

# Dynamic Ionic Crosslinking Polypropylene-based Elastomers with Excellent Mechanical Properties and Antibacterial Performance

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 Electronic Supplementary Information

**Abstract** Polyolefins with intrinsic antimicrobial properties have attracted significant attention. In this study, various ion-functionalized polyolefins were successfully constructed by incorporating iodine-containing comonomers into a polypropylene backbone, followed by post-functionalization strategies that utilized the conversion reactions of pre-introduced iodine groups. The introduction of ionic groups induced notable changes in both the thermal properties and the melt rheological behavior of the material. The dual crosslinking mechanism based on ionic interactions and polypropylene crystallization significantly enhanced the mechanical strength of the material. In addition, imidazolium-based ionomers exhibit highly effective antimicrobial properties against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus*. Specifically, the P5-CCl<sub>3</sub>CO<sub>2</sub><sup>-</sup> sample achieved a sterilization rate of 99.99% against both bacteria and maintained a high bactericidal efficacy of above 90%, even after continuous supplementation with fresh bacterial solutions for 15 days. Consequently, this polypropylene-based ionomer, which combines excellent mechanical strength with outstanding antimicrobial performance, demonstrates substantial application potential in children's toys, food packaging, and medicine.

**Keywords** Ionomer; Antimicrobial; Polypropylene; Binding energy

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## INTRODUCTION

Bacterial infections are the leading cause of death worldwide and have been a threat to human health and social development.<sup>[1–4]</sup> Antibiotics have been substantially developed to eliminate or neutralize bacteria, but the widespread and injudicious use of antibiotics has led to the emergence of antimicrobial-resistant microorganisms, inducing the aggravation of bacterial infections.<sup>[5–7]</sup> At the current rate of bacterial resistance, each year ten million people will be infected with drug-resistant bacteria and die by 2050, and the resulting economic losses would far exceed the cost of treatment for AIDS and cancer.<sup>[8,9]</sup> There is an urgent need to develop more broad-spectrum, efficient, durable, and highly selective novel antimicrobial approaches against bacterial pathogens.

Traditional antibacterial agents are mostly prepared based on small molecular compounds such as bacteriophages, antimicrobial peptides, and antimicrobial enzymes, which can easily produce drug resistance and may lead to environmental pollution and toxicity to the human body.<sup>[10,11]</sup> In contrast, antibacterial polymeric materials provide an effective solu-

tion to these issues by promoting antibacterial efficacy and reducing residual toxicity.<sup>[12,13]</sup> As reported, traditional antimicrobial material /surfaces are based on two bactericidal mechanisms: releasing biocides bound to the polymer and contact killing by the antibacterial polymer.<sup>[14–16]</sup> Small molecular biocides easily penetrate the polymer matrix, and such antimicrobial materials do not guarantee long-term durability.<sup>[17]</sup> Generally, the cationic groups of bactericidal polymers strongly interact with negatively charged bacterial cell membranes through electrostatic interactions and selectively disrupt cell membrane integrity and inactivate bacterial enzymes.<sup>[18]</sup> The majority of cationic polymers can achieve efficient broad-spectrum sterilization with the lowest drug resistance, according to the membrane-breaking mechanism.<sup>[19]</sup> Cationic polymers are typical antimicrobial materials that have been extensively studied and used, including quaternary ammonium,<sup>[20–23]</sup> quaternary phosphonium,<sup>[3,24]</sup> guanidinium,<sup>[25–27]</sup> and metal-ion cationic polymers.<sup>[28–30]</sup> Moreover, the counter anion,<sup>[31,32]</sup> hydrophilic/hydrophobic balance,<sup>[33]</sup> alkyl spacer, and length of the pendant alkyl chains also influenced the antibacterial activity.<sup>[34–37]</sup> Therefore, to achieve efficient antibacterial activity and long-lasting bactericidal effects, it is important to study the best way to select suitable ionic groups and polymer structures.

Polyolefins are the most prevalent thermoplastic polymers

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and are widely used in packaging materials, textile fabrics, children's toys, medical supplies, surgical instruments, etc. It has great research value and application prospects for endowing polyolefin materials with antimicrobial performance.<sup>[38]</sup> Cai *et al.* prepared a series of imidazolium-functionalized polyolefins by post-polymerization functionalization routes; the obtained polyethylene materials displayed excellent antibacterial properties and good mechanical properties.<sup>[39]</sup> Zhang *et al.* reported ionic cyclic olefin polymers with different cationic groups that exhibited high light transmittance and excellent antibacterial properties.<sup>[40]</sup> Raggogna *et al.* investigated the synthesis of quaternary phosphine polymers and found that cationic polymers containing quaternary phosphine groups had good antimicrobial activity and that the antimicrobial effect of hydrophilic group substitution was superior to that of hydrophobic group substitution.<sup>[41]</sup> However, the effect of counter anions on antimicrobial properties has rarely been studied. We previously synthesized polyethylene ionomers bearing  $\text{CH}_3\text{SO}_3^-$ ,  $\text{CF}_3\text{SO}_3^-$  and  $\text{Tf}_2\text{N}^-$ , which showed remarkable antibacterial activities.<sup>[42]</sup> The sterilization rates of the three types of ionomers were different, which was consistent with the regularity of the binding energy between the counter anions and cations. Therefore, we intended to further investigate the effect of counter anions on the antimicrobial effect by calculating the binding energies between different counter anions and cations, as well as by testing the antimicrobial properties. Moreover, suitable cations and anions were selected to obtain inexpensive polyolefin materials with excellent antimicrobial effects.

We previously reported that a dimethyl(pyridylamido)-hafnium catalyst can copolymerize propylene with polar monomers, which can catalyze the copolymerization of propylene with higher  $\alpha$ -olefins to obtain elastomers with excellent mechanical properties. To obtain novel polyolefin elastomers with polar groups, propylene was copolymerized with eicosylene (C20) and  $\omega$ -iodoundecene (IUD) catalyzed by a hafnium catalyst. The flexible C20 unit was beneficial for enhancing chain mobility, and the IUD unit had a suitable side chain length, which was easy to synthesize and could be easily post-functionalized. We then synthesized a series of polypropylene-based ionomers bearing various cationic and counter anion groups *via* a reactive polyolefin intermediate approach, which were expected to show not only high mechanical properties but also excellent antibacterial properties. The thermal, mechanical, and antibacterial properties of these materials have been studied in detail.

## EXPERIMENTAL

Synthesis, characterization, and relevant test data should be in-

corporated into and submitted as part of the electronic supplementary information (ESI).

