Increased Hydrogen-bonding of Poly(m-phenylene isophthalamide) (PMIA) with Sulfonate Moiety for High-performance Easily Dyeable Fiber

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Abstract The demand for high thermal stability and high strength agents is growing steadily as a result of their increasing application in advanced materials. A series of sulfonated poly(m-phenyleneisophthalamide) (SPMIA) copolymers with superior thermal stability and good mechanical properties have been prepared via low temperature polycondensation method. Then the structures of SPMIA copolymers with different content quantities of 2,4-diaminobenzenesulfonic acid (2,4-DABSA) were confirmed by Fourier transform infrared (FTIR). Besides, their superior thermal properties were systematically investigated by differential scanning calorimetry (DSC), thermalgravimetric analysis (TGA), and dynamic mechanical analysis (DMA). SPMIA fibers were obtained by wet spinning using the resultant SPMIA solutions. In addition, the obtained SPMIA fibers were proved to combine enhanced mechanical properties and unprecedented dyeability. Significantly, the SPMIA fiber with great mechanical property, thermal stability, and dyeability shows great potential in easily dyeing high-performance protective fibers.

Keywords Sulfonated poly(m-phenyleneisophthalamide); Copolymer; Sulfonic acid group; High-Performance fiber; Easily dyeable fiber

INTRODUCTION

Poly(m-phenylene isophthalamide) (PMIA/meta-aramid) is one of the most promising high performance aromatic polyamides for commercial applications due to its flame resistance, excellent thermal stability, and low densities. Hence, their fibers have been widely explored, such as military heat-resistant protective clothing, manufacturing protective garments, and aerospace facilities.[1−8] However, the lack of functionalities has limited its wider applications. Furthermore, some performances of PMIA need to be further improved for expanding their future application; in particular, superior mechanical property and easily dyeable ability are essential factors for the application of PMIA in high-performance protective materials, specifically those related with apparels, carpets, etc.

The traditional method for mechanical property modification utilizes the strong and stiff nanofillers reinforcement, like aramid nanofibers,[6] graphene oxide,[7−9] nano-SiO2,[10,11] multiwalled carbon nanotubes, and so on.[12,13] The weak interfacial interaction between nanofiller and polymer matrix and the limitation of nanofillers dispersion severely restrict their reinforcement.[14] Numerous researches toward the enhancement of the mechanical property of high performance polymer are currently being conducted. Most investigations are based on the introduction of new functional groups.[15−18] Meanwhile, introducing additional intermolecular association such as hydrogen bond or chemical cross-linking and incorporating rigid pendent groups have been proved to be two of the most efficient methods. Niu et al.[19] prepared copolyimide with enhanced mechanical property by introducing 2-(4-aminophenyl)-6-amino-4(3H)-quinazolinone (AAQ) into rigid homopolyimide backbones. The result showed that hydrogen bonding formed between AAQ and cyclic imide is the main reason for improved mechanical property. Inter-molecular hydrogen bonding plays a key role in improving the mechanical properties of high-performance polymers. Dai et al.[20] fabricated a series of polyimide copolymers containing phenylenebenzoxazole moiety, and the resultant fibers showed excellent thermal stabilities and enhanced mechanical properties. The FTIR results confirmed that the inter/intra molecular hydrogen bonds formed were expected to be the effective way to improve the fracture strength and initial modulus. When both aromatic heterocyclic rigid pendent units and the intermolecular hydrogen bonding were incorporated into polypyridobisimidazolide (PPIP), the tensile strength and tensile modulus of PIPD fibers reached 4.0 and 360 GPa, respectively.[21] Gan et al.[22] synthesized a novel copolyimide containing pyrimidine rings, and the optimum tensile strength and tensile modulus were up to 3.1 and 90 GPa,
respectively. Feng and coworkers also investigated the effect of molecular rigidity and hydrogen bond interaction on mechanical properties of polyimide fibers; the prepared co-PI fibers possessed the highest tensile strength of 1.82 GPa and initial modulus of 85.7 GPa. The results indicate that high hydrogen bond interaction can lead to better mechanical property.[21]

A series of sulfonated poly(p-sulphonylene terephthalamide) (SPTTA) based on PPTA with a rigid-rod bond and sulfonic acid side groups have been extensively studied for over 3 decades.[24–32] Meanwhile, sulfonic acid group is an anionic functional group, which can create dyeing sites capable of bonding with cationic dyes to improve the dyeing condition.[33,34] To the best of our knowledge, sulfonated poly(m-phenyleneisophthalamide) has not been reported yet.

