose is composed of β -D-anhydroglucopyranose linked by β (1-4') glycosidic bonds^[1] and each repeating anhydroglucopyranose unit (AGU) presents two secondary hydroxyl groups at the C2, C3 positions and one primary hydroxyl group at the C6 position.^[2] The main feature in chemical structure is the hydrogen bond networks between intramolecular and intermolecular hydrogen bond formed in cellulose chains, which affords cellulose insolubility in common solvents and limits its wide application. The hydroxyl groups in cellulose could be modified by etherification, esterification and oxidation reactions to improve the solubility and properties of cellulosic materials.^[3] Hydroxypropyl cellulose (HPC) derived from etherification of cellulose is one of the most important cellulose derivatives, which has been approved by the United States Food and Drug Administration (FDA).^[4] The HPC-based materials with good solubility in water and organic solvents, biodegradability and non-toxicity have been widely used in

food and pharmaceutical products.^[5]

Enormous efforts have been turned to the graft modification of cellulose and its derivatives with tailored synthetic polymers using “grafting from” or “grafting onto”^[1,3,6,7] methods for preparing novel grafted cellulosic materials with improved physical and chemical properties. There are many types of branches in cellulose graft copolymers, such as polystyrene,^[8] polyisoprene,^[9] polyether,^[10] polyester,^[11] polyacrylamide,^[12] polyacrylic acid or polyacrylate^[13,14] and so on. The cellulose acetate-*g*-polystyrene graft copolymers possess enhanced mechanical properties,^[8] and cellulose-*g*-polyisoprene form core-shell nanoparticles by self-assembly.^[9] As far as we know, there is no report on the preparation and properties of soft nonpolar polyisobutylene-grafted HPC materials until now.

Polyisobutylene (PIB) is a typical hydrophobic nonpolar linear saturated polyolefin and exhibits excellent air tightness, thermo-oxidative stability, chemical stability and biocompatibility.^[14–17] Importantly, PIB has also been approved by FDA in the fields of food additives, tissue engineering scaffolds and other biomedical devices.^[18–20] PIB could only be synthesized *via* cationic polymerization of isobutylene^[21–24] and PIBs with various end-functional structures could be produced,^[24–26] which are usually used as the intermediate for further synthesis of PIB-based block copolymers^[27,28] or graft

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copolymers.^[29–31]

In this work, a novel amphiphilic graft copolymer with hydrophilic hard polar HPC backbone and hydrophobic soft nonpolar polyisobutylene (PIB) branches was synthesized through nucleophilic substitution reaction of living PIB chains carrying oxonium ion with the –OH groups along HPC backbone via “grafting onto” method according to our previous work.^[10,32–40] The PIB branch length in the graft copolymers could be designed by living cationic polymerization and the living PIB chains carrying oxonium ions were prepared by transformation of allyl bromide end groups in the presence of AgClO_4 . The grafting density could be adjusted by PIB⁺/–OH molar ratio. The phase-separation morphology was formed in the graft copolymers due to their incompatibility between backbone and branches. The hydrophilicity and hydrophobicity on the surface of graft copolymer films could be mediated by copolymer composition and provided a unique surface via self-assembly for anti-protein adsorption against bovine serum albumin. The small amount of Ag nanoparticles in the copolymers contributed to good antibacterial activities against *Staphylococcus aureus* or *Escherichia coli*. The novel amphiphilic HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposites with good biocompatibility, anti-protein adsorption performance and antibacterial activities might have potential application in the biomedical field.

EXPERIMENTAL

Materials

Hydroxypropyl cellulose (HPC, ~100 kg·mol^{−1}, degree of substitution (DS) (hydroxypropyl, HP)=1.20, molar substitution (MS)=2.4, according to our earlier study^[40]) was heated at 70 °C to remove moisture. Tetrahydrofuran (THF, A.R., Beijing Chemical Company) was dried with sodium wire under distillation. Dichloromethane (DCM, A.R. Beijing Chemical Company) was refluxed with CaH_2 powder before use. Silver perchlorate (AgClO_4 , 99%, Alfa Aesar), lithium bromide (LiBr, 99%, J&K), *n*-hexane and ethanol (A.R., Beijing Yili Fine Chemicals), and regenerated cellulose membranes (MWCO of 8000, Shanghai Yuanye Bio-Technology Co., Ltd.) were used as received. Toluene and acetone (A.R. Beijing Chemical Company) were treated with 4 Å molecular sieve before use.

Synthesis of PIB Macroinitiator with Allyl-Br End Groups (PIB-Br)

The synthesis procedures of PIB-Br were described in our previous work.^[29] Briefly, the living PIB chains with different number-average molecular weights (M_n) react with 1,3-butadiene (BD) to produce PIB with allyl-Cl end groups (PIB-Cl). Then, PIB-Cl reacted with LiBr in toluene/acetone mixed solution through halogen exchange reaction to obtain PIB-Br. PIB-Cl with M_n of 2400–4800 g·mol^{−1} were used in this study.

Typical Procedure for Synthesis of Living PIB-*b*-THF_{*n*}⁺ Chains

Living PIB-THF_{*n*}⁺ chains were synthesized by ring-opening reaction of THF using PIB-Br/ AgClO_4 as an initiating system, as described previously.^[35,38,39] In brief, 0.69 g of PIB-Br (M_n =2400 g·mol^{−1}) and 60 mg of AgClO_4 were added to THF/DCM (30 mL/30 mL) mixed solution at 0 °C in N_2 atmosphere. After stirring for 0.5 h, a small part of the reaction mixture containing

the living PIB-*b*-THF_{*n*}⁺ chains were taken out and quenched with water for parallel characterization of chemical structure and composition. And the remaining part of reaction solution was used to further prepare the graft copolymers.

Typical Procedure for Synthesis of HPC-*g*-(THF_{*n*}-PIB) Graft Copolymers via Nucleophilic Substitution

The HPC-*g*-(THF_{*n*}-PIB) graft copolymers were prepared via nucleophilic substitution (grafting onto method) established by us earlier.^[35,38,39] 0.5 g of HPC with 1.20 mmol of AGU was added to 20 mL of fresh DCM under stirring to form clear homogeneous solution at 0 °C. Then, different volumes of living PIB-*b*-THF_{*n*}⁺ chains solutions above were added into the HPC solution to complete the nucleophilic substitution reaction. After stirring for 5 h, the reaction solution was dialyzed in THF through regenerated cellulose membranes for a week to remove the possible unreacted PIB-*b*-THF_{*n*} chains. Finally, the reaction solution was precipitated in *n*-hexane to obtain the resulting HPC-*g*-(THF_{*n*}-PIB) graft copolymers, followed by drying to determine the final weight of HPC-*g*-(THF_{*n*}-PIB) graft copolymers.

Characterization

Gel permeation chromatography (GPC)

The number-average molecular weight (M_n), weight-average molecular weights (M_w) and molecular weight distribution (MWD, M_w/M_n) of PIB-Cl were determined by GPC (Waters 1515), using THF as a solvent with a flow rate of 1.0 mL·min^{−1} and polystyrene (PS) as a standard.