## RESULTS AND DISCUSSION

### The Preparation of the Cationic Functionalized Polypropylene Copolymers

Based on the unique advantages of the hafnium/borate catalytic system and our previous achievements, we designed and synthesized a series of novel PP-based elastomers. The copolymers had high molecular weights, narrow molecular weight distributions (Fig. 1), high comonomer incorporation, high melting temperatures, and low glass transition temperatures (Figs. S1–S7 in ESI). The typical results are summarized in Table 1. According to the literature, the introduction of ionic groups can improve the mechanical and antibacterial properties of materials.<sup>[40,43,44]</sup> Therefore, we prepared four ionomers with different cations *via* nucleophilic substitution reactions, as shown in Scheme 1. The full conversion of these post-functionalization reactions was identified by  $^1\text{H-NMR}$  analysis (Fig. S8 in ESI).

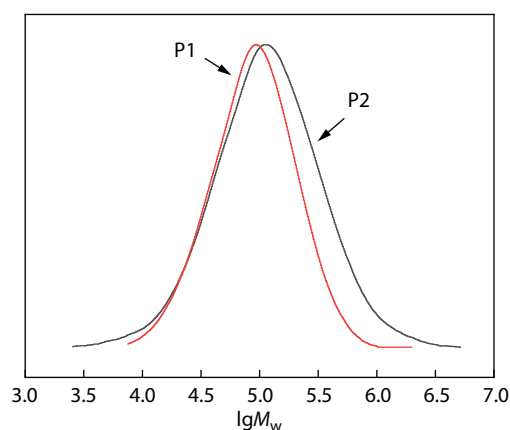


Fig. 1 GPC elution curves of copolymers.

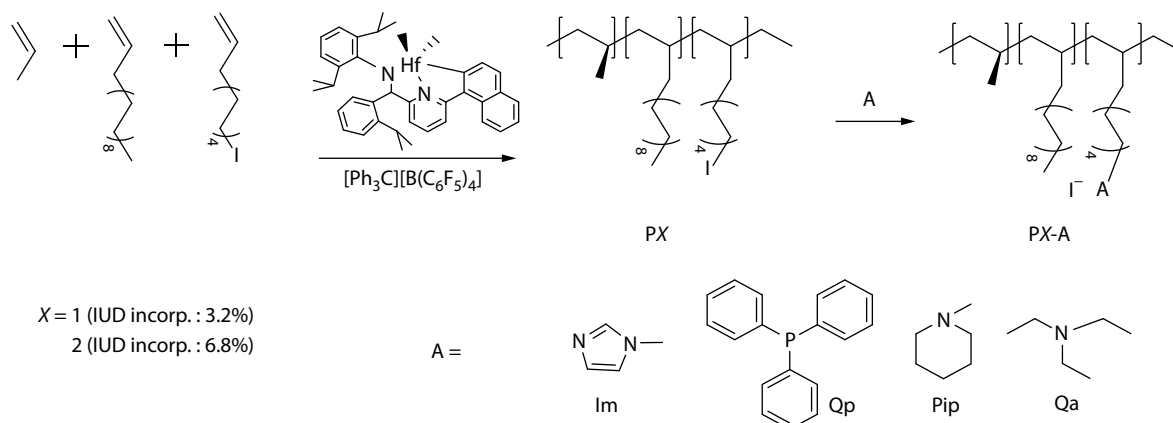
### Thermal Properties of the Cationic Functionalized Polypropylene Copolymers

The thermal properties of the copolymers were significantly altered by the ionic introduction. As shown in the DSC second heating curves (Fig. 2a), P1 exhibited a broad melting peak at approximately 152.6 °C. Following the introduction of ionic groups, a depression in the melting point ( $T_m$ ) was observed, with values decreasing to 152.0 °C for P1-Qp<sup>+</sup>, 152.1 °C for P1-Pip<sup>+</sup>, 152.1 °C for P1-Qa<sup>+</sup>, and 148.3 °C for P1-Im<sup>+</sup>. This trend was consistent with crystallization behavior observed in the cooling curves (Fig. 2b), where the crystallization temperature ( $T_c$ ) of P1

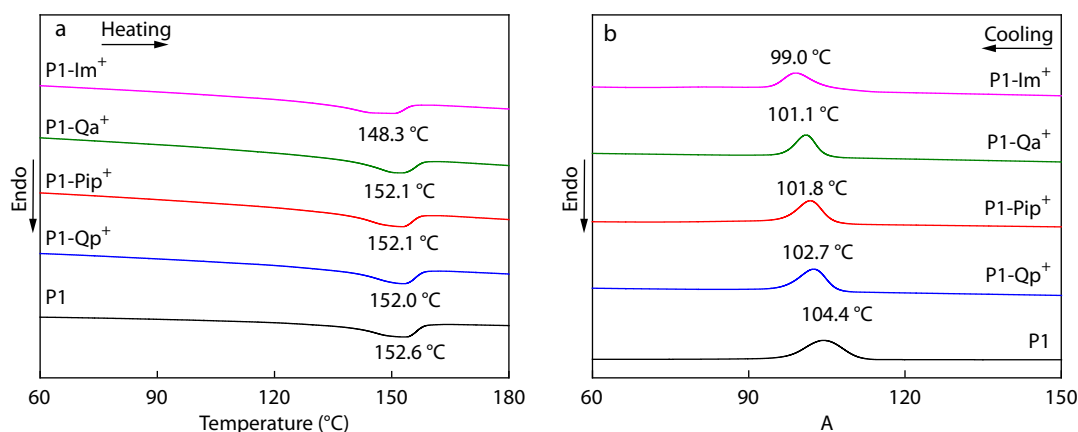
Table 1 Terpolymerization of propylene with IUD and C20. <sup>a</sup>

Code	C20 (mmol)	IUD (mL)	C20 Incorp. <sup>b</sup> (mol%)	IUD Incorp. <sup>b</sup> (mol%)	$M_w$ <sup>d</sup> (kDa)	PDI <sup>d</sup>	$T_m$ <sup>e</sup> (°C)	$\Delta H_m$ (J·g <sup>-1</sup> )	$T_c$ <sup>e</sup> (°C)	$\Delta H_c$ (J·g <sup>-1</sup> )	$T_g$ <sup>f</sup> (°C)
P1	3	1.0	4.5	3.2	132	2.24	152.6	33.1	104.4	54.0	2.3
P2	3	1.5	4.8	6.8	186	2.88	150.3	24.6	96.1	50.8	0.1
P3	4	1.5	7.1	7.9	198	2.85	147.4	24.1	90.7	30.2	-9.7
P4	4	2.0	6.8	9.3	193	2.74	147.1	17.1	88.8	23.5	-12.3
P5	4	2.5	5.1	11.9	173	2.39	145.5	12.2	78.2	19.7	-12.5