Based on the above considerations, we reported the synthesis of novel sulfonated PMIA copolymers. We firstly prepared a kind of long chain diamine monomer (LCDM) in the presence of 2,4-DABSA and used it as a monomer. Then a series of sulfonated PMIA (SPMIA) with different molar ratios of LCDM was synthesized via low temperature solution polycondensation. Notably, compared with homopolymer, the impressive thermal property and mechanical property of the copolymers were extremely enhanced even at the low addition of 2,4-DABSA due to the enhanced hydrogen bonding between sulfonic acid group and the proton of the amide bond. Significantly, the obtained SPMIA fibers not only were easily dyed with cationic dyes, but also achieved satisfactory color fastness.

**EXPERIMENTAL**

**Materials**

m-Phenylenediamine (MPD), 2,4-diaminobenzenesulfonic acid (2,4-DABSA), and isophthaloyl dichloride (IPC) were purchased from TCI and used as received. Anhydrous lithium chloride (LiCl) was received from Sigma-Aldrich. Calcium hydroxide (Ca(OH)2, > 99%) was received from Long You Hai Fa Chemical Co., Ltd. (Shanghai, China) and used directly. N,N-dimethylacetamide (DMAc) was obtained from Long Feng Chemicals Co., Ltd. (Shanghai, China) and used as received. Commercial grade cationic dyes (Basic Red 46, Basic Yellow 28 and Basic Blue 41) were obtained from Sigma-Aldrich.

**Preparation of Long Chain Diamine Monomer (LCDM)**

For the synthesis of long chain diamine monomer containing sulfonic acid groups depicted in Scheme 1, 150 mL four-necked bottomed flask was put into water and finally obtained after was dried containing a mechanical stirrer and a thermometer, and the flask was passed through with nitrogen. For the synthesis of long chain diamine monomer containing sulfonic acid groups depicted in Scheme 1, 150 mL four-necked bottomed flask was dried containing a mechanical stirrer and a thermometer, and the flask was passed through with nitrogen for 1 h. The long chain diamine monomer (LCDM) was obtained.

**Synthesis of Sulfonated PMIA Based on Solution Polycondensation**

The polycondensation was carried out in flame-dried four-necked bottomed flask under nitrogen atmosphere due to the high water vapour sensitivity of the monomers. Based on as-conformed LCDM, a different molar ratio of MPD was added to dissolve in 100 mL of DMAC containing LCDM. The mixture was cooled down to 0 °C and 18.27 g of IPC was added dropwise within 20 min. Then the reaction was conducted at room temperature for 20 min. Finally, residual IPC was added dropwise with high-speed stirring for 1 h. Ca(OH)2 (7.49 g) was added to neutralize HCl. With this preparation process, sulfonated PMIAs with different MPD/LCDM molar ratios (10/0, 9.5/0.5, 9/1, 8.5/1.5, 8/2, and 7.5/2.5) were synthesized, and the chemical structure of SPMIA synthesized in this work is shown in Scheme 2.

**Preparation and Dyeing Experiment of SPMIA Fibers**

SPMIA nascent fibers were prepared via wet spinning. The viscous copolymer solution was pumped through a spinneret...
(total 50 holes, 0.08 mm of each hole) to the mixed solution of DMAC/H2O (45/55, W/W) at 25 °C. The as-spun fibers were then drawn between the two drawing rollers with a draw ratio of 2 in the second coagulation bath of DMAC/H2O (35/65, W/W) at 60 °C. The drawn fibers were washed with hot water and dried in an oven at 100 °C for 6 h. Finally, SPMIA fibers were obtained by hot stretching in a hot tube with a draw ratio of 2.5 to 310 °C.

Dyeing experiment was carried out in aqueous solution. In each beaker, 1-g fiber sample was added to 50 mL dyebath of known dye concentration 2% owf (on fiber weight) together with pH of 3–5 and the temperature raised to 100 °C for 1 h. Then the dyed fibers were held for 30 min at 60 °C. Subsequently, the fibers were rinsed with cold water, followed by drying in an oven at 60 °C.