Nuclear magnetic resonance (NMR)

¹H-NMR spectra of PIB-Cl, PIB-Br and HPC-*g*-(THF_{*n*}-PIB) graft copolymers were recorded by Bruker AV400 in CDCl_3 , using tetramethylsilane (TMS) as an internal standard.

As described in our earlier work,^[39] the number of THF connecting units (n_{THF}) between HPC backbone and PIB branch was calculated by ¹H-NMR characterization according to Eq. (1):

$$n_{\text{THF}} = \frac{A_{1.6}/4}{A_{1.1}/6} \times \frac{M_{n,\text{PIB}}}{M_{\text{IB}}} \quad (1)$$

where $A_{1.6}$ refers to the integral value of methylene groups at 1.6 ppm belonging to THF units between HPC backbone and PIB branches and $A_{1.1}$ is the integral value of methyl groups at 1.1 ppm in PIB branches.

Based on our earlier work,^[10,40] the average grafting number (G_N) of PIB branches in HPC-*g*-(THF_{*n*}-PIB) graft copolymers could be calculated by the molar ratio of PIB branches to per 1000 AGU of HPC backbone according to Eq. (2):

$$G_N = \frac{m_{\text{PIB}}}{M_{n,\text{PIB}} \times N_{\text{AGU}}} \times 1000 \quad (2)$$

where m_{PIB} stands for the total weight of PIB branches grafted onto HPC backbone, N_{AGU} stands for the total mole of AGU in 0.5 g of HPC. Herein, N_{AGU} was determined to be 1.20 mmol, as described previously.^[40] The as-prepared graft copolymer was denoted as HPC- g_{G_N} -(THF_{*n*}-PIB) _{M_n}).

Fourier transform infrared spectroscopy (FTIR)

FTIR spectra (4000–400 cm^{−1} region) of PIB-Cl, PIB-Br and HPC-*g*-(THF_{*n*}-PIB) graft copolymers were recorded by Thermo Fisher Scientific Nicolet 6700 infrared spectrometer. The related sample solutions (12.0 mg·mL^{−1} in THF) were dropped on potassium bromide (KBr) tablet for FTIR measurement after

solvent evaporation.

Transmission electron microscopy (TEM)

The micromorphology of HPC-*g*-(THF_{*n*}-PIB) graft copolymers was observed by TEM Japan Hitachi HT-7700. 10 μL of sample solutions (0.5 $\text{mg}\cdot\text{mL}^{-1}$ in THF) were dropped onto a carbon-coated copper grid. The TEM samples were annealed at 50 $^{\circ}\text{C}$ for 5 h after solvent evaporation, and then dyed with RuO_4 for 20 min.

High resolution transmission electron microscopy (HR-TEM)

The micromorphology of HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposites was observed by HR-TEM JEOL JEM-3010. 10 μL of supernatant liquor related sample solutions (0.5 $\text{mg}\cdot\text{mL}^{-1}$ in THF) were dropped onto a carbon-coated copper grid and dried for further observation.

X-ray photoelectron spectroscopy (XPS)

XPS characterization of HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposite was performed on a Thermo Fisher Scientific USA ESCALAB 250.

Thermal gravimetric analysis (TGA)

TGA measurement of HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposite powder (5.0–10.0 mg) was performed with a TA Instrument Q50 (with a scan rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$, 25–600 $^{\circ}\text{C}$, air atmosphere). $W_{\text{Ag,TGA}}$ refers to the Ag content measured by TGA analysis (the final percentage of residues at 600 $^{\circ}\text{C}$). $W_{\text{Ag,theo}}$ refers to the theoretical data of Ag content, which could be calculated according to our earlier work.^[38]

Atom force microscopy (AFM)

The surface micromorphology of HPC-*g*-(THF₅-PIB) films was observed by Bruker-Fastscan ultrafast DI AFM with tapping mode. The related sample solutions (10 μL , 0.5 $\text{mg}\cdot\text{mL}^{-1}$ in THF) were dropped onto a silicon slice and treated by spinning coater to form a film. Then the samples were annealed at 50 $^{\circ}\text{C}$ for 5 h for further observation.

Water contact angle (WCA) measurement

WCA measurements on HPC-*g*-(THF_{*n*}-PIB) graft copolymer films were carried out by JC2000D2M (Shanghai Zhongchen Digital Technology Equipment Co., Ltd.). The related sample solutions (10.0 $\text{mg}\cdot\text{mL}^{-1}$ in THF) were dropped onto glass slide to form a film after solvent evaporation. The WCA values were measured parallelly at three different positions.

Nonspecific protein adsorption test

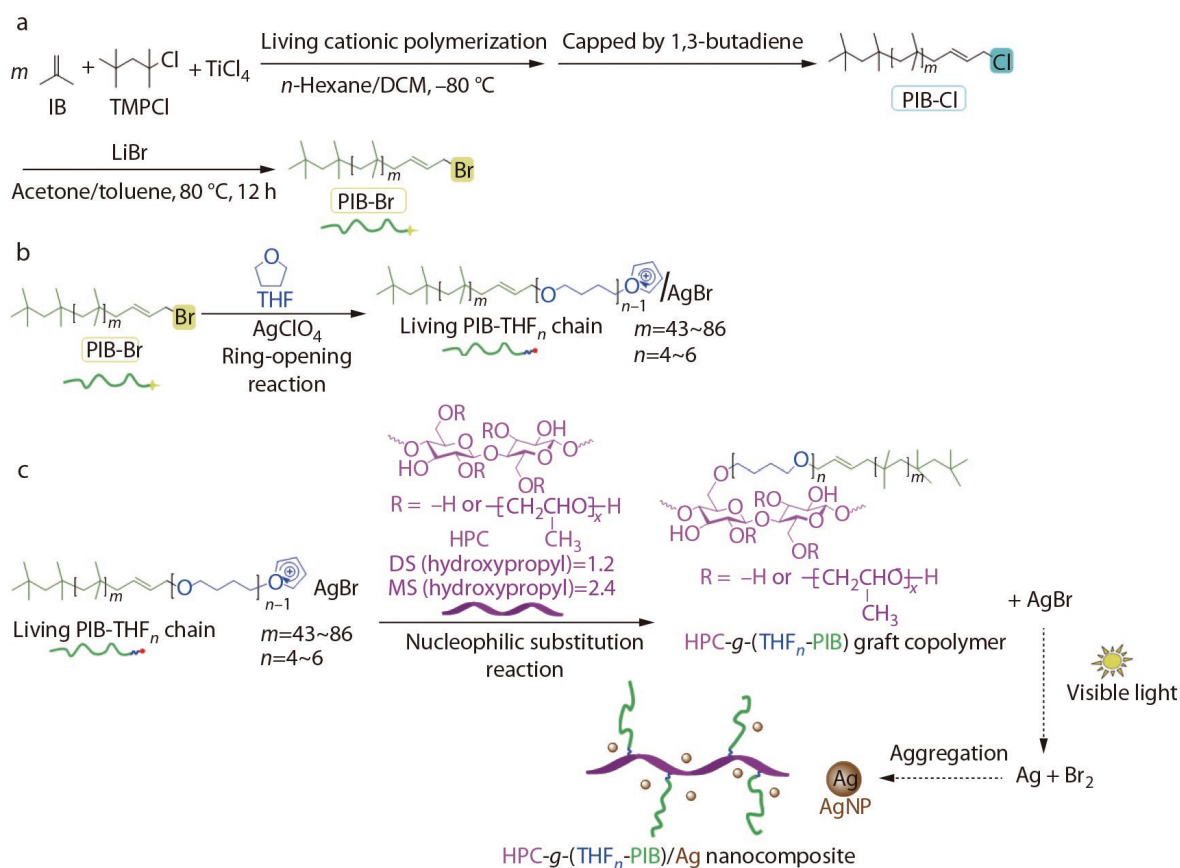
The detailed measurement procedure was described in our earlier work.^[35,38,39]