<sup>a</sup> Reaction conditions: 10  $\mu\text{mol}$  of catalyst,  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  20  $\mu\text{mol}$ ,  $^i\text{Bu}_3\text{Al}$  1 mmol, propylene 0.1 MPa, toluene solution,  $V_{\text{total}} = 80$  mL, copolymerization at 25 °C for 10 min. <sup>b</sup> Comonomer incorporation (mol%) was determined by  $^{13}\text{C-NMR}$  spectroscopy. <sup>c</sup> Catalytic activity:  $10^6$  g·mol<sup>-1</sup>·h<sup>-1</sup>. <sup>d</sup> Estimated by GPC at 150 °C in 1,2,4-trichlorobenzene versus a polystyrene standard. <sup>e</sup> Determined by DSC at a heating and cooling rate of 10 °C·min<sup>-1</sup>. <sup>f</sup> Determined by DMA.



**Scheme 1** Synthetic route of polypropylene ionomers bearing various cations.



**Fig. 2** DSC thermograms of P1 and ionomers (a) in the second heating process and (b) in the first cooling process.

(104.4 °C) dropped to values as low as 99.0 °C for P1-Im<sup>+</sup>. This phenomenon is primarily attributed to the introduced ionic groups, which restrict the segmental motion of the polymer chains and disrupt their regular arrangement, thereby leading to a reduction in crystallinity. Overall, the intensity of the electrostatic interactions varied with different cation-anion pairs, and the specific nature of these interactions directly influenced the melting and crystallization temperatures of the ionomers.

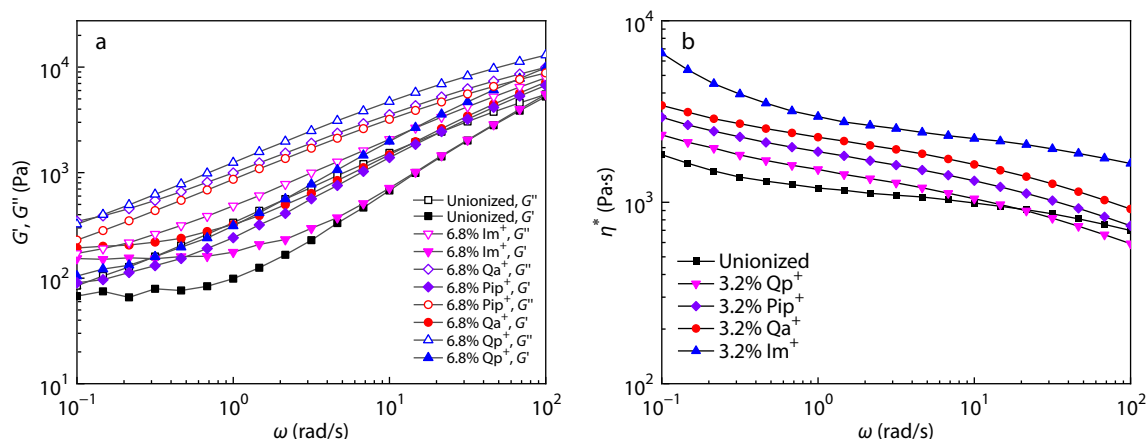
### Melt Rheological Properties of the Cationic Functionalized Polypropylene Copolymers

To investigate the effect of ionic groups on the rheological properties of the copolymer melts, small-amplitude oscillatory shear tests were conducted. As depicted in Figs. 3(a) and 3(b), the black curves correspond to the storage modulus ( $G'$ ), loss modulus ( $G''$ ), and complex viscosity ( $\eta^*$ ) of P1. The incorporation of ionic groups led to notable increases in  $G'$ ,  $G''$ , and  $\eta^*$ , which could be attributed to the combined influence of ionic interactions and chain entanglements on the flow behavior of the ionomers. The strong aggregation tendency of the ionic groups significantly impeded chain mobility, resulting in enhanced melt viscosity. Moreover, the  $\eta^*$  curves of the ionomers displayed marked shear-thinning behavior across the entire frequency range investigated.

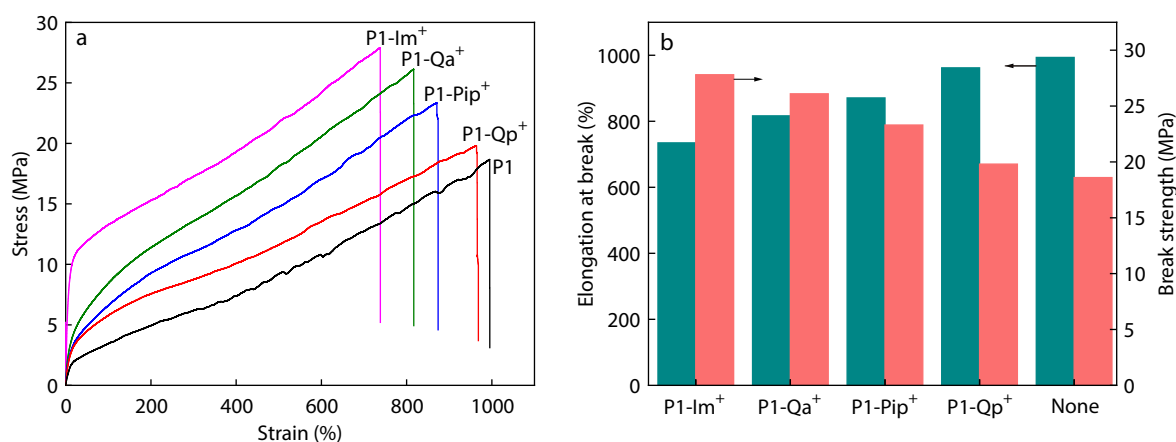
### Mechanical Properties of the Cationic Functionalized Polypropylene Copolymers