Characterization
Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Nexus 670 spectrometer with an attenuated total reflection (ATR) accessory at a resolution of 4 cm⁻¹. Curve-fitting deconvolution of the infrared spectra was performed using Origin 8.5 Software to separate individual absorption contributions in the spectral region of 1620–1720 cm⁻¹. They were identified by a second-derivative analysis. The non-linear least squares fitting method was used to obtain the best fit of the sum of the calculated peaks to that of the measured peaks.

1H-NMR spectra were recorded on a Bruker AV 600 FT-NMR spectrometer at 600 MHz using deuterated dimethyl sulfoxide (DMSO-d6) as the solvent. Elemental analysis was carried out using a Perkin-Elmer model 2400 CHN analyser. Gel permeation chromatography (GPC) measurements were performed by a Waters 2414 instrument consisting of a Waters 2414 refractive index (RI) detector and a Water 1515 pump. DMAC was used as eluent at a flow rate of 0.8 mL/min at 50 °C. Polystyrene (PS) was used as standard.

Thermalgravimetric analysis (TGA) measurements were performed on a TA instrument TG209F1 system. Samples weighing about 6.0 mg were heated from 30 °C to 900 °C at a heating rate of 20 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) analyses were conducted on a 204F1 Netzsch Phenix at the heating rate of 20 °C/min under nitrogen atmosphere. Thermal dynamic mechanical behaviors were recorded on a dynamic mechanical analysis (DMA) system of Q800 with the temperature from 30 °C to 400 °C. The frequency used was 1.0 Hz and the heating rate of 5 °C/min.

Mechanical properties of samples with width of 10 mm and thickness of 0.02–0.03 mm were measured on an MTS model C44-104 electromechanical universal testing machine at room temperature. At least 5 samples were tested with a drawing rate of 40 mm/min.

Ultraviolet-Visible spectra of the membranes were recorded on a Perkin-Elmer Lambda 950 Ultraviolet-visible spectrophotometer (UV-Vis) in the 250–850 nm spectral regions.

An XD-1 fineness tester and XQ-1 strength tester were applied to measure the intensities of fibers.

Dyeability was investigated by testing the color strength value (K/S) using a Datacolor 850 Tester. The K/S value determining the color depth of dyed sample was calculated as Eq. (1):

\[ K/S = \left(1 - R^2\right)/2R \]  

where K is the absorption coefficient, S is scattering coefficient, and R is reflectance of tested sample. Rubbing fastness was measured according to the GB/T 3920-2008 standard. Washing fastness was evaluated according to the GB/T 5713-2013 standard.

RESULTS AND DISCUSSION
Synthesis of SPMIA in Solutions
In general, the molecular weight of the copolymer plays a key role in the ultimate properties. In our previous work,[35] 3,4'-oxydianiline (3,4'-ODA) containing electron-donating ether group enhanced the diamine monomer reactivity. Since 3,4'-ODA behaved more actively than MPD, ideal high molecular weight OPMIA copolymers were obtained by direct low temperature polycondensation. In contrast, the sulfonic acid group on the benzene ring is an electron-withdrawing group, which extremely reduces the reactivity of amino groups toward chloride groups.[36] Herein, a sulfonated long chain diamine monomer (LCDM) in the presence of 2,4-DABSA was prepared by a facile and low-cost method. The GPC results of SPMIA copolymers with different MPD/LCDM molar ratios are presented in Table 1. All SPMIA copolymers achieved relatively high molecular weight (Mw) of 1.59 × 10⁷–2.06 × 10⁸ g/mol, with polydispersity index (PDI) in the range of 2.82–2.91, indicating the successful copolymerization.

| Polymer | MPD/LCDM (molar ratio) | Mw × 10⁸ (g/mol) | PDI |
|---------|------------------------|-----------------|-----|
| PMIA    | 100/0                  | 17.7            | 3.26|
| SPMIA-5 | 95/5                   | 20.6            | 2.91|
| SPMIA-10| 90/10                  | 19.7            | 2.90|
| SPMIA-15| 85/15                  | 18.6            | 2.90|
| SPMIA-20| 80/20                  | 16.5            | 2.82|
| SPMIA-25| 75/25                  | 15.9            | 2.83|

*Weight-average molecular weight. Polydispersity.