Antibacterial activity

The antibacterial properties of HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposites were tested by live/dead staining, using the reported method.^[41]

RESULTS AND DISCUSSION

The synthetic route for preparing the PIB-Br macroinitiator by halogen exchange reaction and HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposite by nucleophilic substitution reaction is given in



Scheme 1 Synthetic routes to (a) PIB-Cl by living cationic polymerization and PIB-Br macroinitiator by halogen exchange reaction, (b) living PIB-THF_{*n*}⁺ chains with oxonium ion end group and (c) HPC-*g*-(THF_{*n*}-PIB)/Ag nanocomposite by nucleophile substitution reaction.

Scheme 1. To improve the initiating efficiency of PIB macro-initiator, PIB-Cl with allyl chloride end groups was converted to PIB-Br with allyl bromide end groups. Then, PIB-Br was used conveniently as a macroinitiator to prepare oxonium ion-contained living PIB-THF_n⁺ chains, which were further grafted onto HPC backbone *via* nucleophilic substitution reaction of living PIB-THF_n⁺ chains with hydroxyl side groups in HPC to construct hydroxypropyl cellulose-*g*-(tetrahydrofuran_n-polyisobutylene) (HPC-*g*-(THF_n-PIB)). The HPC-*g*-(THF_n-PIB) graft copolymers with various average grafting numbers (G_N) and lengths of PIB branches could be achieved by using PIB-Br macroinitiators with different M_n 's and by changing the molar ratio of living PIB-THF_n⁺ chains to -OH side groups. Moreover, AgNPs were *in situ* generated from AgBr in the presence of the AgClO₄ coinitiator under visible light and well-dispersed in HPC-*g*-(THF_n-PIB) graft copolymer matrix to produce HPC-*g*-(THF_n-PIB)/Ag nanocomposite.

Preparation of PIB-Br Macroinitiator

A series of polyisobutylene-allyl-Cl (PIB-Cl) with allyl-Cl end groups and different M_n 's could be successfully synthesized by living cationic polymerization of isobutylene (IB) using TiCl₄/TMPCl as an initiating system, followed by quantitative termination reaction according to the earlier work.^[16,17,21–27] PIB-Br with M_n from 2400 g·mol⁻¹ to 4800 g·mol⁻¹ ($M_w/M_n=1.27–1.49$) was further prepared by the reaction of PIB-Cl with LiBr through halogen exchange reaction. ¹H-NMR spectra of PIB_{3.7k}-Cl and PIB_{3.7k}-Br (Fig. S1 in the electronic supplementary information, ESI) show that the new characteristic peaks appeared at $\delta=5.69$ and 3.98 ppm attributed to the methylene protons and methine proton in the allyl bromide group of PIB_{3.7k}-Br and the characteristic peaks at $\delta=5.61$ and 4.06 ppm belonging to the allyl chloride group of PIB_{3.7k}-Cl completely disappeared, which reveals that the PIB-Br was successfully synthesized.

Preparation of Living PIB⁺ Chains Carrying Short THF Unit Connection with Oxonium Ion

PIB-Br was employed as a macroinitiator to prepare living PIB⁺ chains carrying short THF connection units (4–6 units) with oxonium ion at chain-end by ring-opening reaction of THF in the presence of AgClO₄ coinitiator at 0 °C. The living polymer chains with oxonium ion end groups were terminated with model molecule (water) for confirmation of nucleophilic substitution reaction and for characterization of the terminal groups. It can be seen from Fig. S2 (in ESI) that new bands appear at 3446 and 1114 cm⁻¹, which are attributed to terminated -OH groups and C—O—C bond in the PIB_{3.7k}-THF_n-OH, respectively. It is proved by FTIR analysis that the hydroxyl group-terminated PIB could be successfully synthesized *via* nucleophilic substitution reaction with H₂O end-capping agent. The ¹H-NMR spectra in Fig. 1 show that new signals appeared at 1.6 (peak f) and 3.4 ppm (peak e) belonging to the two middle methylene groups and the methylene groups next to oxygen atom in the short THF connection units, respectively. And signal d at 3.63 ppm is attributed to the methylene group between allyl group and oxygen atom, while the characteristic signals at $\delta=4.0$ ppm attributed to the methylene group between allyl group and bromine atom completely disappeared, suggesting that the extremely high reaction efficiency could be obtained and PIB-THF_n⁺ living

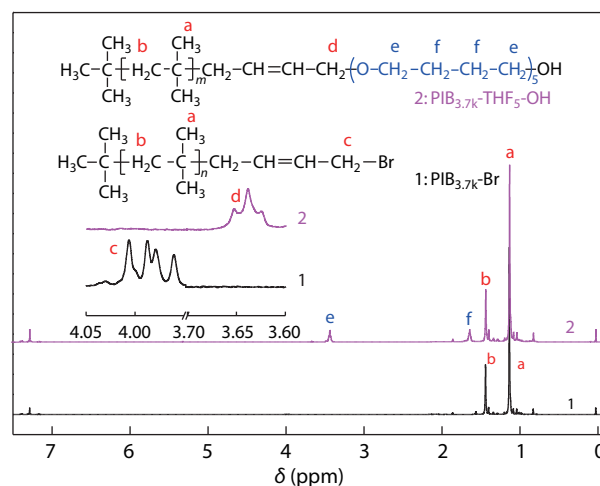


Fig. 1 Typical ¹H-NMR spectra of PIB_{3.7k}-Br and PIB_{3.7k}-THF₅-OH.

chains having *ca.* 100% of oxonium ions at chain ends could be synthesized. The average number (n) of connecting THF structural units in PIB-THF_n⁺ was calculated to be 4–6 according to NMR characterization, *i.e.* the average number of the connecting THF units was set at 5 in this work. On the other hand, Ag was generated by decomposition of AgBr under visible light during this reaction, and Ag nanoparticles were formed *via* aggregation.