Typical stress-strain curves of cationic functionalized polypropylene

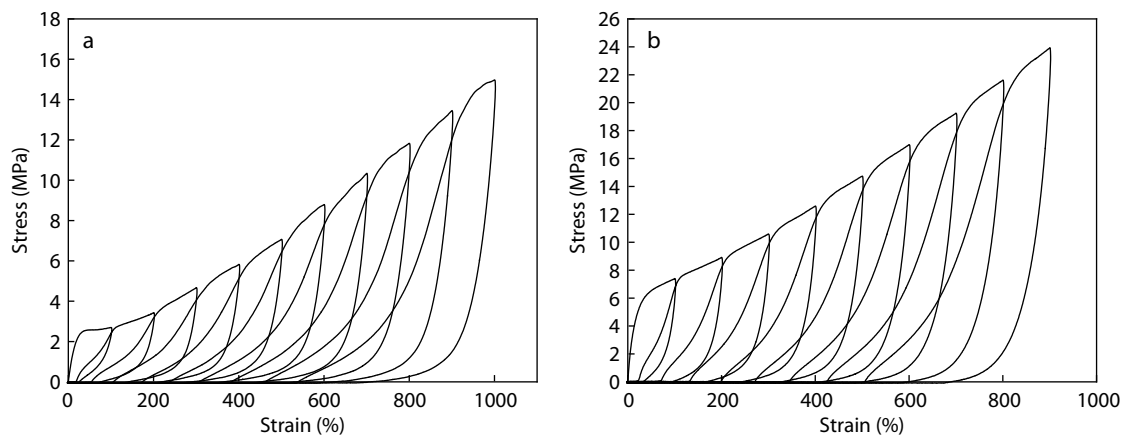
are displayed in Fig. 4(a). Clearly, the copolymer showed typical elastomer characteristics without yield point and the breaking strength of it increased significantly after the introduction of ionic groups, from 18.7 MPa (P1) in the original polymer to 19.8 (P1-Qp<sup>+</sup>), 23.3 (P1-Pip<sup>+</sup>), 26.1 (P1-Qa<sup>+</sup>) and 27.9 MPa (P1-Im<sup>+</sup>), respectively. The toughness of the ionomers was significantly increased. This is because ionic aggregation forms physical cross-links that tightly bind copolymer chains via strong electrostatic interactions.<sup>[43]</sup> The tensile properties of the polypropylene ionomers improved considerably, and the cations affected the tensile properties considerably. For ionomers paired with different cations, the tensile strength increased in the order P1-Qp < P1-Pip < P1-Qa < P1-Im. According to a previous study,<sup>[44]</sup> the breaking strength of the ionomers increased with increasing binding energy between the ion pairs. The binding energy between I<sup>-</sup> and different cations increased in the order Qp<sup>+</sup>I<sup>-</sup> (-56.0 kcal/mol) < Pip<sup>+</sup>I<sup>-</sup> (-75.9 kcal/mol) < Qa<sup>+</sup>I<sup>-</sup> (-78.5 kcal/mol) < Im<sup>+</sup>I<sup>-</sup> (-78.9 kcal/mol), indicating that the Im<sup>+</sup>I<sup>-</sup> interaction was the strongest and the Qp<sup>+</sup>I<sup>-</sup> interaction was the weakest (all calculations were based on the RB3LYP/6-31G(D) calculation method of Gaussian 09 software).<sup>[45,46]</sup> As shown in Fig. 4(b), the physical cross-links formed by stronger ionic aggregation increased the breaking strength while decreasing the elongation at break. Therefore, the mechanical properties of copolymers can be modulated by calculating the binding energy to select the appropriate ion



**Fig. 3** (a) Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of the copolymers and ionomers paired with different counteranions plotted as functions of frequency at 180 °C; (b) Complex viscosity ( $\eta^*$ ) of copolymers and ionomers plotted as functions of frequency for different ion contents at 180 °C.



**Fig. 4** (a) Stress-strain curves of polypropylene ionomers paired with different cations; (b) Break strengths and elongations at break of ionomers and copolymer.

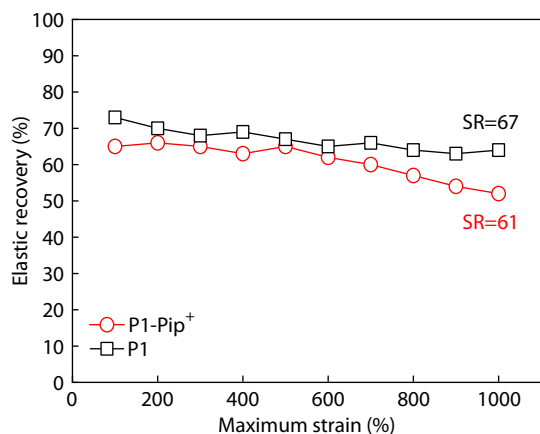


**Fig. 5** Hysteresis curves of (a) P1 and (b) P1-Pip<sup>+</sup>.

pair.

We further investigated the elastic properties of these copolymers and their corresponding ionomers. The samples were extended to a fixed strain and then returned to 0. The formula for the elastic recovery values (SR) was  $SR = 100(e_1 - e_2)/(e_1 - e_3)$ , where  $e_1$  refers to the predefined strain value in each tensile cycle,  $e_2$  is the strain at 0 load after the ap-

plication of strain in the cycle, and  $e_3$  represents the initial strain of each cycle. The hysteresis loops and SR values are shown in Figs. 5 and 6, respectively. The average SR for copolymer P1 was 67%, whereas after the introduction of the ionic groups, the SR decreased to 61%. The reduction in elastic recovery was attributed to two factors: its inherent high crystallinity and the introduction of ionic groups. The ionic



**Fig. 6** Elastic recovery of P1 and P1-Pip<sup>+</sup>.

aggregation created additional physical crosslinks, which further restricted the chain mobility by reducing the free volume, ultimately leading to a decline in elastic recovery.

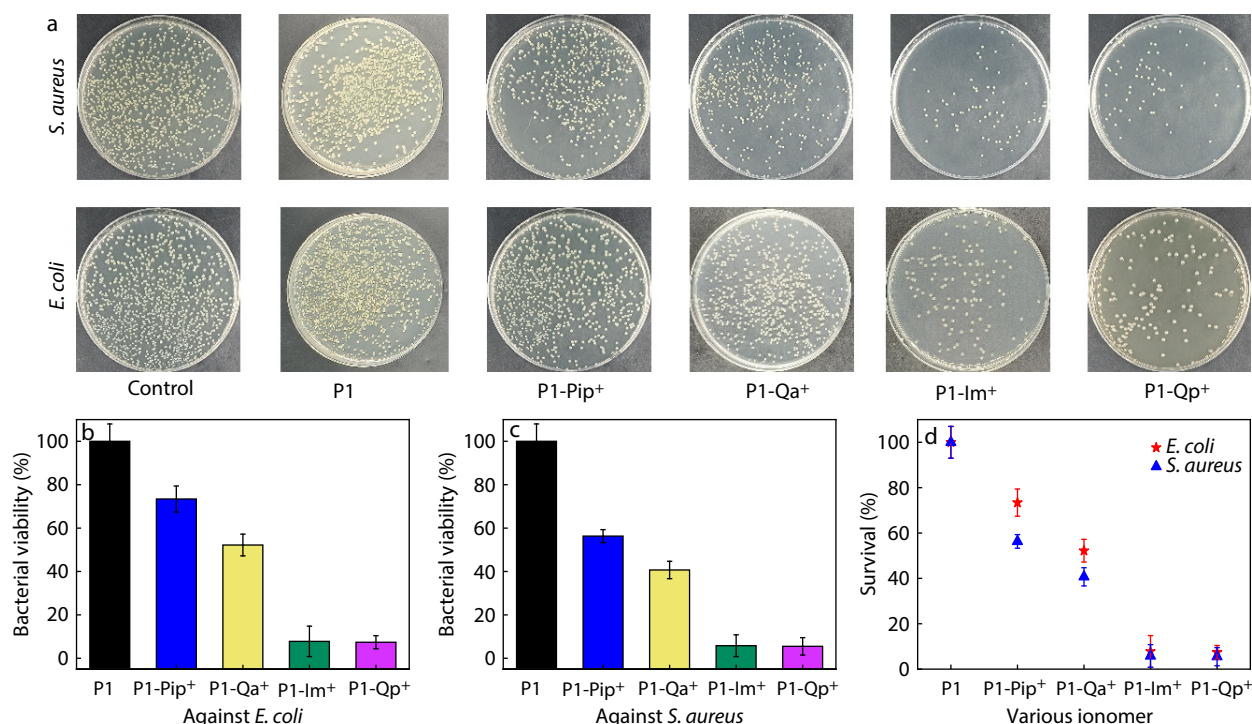
### Antibacterial Properties of the Cationic Functionalized Polypropylene Membranes

*S. aureus* is a common bacterial pathogen that causes a variety of infectious diseases. *E. coli* is a representative gram-negative bacterium that is difficult to kill using antibacterial agents.<sup>[47–50]</sup> The antimicrobial properties of P1, P1-Pip<sup>+</sup>, P1-Qa<sup>+</sup>, P1-Im<sup>+</sup> and P1-Qp<sup>+</sup> were studied against *S. aureus* and *E. coli* were studied. As expected, the nonionized polymer P1 exhibited negligible antimicrobial activity, confirming that the introduction of ionic groups is essential for achieving significant antibacterial efficacy.

The IUD units served as a reaction intermediate with an appropriate side chain length so that the terminal ionic groups could easily migrate to the surface. All the materials showed certain antimicrobial abilities against *S. aureus* and *E. coli* (Figs. 7a–7d). P1-Qp<sup>+</sup> and P1-Im<sup>+</sup> exhibited excellent antibacterial properties among the four materials, and P1-Qa<sup>+</sup> and P1-Pip<sup>+</sup> showed poor antibacterial ability. For P1-Pip<sup>+</sup>, P1-Qa<sup>+</sup>, P1-Im<sup>+</sup> and P1-Qp<sup>+</sup> (the ionic content of 3.2 mol%), the survival rates of *E. coli* were 73.4%, 52.2%, 7.8% and 7.4%, respectively. In comparison, the antimicrobial activities against *S. aureus* followed the order P1-Pip<sup>+</sup>, P1-Qa<sup>+</sup>, P1-Im<sup>+</sup> and P1-Qp<sup>+</sup>; the survival rates of *S. aureus* were 56.3%, 40.7%, 5.8%, and 5.5%, respectively. The four materials were more effective against *S. aureus* than *E. coli*, according to relevant literature reports.<sup>[51,52]</sup> The cell membrane of *S. aureus* carried more negative electricity and was more likely to have electrostatic interactions with the cations of the ionomers. However, triphenylphosphine has a large site resistance owing to conjugated double bonds, and its synthesis is considerably more difficult than that of other materials. Thus, the outstanding antimicrobial properties of Im-based ionomers prompted us to study them.

### The Preparation of Imidazolium-functionalized Polypropylene Copolymers

Imidazolium-functionalized polypropylenes exhibited excellent sterilization effects, favorable mechanical properties, and easy synthesis. However, the effect of counter anions on antimicrobial properties has rarely been investigated. To explore this issue, a series of imidazole-functionalized polypropylene membranes was developed against *S. aureus* and *E. coli* (Scheme 2).



**Fig. 7** (a) Photographs of bacterial colonies of *S. aureus* and *E. coli* after incubation with the ionomer membranes at 37 °C for 4 h in the sandwich test with a bacterial suspension as a control. (b) Bacterial viabilities of *E. coli* of P1-Pip<sup>+</sup>, P1-Qa<sup>+</sup>, P1-Im<sup>+</sup>, P1-Qp<sup>+</sup> and P1 via the sandwich test. (c) Bacterial viabilities of *S. aureus* of P1-Pip<sup>+</sup>, P1-Qa<sup>+</sup>, P1-Im<sup>+</sup>, P1-Qp<sup>+</sup> and P1 via the sandwich test. (d) Comparison of the bactericidal effect of polymers on *E. coli* and *S. aureus*.