In Situ Preparation of HPC-*g*-(THF₅-PIB)/Ag Nanocomposite

The successful synthesis of hydroxyl group-terminated PIB *via* nucleophile substitution reaction with H₂O provides an effective way for preparation of HPC-*g*-(THF₅-PIB) graft copolymers using the similar nucleophile substitution reaction. The average grafting efficiency (G_e) of living PIB-*b*-THF₅⁺ chains grafted onto the HPC backbone could reach *ca.* 100%, and briefly stated as follows. The oxonium ion-terminated living PIB-THF₅⁺ chain as a strong electrophile could efficiently reacted with a protic compound (nucleophile), *e.g.* HPC with lots of -OH side groups, which followed the S_N1 mechanism. On the other hand, the dialysate from reaction solution of HPC-*g*-(THF₅-PIB) graft copolymer was examined by FTIR analysis, indicating that there was no characteristic peak for C—O—C band at about 1100 cm⁻¹. These results are also in agreement with our earlier reports.^[10,39] The average grafting numbers (G_N) of PIB branches in the HPC-*g*-(THF₅-PIB) were determined to be 6 to 23 per 1000 AGU in HPC backbone with gravimetric method (based on Eq. 2).

The chemical structure of the as-prepared HPC-*g*-(THF₅-PIB) graft copolymers was first characterized by FTIR. The FTIR spectra of HPC and HPC-*g*₂₂-(THF₅-PIB_{4.8k}) graft copolymer are presented in Fig. 2(a). For HPC-*g*₂₂-(THF₅-PIB_{4.8k}) graft copolymer, the presence of the short THF connection units between HPC backbone and PIB branches was verified by C—O—C band stretching at about 1088 cm⁻¹. The band at 3438 cm⁻¹ ascribed to -OH group decreased and bands from 2980 cm⁻¹ to 2850 cm⁻¹ attributed to C—H vibration and 1338, 1367 cm⁻¹ attributed to -C(CH₃)₂- group from PIB branches increased with increasing length of PIB branches and G_N , compared to HPC. The FTIR results preliminarily verify the suc-

successful preparation of HPC- g_{22} -(THF₅-PIB_{4.8k}) graft copolymers.

To further confirm the successful preparation of the HPC- g -(THF₅-PIB) graft copolymers, HPC- g_{22} -(THF₅-PIB_{4.8k}) graft copolymer was selected for structural characterization by ¹H-NMR spectroscopy, as shown in Fig. 2(b). The characteristic chemical shifts of $\delta=1.4$ ppm (peak a) and $\delta=1.1$ ppm (peak c) were assigned to the proton of methylene and methyl in PIB repeat unit, respectively. The series of proton signals from 2.9 ppm to 4.3 ppm were ascribed to the inner proton of methylene and methine on AGU and hydroxypropyl. The proton characteristic peak of methyl end group on hydroxypropyl (peak d) totally overlapped with that of methyl proton in PIB repeat unit at 1.1 ppm (peak c). Peak at 1.6 ppm (peak b) belongs to the protons of two middle methylene groups in the short THF connection units between HPC backbone and PIB branches.

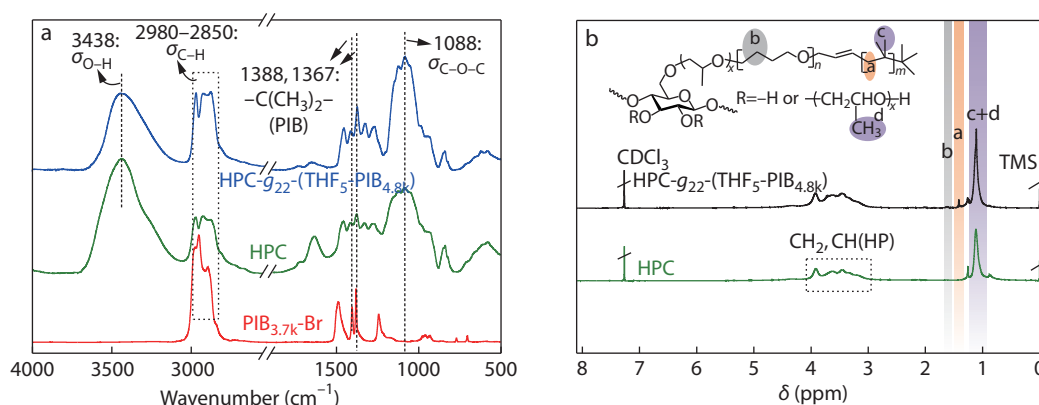


Fig. 2 (a) Typical FTIR spectra of PIB-Br, HPC and resultant HPC- g_{22} -(THF₅-PIB_{4.8k}) graft copolymer; (b) Typical ¹H-NMR spectra of HPC and the obtained HPC- g_{22} -(THF₅-PIB_{4.8k}) graft copolymer.

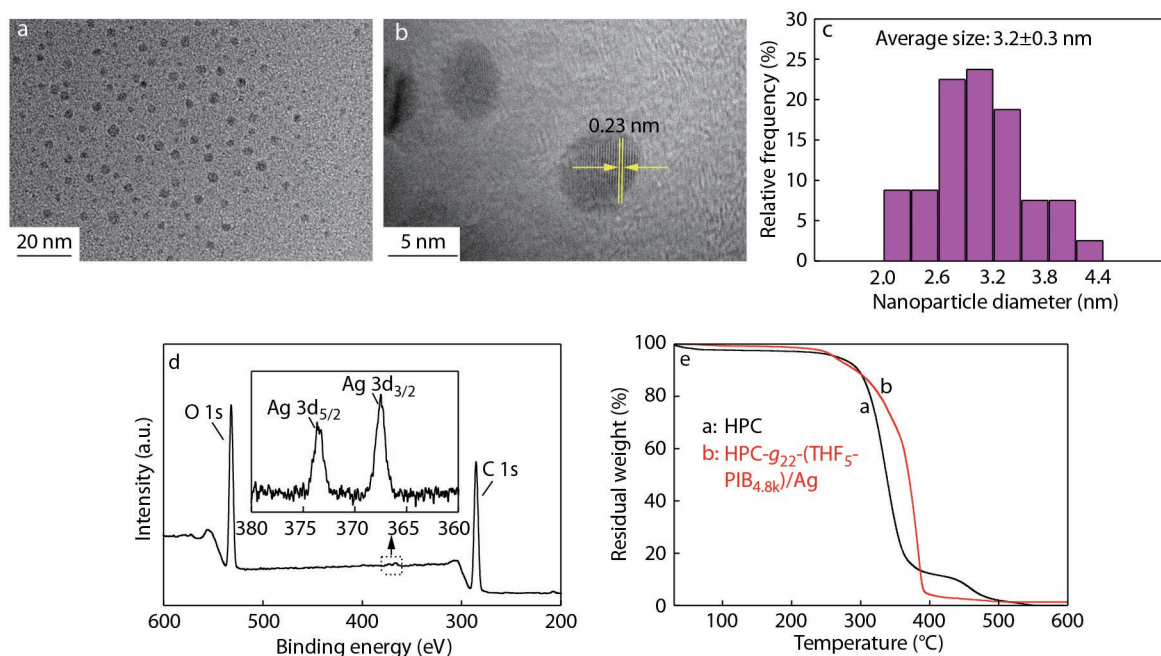


Fig. 3 (a, b) HR-TEM images (scale bar = 20 nm (a) and 5 nm (b)) and (c) size distribution of AgNPs in HPC- g_{22} -(THF₅-PIB_{4.8k}) graft copolymer, as evaluated from 80 measurements; (d) Typical XPS survey spectra and Ag 3d spectra of AgNPs in HPC- g_{22} -(THF₅-PIB_{4.8k})/Ag nanocomposite; (e) TGA curves of HPC and HPC- g_{22} -(THF₅-PIB_{4.8k})/Ag nanocomposite in air atmosphere at 10 °C·min⁻¹.

The TGA analysis under air atmosphere was further employed to measure the mass content of AgNPs as well as thermal properties of HPC-*g*-(THF₅-PIB)/Ag nanocomposites. The TGA curves of HPC and representative HPC-*g*₂₂-(THF₅-PIB_{4.8k})/Ag nanocomposites are shown in Fig. 3(e). It can be seen that for HPC-*g*₂₂-(THF₅-PIB_{4.8k})/Ag nanocomposite, a residue at 600 °C was observed ascribed to the AgNPs, while the HPC exhibited nearly 0% char residue under the same conditions. And the total mass percentage of Ag in the HPC-*g*-(THF₅-PIB)/Ag nanocomposites determined by TGA ranges from 0.7 wt% to 1.8 wt%. The mass content of Ag determined by TGA ($W_{\text{Ag,TGA}}$) was very close to that by theoretical calculation ($W_{\text{Ag,theo}}$) (Fig. S3 in ESI). Additionally, it can also be clearly observed from Fig. 3(e) that two steps of weight loss occur in TGA curves of HPC-*g*-(THF₅-PIB)/Ag nanocomposites. The first step of weight loss took place from 300 °C to 350 °C belonging to the HPC backbones and the second step of weight loss took place from 350 °C to 450 °C was attributed to the decomposition of PIB branches. Interestingly, the thermal property of HPC-*g*-(THF₅-PIB) graft copolymer was enhanced compared to that of HPC, which might results from the branched polymeric structures that PIB branches were grafted onto HPC backbone.

The above-mentioned results indicate that the HPC-*g*-(THF₅-PIB)/Ag nanocomposites have been successfully prepared by green method with highly efficient and silver atom economy.

Micromorphology of HPC-*g*-(THF₅-PIB) Graft Copolymers

The branched polymeric HPC-*g*-(THF₅-PIB) graft copolymers could form obvious phase-separation morphologies due to the incompatibility between the hydrophobic soft nonpolar PIB branches and the hydrophilic hard polar HPC backbone. The phase-separation morphologies of HPC-*g*-(THF₅-PIB) graft copolymers with different PIB branch lengths and G_N values were observed by TEM, as given in Fig. 4. The HPC backbone

domains with —OH side groups in HPC-*g*-(THF₅-PIB) graft copolymer are prioritized to be oxidized by RuO₄ to produce highly scattering RuO₂. The dark regions represent HPC backbone domains while the bright areas represent PIB branch domains. For TEM images of HPC-*g*-(THF₅-PIB) graft copolymers, all the samples (Figs. 4a–4c) could form nano-sized phase-separation morphology compared to a blank copper grid (Fig. 4d). Besides, the HPC-*g*-(THF₅-PIB) graft copolymers with different PIB branch lengths and G_N values (the HPC mass contents of HPC-*g*-(THF₅-PIB) graft copolymers are listed in Table 1) could form different phase-separation sized morphologies.

Taking HPC and HPC-*g*₁₂-(THF₅-PIB_{3.7k}) graft copolymer as examples, we prepared the electrospinning HPC solution with a concentration of 15 mg·mL^{−1} and HPC-*g*₁₂-(THF₅-PIB_{3.7k}) solutions with concentrations of 10 and 15 mg·mL^{−1} in THF/toluene (8/2, V/V) mixed solvent and then used electrospinning method for treating these solutions to prepare the polymer films. The corresponding SEM images are presented in Fig. 5. It can be seen that HPC sample forms the relatively spherical adhesive particles, whereas all the film samples of HPC-*g*₁₂-(THF₅-PIB_{3.7k}) graft copolymers form the irregularly adhesive particles rather than electrospun nanofibers and the particle size increases with increasing polymer concentration. The reason might be that the branched polymeric structure of HPC-*g*₁₂-(THF₅-PIB_{3.7k}) would be adverse to fibrillating procedure. On the other hand, the incompatibility between hard hydrophilic HPC backbone and soft hydrophobic PIB branches

Table 1 The HPC mass contents of HPC-*g*-(THF₅-PIB) graft copolymers.

Sample	HPC mass contents (%)
HPC- <i>g</i> ₂₂ -(THF ₅ -PIB _{2.4k})	88.8
HPC- <i>g</i> ₂₃ -(THF ₅ -PIB _{3.7k})	83.0
HPC- <i>g</i> ₁₁ -(THF ₅ -PIB _{4.8k})	88.8
HPC- <i>g</i> ₂₂ -(THF ₅ -PIB _{4.8k})	79.8

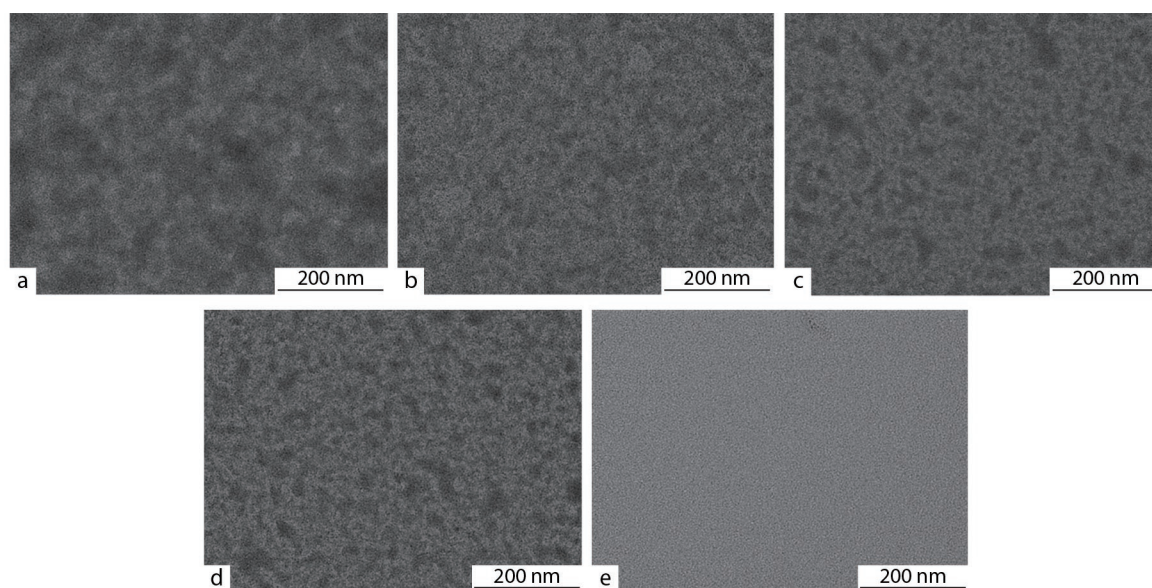


Fig. 4 TEM images of the (a) HPC-*g*₂₂-(THF₅-PIB_{2.4k}), (b) HPC-*g*₂₃-(THF₅-PIB_{3.7k}), (c) HPC-*g*₁₁-(THF₅-PIB_{4.8k}), (d) HPC-*g*₂₂-(THF₅-PIB_{4.8k}) graft copolymer dyed with RuO₄ and (e) blank carbon-coated copper grid.