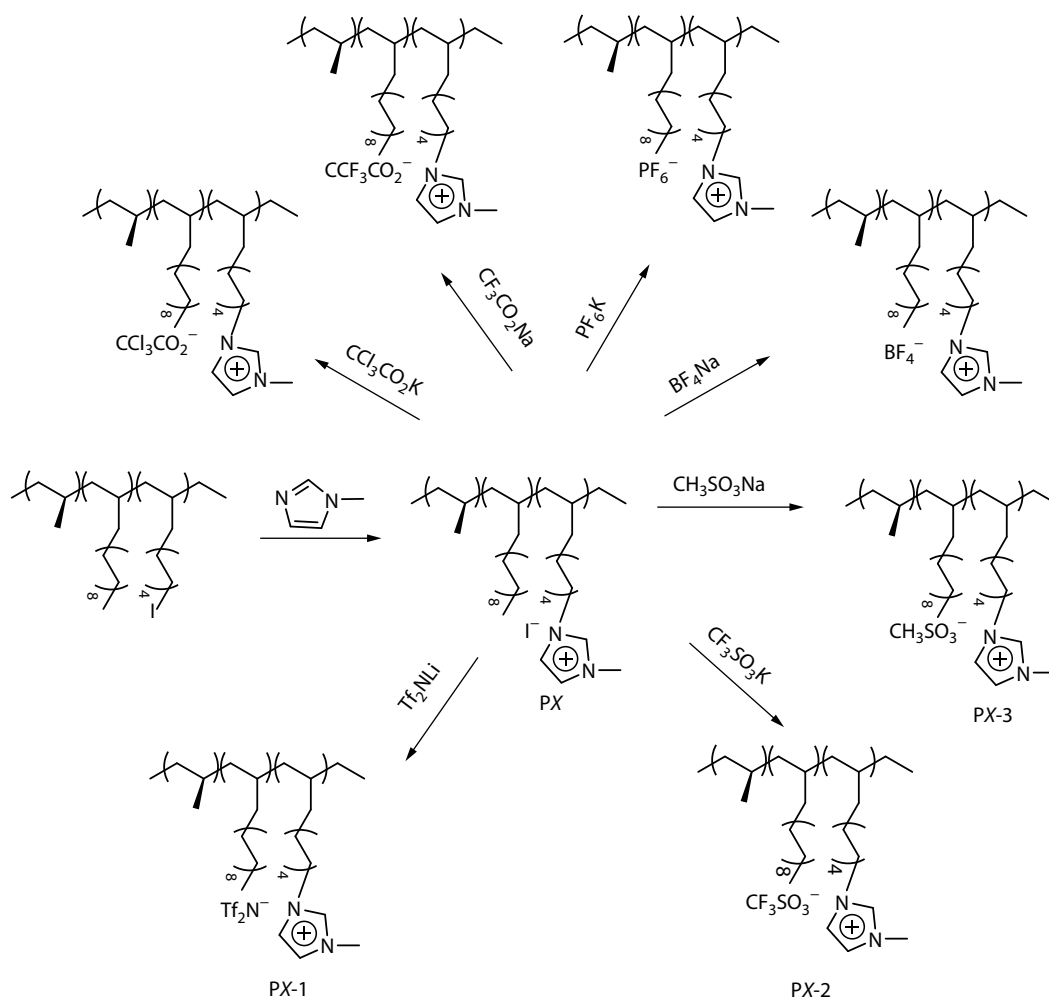
The imidazolium-functionalized polypropylene copolymer was first dissolved in a suitable amount of xylene at 80 °C.  $\text{BF}_4\text{K}$  was dissolved in a mixture of deionized water and acetonitrile, and the resulting solution was added dropwise to the copolymer solution. The reaction mixture was refluxed at 80 °C for 48 h. After completion, the product precipitated into a large volume of ethanol. To remove the residual  $\text{BF}_4\text{K}$ , the ionomer was thoroughly washed with a mixed solvent of deionized water and acetonitrile. Ionomers containing other counteranions were synthesized using the same procedure.

### Antibacterial Properties of Imidazolium-functionalized Polypropylene Copolymers

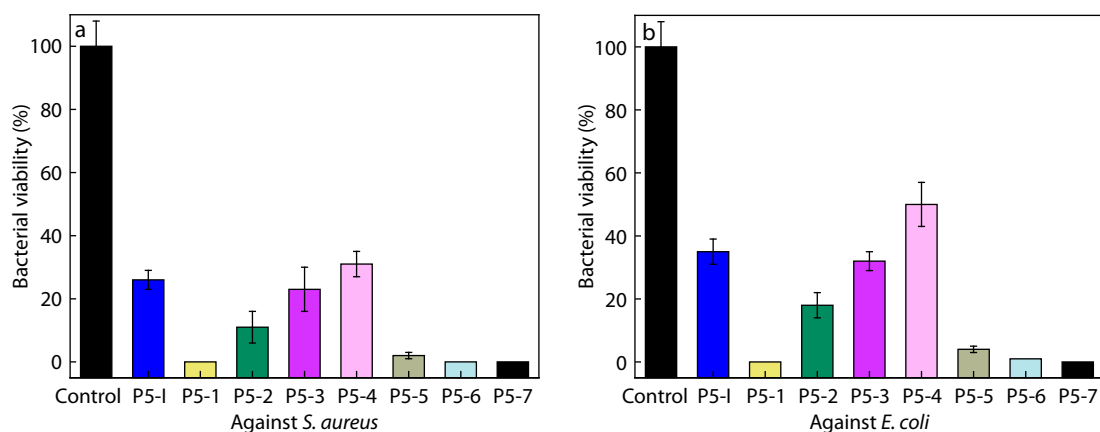
As shown in Figs. 8(a) and 8(b), we evaluated the antibacterial ability of the ionomer membranes using *S. aureus* and *E. coli* with a bacterial suspension as a control. These results indicated that the ionomer membranes exhibited excellent antimicrobial properties. This observation could be attributed to the fact that the cations in the ionomer can interact strongly with the negatively charged bacterial cell membrane through electrostatic interactions, thus selectively destroying the integrity of the bacterial cell membrane and killing the bacteria.<sup>[40]</sup> For P5 with the ionic content of 11.9 mol%, after incubation with P5- $\text{I}^-$ , P5- $\text{PF}_6^-$ , P5- $\text{Tf}_2\text{N}^-$ , P5- $\text{CCl}_3\text{CO}_2^-$ , P5- $\text{CF}_3\text{SO}_3^-$ , P5- $\text{BF}_4^-$ , P5- $\text{CF}_3\text{CO}_2^-$ , P5-

$\text{CH}_3\text{SO}_3^-$ , the bacterial viability of *E. coli* was 0%, 0%, 0%, 0%, 1%, 4%, 5% and 15%, respectively. However, the bacterial viability against *S. aureus* decreased from 100% for the control to 0% for ionomer with  $\text{I}^-$ , to 0% for ionomer with  $\text{PF}_6^-$ , to 0% for ionomer with  $\text{Tf}_2\text{N}^-$ , to 0% for ionomer with  $\text{CCl}_3\text{CO}_2^-$ , to 0% for ionomer with  $\text{CF}_3\text{SO}_3^-$ , to 2% for ionomer with  $\text{BF}_4^-$ , to 3% for ionomer with  $\text{CF}_3\text{CO}_2^-$  and to 10% for ionomer with  $\text{CH}_3\text{SO}_3^-$ . Overall, ionomer membranes exhibited excellent bactericidal properties. Kanazawa *et al.* reported a series of ionomers with different counter anions, which affected the antimicrobial performance. It was speculated that cations dissociated more readily to free ions and had better antimicrobial activity, while the activity was increased for ionomers bearing counter anions, forming loose ion pairs with cations.<sup>[53]</sup>