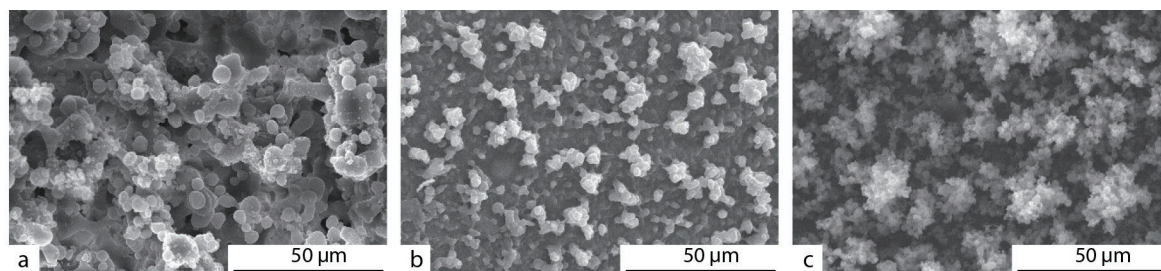


Fig. 5 SEM images of (a) HPC (15 mg·mL⁻¹) and HPC-*g*₁₂-(THF₅-PIB_{3.7k}) graft copolymer with different concentrations of (b) 15 mg·mL⁻¹, (c) 10 mg·mL⁻¹ in THF/toluene (8/2, V/V) mixed solvent by electrospinning.

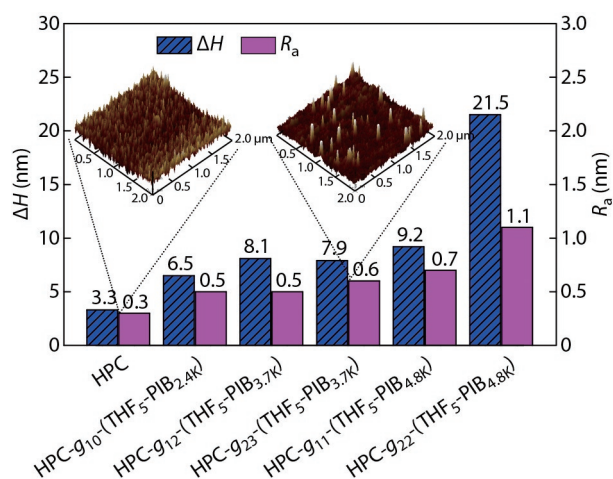


Fig. 6 Height difference (ΔH) and average surface roughness (R_a) of the corresponding HPC and HPC-*g*-(THF₅-PIB) graft copolymers (inset: the AFM height images of HPC (left) and HPC-*g*₂₃-(THF₅-PIB_{3.7k}) graft copolymer (right)).

tend forming split phase after electrospinning, further forming particles by self-assembly to decrease the interface energy.

The surface morphology of HPC-*g*-(THF₅-PIB) graft copolymers influenced by G_N and PIB length was further studied by AFM after annealing at 50 °C for 5 h and the corresponding AFM height images and diagram for the average surface roughness (R_a) and height differences (ΔH) are given in Fig. 6. The HPC film surface was relatively smooth and R_a value was just 0.3 nm. The ΔH values gradually increased from 6.5 nm to 9.2 nm and the R_a values correspondingly increased from 0.5 nm to 0.7 nm with increasing PIB length (M_n) from 2400 g·mol⁻¹ to 4800 g·mol⁻¹ at almost the same G_N (Fig. 6). For the film surfaces of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymers, the ΔH values increased from 9.2 nm to 21.5 nm and the R_a values increased from 0.7 nm to 1.1 nm with increasing G_N from 11 to 22 (Fig. 6). The changes on HPC-*g*-(THF₅-PIB) graft copolymer film surface might be caused by the random coils of PIB segments, which is similar to the results in our previous work.^[39]

Hydrophilicity/Hydrophobicity of HPC-*g*-(THF₅-PIB) Graft Copolymer Films

The hydrophilicity/hydrophobicity of HPC-*g*-(THF₅-PIB) amphiphilic graft copolymers was characterized by static water contact angle (WCA) measurement, and the relevant data are shown in Fig. 7. The WCA of HPC film was determined to be

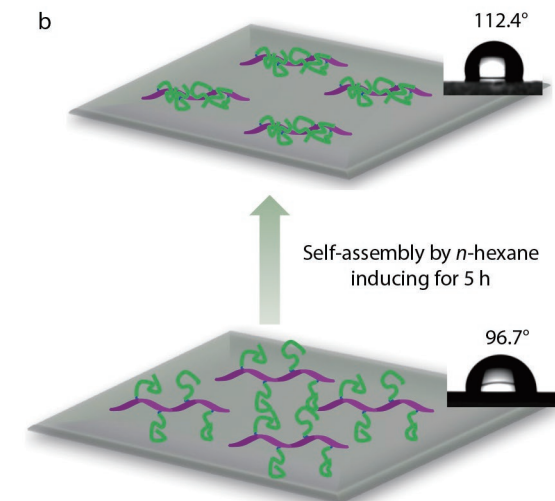
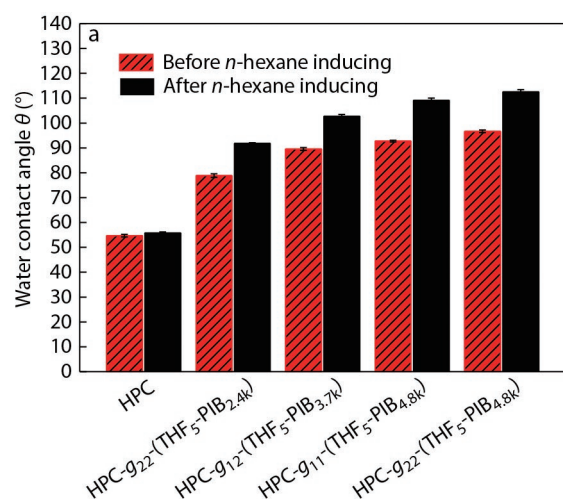


Fig. 7 (a) Water contact angles on film surfaces of HPC and HPC-*g*-(THF₅-PIB) graft copolymers with different length of PIB branches and G_N before and after *n*-hexane inducing. (b) Schematic illustration of self-assembly behavior of HPC-*g*-(THF₅-PIB) graft copolymer after *n*-hexane inducing (inset: the WCAs of HPC-*g*₂₂-(THF₅-PIB_{4.8k}) film before and after self-assembly by inducing in *n*-hexane).

54.1°, while the WCAs of HPC-*g*-(THF₅-PIB) graft copolymer films with different PIB branch lengths and G_N values were obviously higher than that of HPC, ranging from 78.1° to 96.7°. These results confirm that the hydrophobicity of HPC-*g*-(THF₅-PIB)

graft copolymers could be enhanced with increasing length of PIB branches and G_N due to the grafted hydrophobic PIB branches. The HPC-*g*-(THF₅-PIB) graft copolymer films were further induced by *n*-hexane since *n*-hexane is poor solvent for HPC backbone and good solvent for PIB branches. It can be seen clearly from Fig. 7(a) that the corresponding WCAs of HPC-*g*-(THF₅-PIB) graft copolymer films increased after inducing in *n*-hexane for 5 h. The larger $M_{n,PIB}$ and G_N in HPC-*g*-(THF₅-PIB) graft copolymers, the more significant increase of WCA. The hydrophobicity of HPC-*g*-(THF₅-PIB) graft copolymers could be increased since the soft hydrophobic nonpolar PIB branches could easily move to the surface of HPC-*g*-(THF₅-PIB) graft copolymer films to enhance their hydrophobicity, as shown in Fig. 7(b). For HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymers, the long PIB branches might tend to form intra-molecular entanglement, which further formed a hydrophobic shell around HPC backbones.

Compared to our previous work about the amphiphilic copolymers of acylated sodium alginate-*g*-(tetrahydrofuran₅-*b*-polyisobutylene)^[38] and chitosan-*g*-polyisobutylene graft copolymers,^[39] we found that obvious phase separation could be formed in these PIB-grafted polysaccharide amphiphilic copolymers due to the incompatibility between hydrophobic soft nonpolar PIB branches and hydrophilic hard polar polysaccharide backbone. Besides, these polysaccharide amphiphilic graft copolymers with hydrophobic soft nonpolar PIB branches show self-assembly behavior after *n*-hexane solvent inducing or annealing, resulting in further enhanced roughness and hydrophobicity on the surface of copolymer films. The films with facilely adjustable hydrophobic property

would be used in biomedical application.^[42]

Anti-protein Adsorption Performance of HPC-*g*-(THF₅-PIB) Graft Copolymer Films

The anti-protein adsorption performance against BSA of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films was studied according to the facilely enhanced surface roughness and hydrophobicity mentioned above. The representative CLSM images (Figs. 8a and 8b) show that the HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films after annealing present more effective anti-protein adsorption performance against BSA, compared to that of PIB-Br macroinitiator film. The detailed fluorescence intensity (Fig. 8c) reveals that the fluorescence intensity of PIB_{3.7k}-Br macroinitiator film is 16.7%, whereas the fluorescence intensity of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films was greatly reduced and decreased from about 2.6% to 1.0% with increasing the length of PIB branches. And the fluorescence intensity of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films further decreased after annealing at 50 °C for 5 h. The above results suggest that the enhanced surface roughness of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films might benefit for the repulsion of BSA since the BSA could not be stably adsorbed in the HPC-*g*-(THF₅-PIB_{4.8k}) film surface. In addition, the enhanced hydrophobic surface of HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer films with WCA of about 110° might also do a favor to suppress the adsorption of BSA.

Antibacterial Properties of HPC-*g*-(THF₅-PIB)/Ag Nanocomposite Against *E. coli* or *S. aureus* Bacteria

It is well known that the AgNP with a size of 1–10 nm is an efficient antibacterial agent due to its large surface area and high interfacial free energy.^[43] As illustrated in Scheme 1,

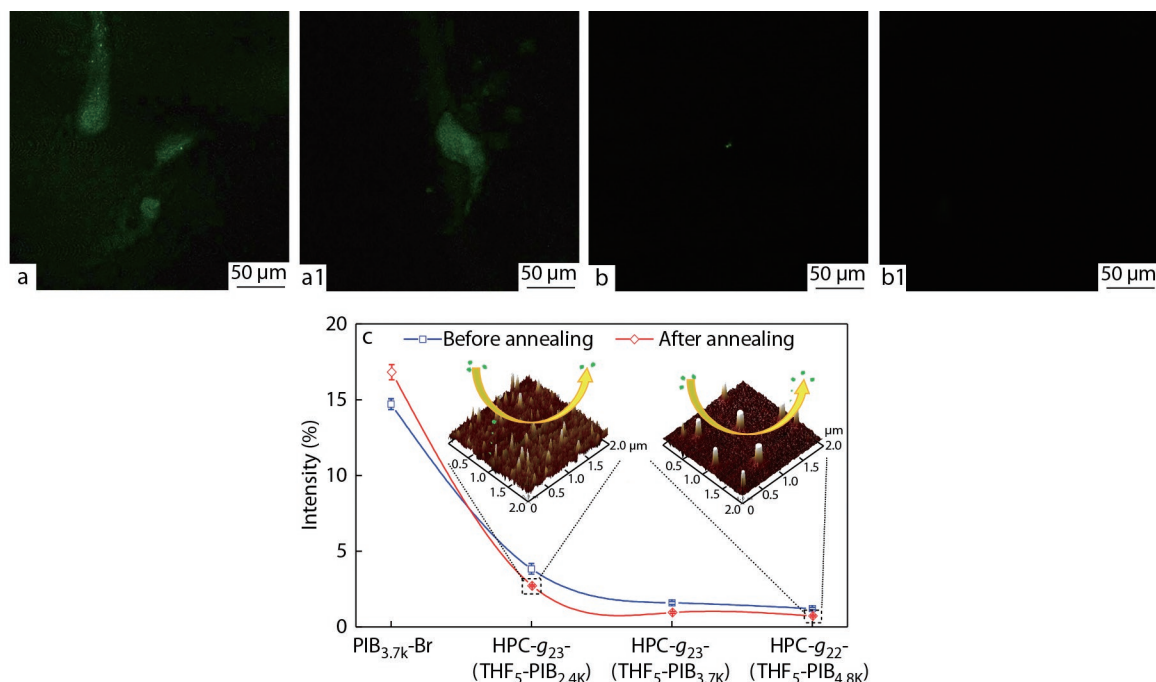


Fig. 8 Representative CLSM images of samples before annealing: (a) HPC-*g*₂₂-(THF₅-*b*-PIB_{2.4k}), (b) HPC-*g*₂₂-(THF₅-PIB_{4.8k}) graft copolymer film and after annealing: (a1) HPC-*g*₂₂-(THF₅-PIB_{2.4k}), (b1) HPC-*g*₂₂-(THF₅-PIB_{4.8k}) graft copolymer film and (c) fluorescence intensity statistics of HPC-*g*-(THF₅-PIB) graft copolymer films with different length of PIB branches and G_N after 2 h incubation with the FITC labeled BSA protein (inset: schematic illustration of possible mechanism for anti-protein adsorption performance of HPC-*g*₂₂-(THF₅-PIB_{2.4k}) and HPC-*g*-(THF₅-PIB_{4.8k}) graft copolymer film surface after annealing at 50 °C for 5 h).

AgClO₄ coinitiator could generate AgBr, *in situ* form AgNPs under visible light, and then be well dispersed in HPC-*g*-(THF₅-PIB) graft copolymer matrix, endowing the HPC-*g*-(THF₅-PIB)/Ag nanocomposite with potential antibacterial property. The typical *E. coli* (Gram-negative bacteria) and *S. aureus* (Gram-positive bacteria) were used to study the antibacterial activities of HPC-*g*-(THF₅-PIB)/Ag nanocomposites with various Ag mass contents. The representative CLSM images and bacteria viability of *E. coli* and *S. aureus* after culturing with HPC-*g*-(THF₅-PIB)/Ag nanocomposites containing various AgNPs mass contents are given in Fig. 9.