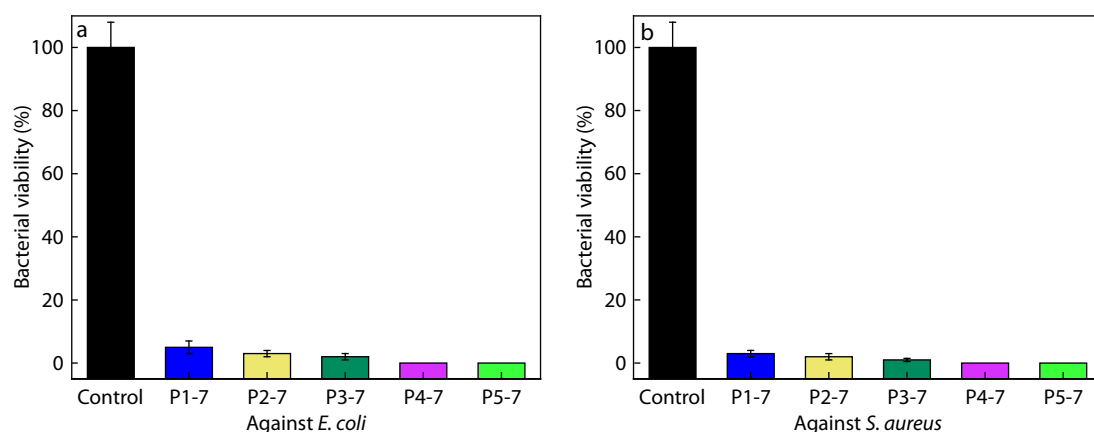
Further testing was conducted based on the remarkable bactericidal properties and easily accessible raw materials of the ionomer with  $\text{Im}^+\text{CCl}_3\text{CO}_2^-$ . We tested the antibacterial properties of ionomers with different ionic contents, and the results are shown in Figs. 9(a) and 9(b). The observed results showed that all the ionomer membranes exhibited excellent antimicrobial efficiency. P3-7, P4-7, and P5-7, with ionic contents more than 7.9 mol%, showed excellent antibacterial properties against *S. aureus* and *E. coli* (survival rates were less



**Scheme 2** Synthetic routes of polypropylene ionomers bearing various counter anions.



**Fig. 8** Bacterial viabilities of (a) *S. aureus* and (b) *E. coli* of ionomers via the sandwich test.



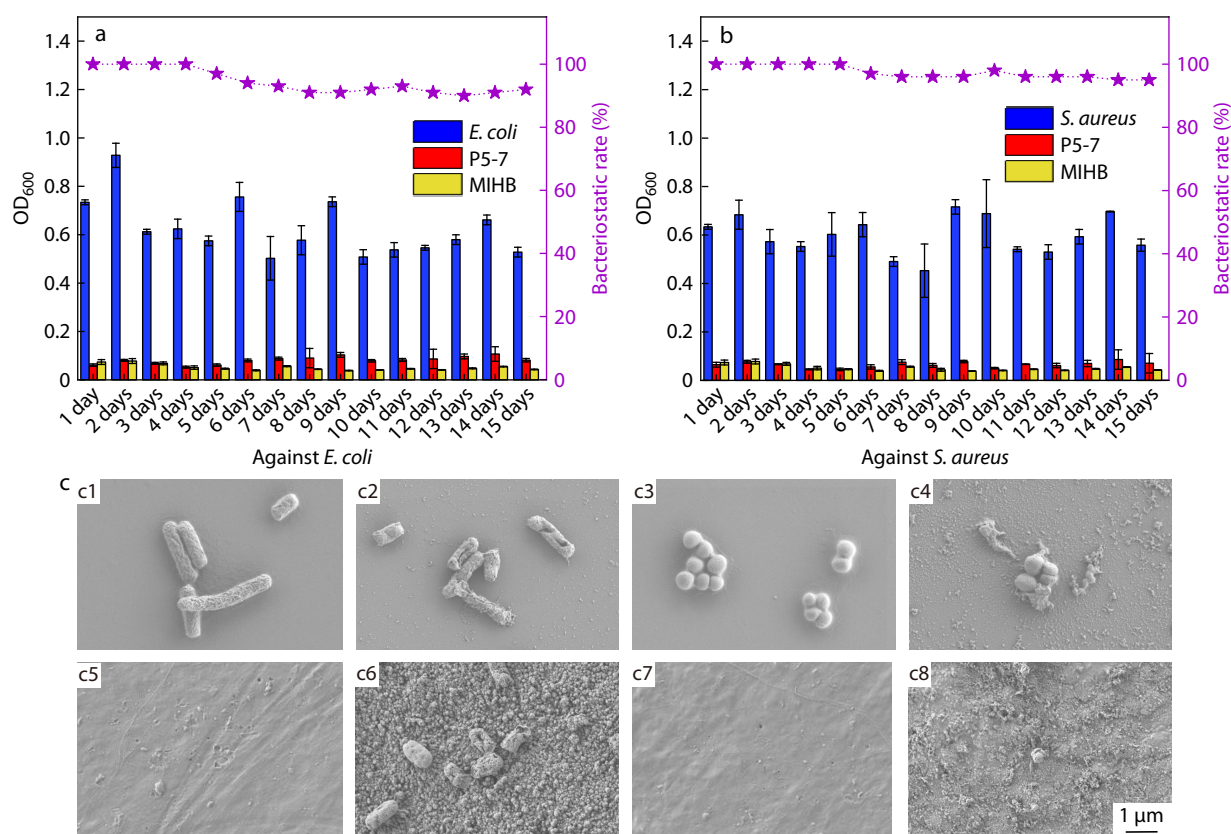
**Fig. 9** Bacterial viabilities of (a) *E. coli* and (b) *S. aureus* of control and ionomer with different ion contents.

than 1%). P1-7 had the lowest ionic content of 3.2 mol%, and more than 95% of *E. coli* and 97% of *S. aureus* were killed. Clearly, the materials exhibited excellent antibacterial properties at low ionic contents. In ionomer membranes, bacterial inhibition is significantly enhanced with increasing ionic content. This phenomenon was attributed to an increase in the localized positive charge density, which ultimately enhanced its interaction with the bacterial cell membrane and improved the penetration of the ionic polymer into the biofilm, significantly inhibiting the growth of bacteria in the biofilm.