For HPC example, both the fluorescence images of stained *E. coli* and *S. aureus* show green color, indicating that the HPC example behaves minimal antibacterial activity. After *E. coli* and *S. aureus* bacteria were incubated with the HPC-*g*-(THF₅-PIB)/Ag nanocomposite with Ag NPs content of 0.7%, some of the bacteria were killed. Most of bacteria could be killed when the AgNPs content in the nanocomposite was 1.8%. These results indicate that the antibacterial activities of HPC-*g*-(THF₅-PIB)/Ag nanocomposites were mainly caused by the *in situ* formed AgNPs. The more the Ag NPs mass content in HPC-*g*-(THF₅-PIB)/Ag nanocomposites, the stronger the antibacterial

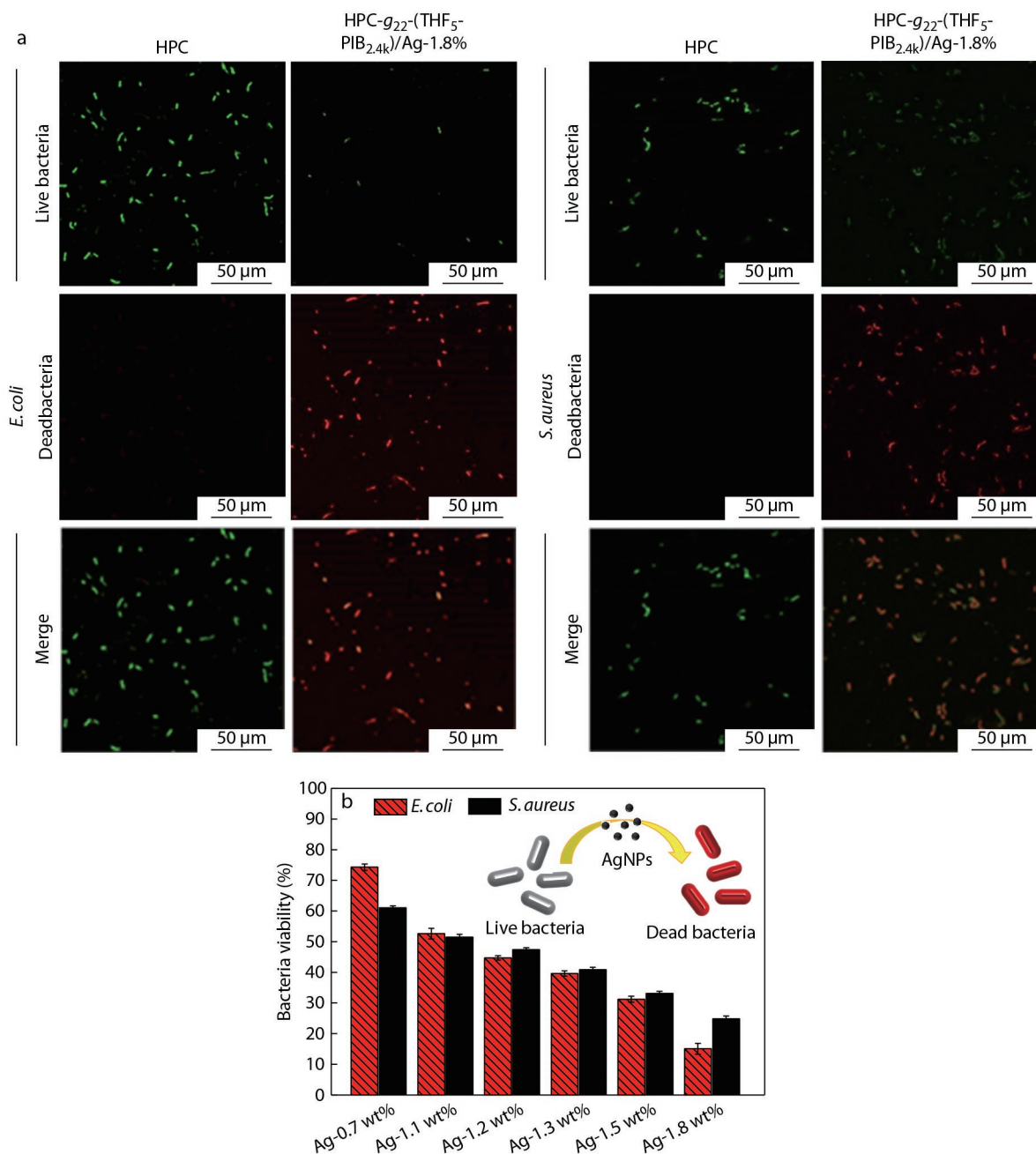


Fig. 9 (a) Representative CLSM images of *E. coli* and *S. aureus* interacted with HPC-*g*-(THF₅-PIB)/Ag nanocomposites after incubating for 6 h; (b) Relationship between bacteria viability of *E. coli* and *S. aureus* and Ag mass content (inset: schematic illustration of antibacterial property of HPC-*g*-(THF₅-PIB)/Ag nanocomposite).

property (Fig. 9b). For the HPC-*g*₂₂-(THF₅-PIB_{2.4k})/Ag-1.8% nanocomposite with Ag content of 1.8%, the bacteria viability of *E. coli* and *S. aureus* were determined as 15.1% and 23.6%, respectively.

CONCLUSIONS

A series of novel HPC-*g*-(THF_{*n*}-PIB) graft copolymers (*n*=4–6) have been successfully prepared via highly efficient nucleophilic substitution reaction of living oxonium ion-contained PIB-THF_{*n*}⁺ chains with hydroxyl groups on the HPC backbone and the grafting efficiency could reach ca. 100%. The PIB-Br macroinitiators with *M_n* from 2400 g·mol^{−1} to 4800 g·mol^{−1} could be synthesized by controlled/living cationic polymerization of isobutylene. The *G_N* of HPC-*g*-(THF_{*n*}-PIB) graft copolymers could be mediated from 6 to 23 per 1000 AGU by changing the molar ratio of living PIB-THF_{*n*}⁺ chains to —OH side groups. HPC-*g*-(THF_{*n*}-PIB) graft copolymers could form obvious nano-sized phase-separation morphology due to the incompatibility between the hydrophobic soft nonpolar PIB branches and the hydrophilic hard polar HPC backbone. Both the average surface roughness (*R_a*) and height difference (ΔH) of HPC-*g*-(THF_{*n*}-PIB) increased with increasing *G_N* and length of PIB branches. And the WCAs of HPC-*g*-(THF_{*n*}-PIB) graft copolymer films after *n*-hexane inducing could be increased, which behaved an enhanced hydrophobicity, following anti-protein adsorption performance against BSA. The *in situ* formed AgNPs with 3.2±0.3 nm (0.7 wt% to 1.8 wt%) under visible light could be well-dispersed in HPC-*g*-(THF₅-PIB) graft copolymer matrix, making the HPC-*g*-(THF₅-PIB)/Ag nanocomposite behave bacteriostasis rate of 84.9% against *E. coli* and 76.4% against *S. aureus*, respectively.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-021-2546-7>.

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