Encouraged by the antibacterial performance of P5- $\text{CCl}_3\text{CO}_2^-$ , we further studied the long-term sterilization effect of the ionomer membranes, as shown in Figs. 10(a) and 10(b). As observed, P5- $\text{CCl}_3\text{CO}_2^-$  showed 100% bactericidal effect against *E. coli* and *S. aureus* within 4 days or 5 days with continuous supplementation of a new bacterial solution. From the 5<sup>th</sup> day to 15<sup>th</sup> day, the materials still maintained over 90% bacterial inhibition against *E. coli* and *S. aureus*. According to the relevant literature, the decrease in bacterial inhibition was due to the fact that during killing of the bacteria and the continuous replenishment of new bacterial sources, some dead bacteria and contents adhered to the surface of the ionomer membrane, which hindered contact with bacteria.<sup>[51]</sup> We used a bacterial solution concentration of  $10^8$ – $10^9$  CFU/mL of *E. coli* and *S. aureus*, and the experimental conditions were much higher than those of the bacteria in our daily lives; therefore, the ionomer film had an excellent and long-

lasting bactericidal effect.

The morphological changes of the two tested bacteria and ionomer membranes were studied using SEM, and the results are shown in Fig. 10(c). Wrinkled bacterial membranes and debris were clearly observed by SEM after 4 h of treatment with ionomer membranes, especially for *S. aureus*, indicating that P5-7 disrupted the cell membranes. As shown in Figs. 10(c2) and 10(c4), *E. coli* had pores and depressions after 4 h of interaction with P5-7, while *S. aureus* showed burst bacterial membranes and leakage of cellular content. This proved that the ionomer membranes killed both bacteria by damaging the bacterial membranes.<sup>[54]</sup> Compared with the ionomer film that had been in contact with the bacterial solution for 4 h (Figs. 10c5 and 10c7), some dead bacteria and lumps were clearly attached to the surface of the ionomer film after 15 days of continuous replenishment of new bacterial solutions (Figs. 10c6 and 10c8). This may be the result of cell contents leaking out after bacterial death and adhering to the surface of the ionomer membranes.<sup>[55]</sup> This observation also demonstrated that the decrease in the ionomer membrane bacteriostatic efficiency in the bacterial inhibition persistence experiment was due to the adhesion of dead bacteria and their contents to the surface of the film. In conclusion, these findings further proved that P5-7 had an excellent sterilizing effect, even though larger dead bacterial cell fragments were attached to its surface.



**Fig. 10** (a) OD<sub>600</sub> values of MHB, bacterial solutions and the bacterial suspensions treated with P5-7 and bacteriostatic rate against *E. coli* for 15 days. (b) OD<sub>600</sub> values of MHB, bacterial solutions and the bacterial suspensions treated with P5-7 and bacteriostatic rate against *S. aureus* for 15 days. (c) SEM images of (c1) original *E. coli* form; (c2) *E. coli* treated with P5-7 for 4 h; (c3) original *S. aureus* form; (c4) *S. aureus* treated with P5-7 for 4 h; (c5) the surface of ionomer membranes after 4 h interaction with *E. coli*; (c6) the surface of ionomer membranes after 15 days interaction with *E. coli*; (c7) the surface of ionomer membranes after 4 h interaction with *S. aureus*; (c8) the surface of ionomer membranes after 15 days interaction with *S. aureus*.

## CONCLUSIONS

In summary, we employed hafnium complexes to catalyze the copolymerization of propylene with C20 and IUD and subsequently converted the resulting copolymers into a series of ionomers bearing diverse cations and counter anions. The obtained materials exhibited high molecular weights and narrow molecular weight distributions, with the ionization reaction proceeding to complete the conversion. The thermal properties of the copolymers and the rheological properties of the copolymer melts were significantly altered by ionic introduction. In addition, the introduction of ionic groups leads to significant alterations in the mechanical strength and elastic recovery of the material. This phenomenon can be attributed to the formation of ionic clusters through electrostatic interactions between the cations and anions, which created additional physical crosslinking points between the molecular chains. Moreover, ionomers can kill bacteria by selectively disrupting the integrity of the bacterial cell membrane through strong electrostatic interactions with the negatively charged bacterial cell membrane. The ionomers obtained exhibited high bactericidal properties against *S. aureus* and *E. coli*. In particular, the ionomer containing  $\text{Im}^+\text{CCl}_3\text{CO}_2^-$  exhibited an excellent sterilization rate of up to 99.99% for both bacteria. The ionomer membranes had a long-lasting bactericidal effect, which was maintained a high bactericidal effect against *E. coli* (>90%) and *S. aureus* (>95%) for 15

days. This work demonstrates that ionic polypropylene-based copolymers have great potential for auto parts, food packaging, biomedical equipment, and children's toys owing to their outstanding antimicrobial and mechanical properties.

## Conflict of Interests

The authors declare no interest conflict.

## 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/s10118-025-3523-3>.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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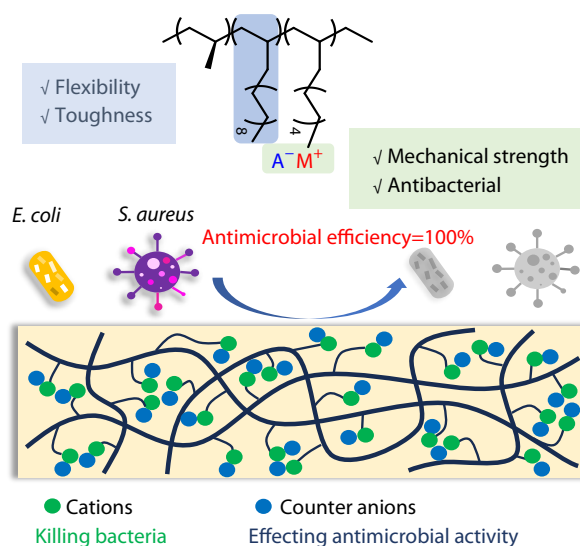
## Graphical Abstract

### Dynamic Ionic Crosslinking Polypropylene-based Elastomers with Excellent Mechanical Properties and Antibacterial Performance

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Iodine-containing comonomers were introduced into a polypropylene backbone and functionalized via iodine group conversion to prepare various ionomers. The resulting ionic groups enhanced the thermal properties, melt rheology, and mechanical performance of the materials. The ionomers also exhibited excellent antibacterial efficacy against both *Escherichia coli* and *Staphylococcus aureus*.



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