Structure Characterization of Prepared SPMIA Copolymers
FTIR characterization was utilized to confirm the chemical structure, and the results are shown in Fig. 1. Three apparent absorption bands centered at 1654, 1544, and 1250 cm⁻¹ are

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observed, which were ascribed to amide I, II, and III, respectively, demonstrating the formation of amide groups. The characteristic bands around 1610 cm\(^{-1}\) were related to the presence of C=\(\equiv\)C stretching vibration together with C—H stretching vibration at 3063 cm\(^{-1}\). The distinctive bands at 3495 and 3307 cm\(^{-1}\) were corresponding to “free” N—H stretching and hydrogen-bonded N—H stretching of the amide groups. Furthermore, the band corresponding to H-bonded N—H stretching gradually shifted from high frequency to low frequency with the increasing content of LCDM. This phenomenon was consequently attributed to the formation of intermolecular hydrogen bonding in sulfonated copolymers (see later in Discussion). Notably, the apparent band at 1022 cm\(^{-1}\) was attributed to sulfonic acid group, and its intensity increased with the increasing molar content of LCDM.

**Mechanical Properties**

Mechanical property is deemed to be a most significant parameter for high performance polymers. The appearance of transparent sulfonated PMIA membranes is shown in Fig. 2. The variation of the mechanical properties with different LCDM molar contents is shown in Fig. 3 and the detailed data are listed in Table 2. As can be observed, without the addition of LCDM, the pristine PMIA possessed fracture strength and tensile modulus of 95 MPa and 1.67 GPa, respectively. From SPMIA-5 to SPMIA-25, their tensile strengths were 112, 119, 107, 105, and 104 MPa, and tensile moduli were 2.19, 2.70, 3.27, 3.49, and 3.51 GPa, respectively. Remarkably, the tensile strengths of SPMIA copolymers with the low LCDM contents were obviously higher than that of neat PMIA. Particularly, SPMIA-10 exhibited a superior fracture strength of 119 MPa, while the maximum tensile modulus was observed for SPMIA-25. It can be explained by the fact that the sulfonated copolymers had superior ability to resist against the tensile force with the assistance of increased molecular chain rigidity. With the continuous increase in applied stress, however, it became easier to reach the stress concentration point due to the increased molecular chain rigidity. Hence, the break of SPMIA membrane happened subsequently and the applied stress was reduced. Then, the slight decrease in strength of SPMIA membranes was observed. Overall, the SPMIA membranes still possessed good mechanical properties.

**Hydrogen Bonding Interaction in SPMIA Copolymers**

The locations of infrared absorption bands of the hydrogen bonded functional groups and “free” groups obtained by FTIR spectra were processed by fitting peak-splitting technique.\(^{[37,38]}\) It is well accepted that the corresponding band moves towards the lower wavenumber due to the formation of intermolecular hydrogen bonding.\(^{[39]}\) The presence of sulfonic acid groups in the copolymer chains is expected to create strong intermolecular interaction, especially hydrogen bonding between CONH groups and sulfonic acid groups. To confirm this hypothesis, the FTIR spectra were deconvoluted in the range of 1620–1720 cm\(^{-1}\) to determine the attribution bands of carbonyl groups, and then the non-linear least square method was used to fit corresponding bands. Fig. 4 shows the deconvoluted FTIR spectra in a wavenumber range of 1620–1720 cm\(^{-1}\). Five displayed peaks at approximately 1681, 1670, 1661, 1655, and 1645 cm\(^{-1}\) were separately identified for PMIA and sulfonated PMIAs. The detailed curve-fitting results of the FTIR spectra are listed in Table 3. Additionally, compared with the pristine PMIA,
the position of the five peaks red-shifted to the lower wavenumber upon LCDM incorporation.

All these observations suggested the obviously increased hydrogen bonds in SPMIA copolymers, and thus indicated that the introduction of sulfonic acid group could strengthen the interchain hydrogen bonding.

Thermal Stability and Glass Transition Temperature

The glass transition temperatures \(T_g\) of prepared aromatic polyimides were investigated by DSC and DMA, and the thermal stability was evaluated by TGA under nitrogen atmosphere. Although there were some deviations in \(T_g\) received from DSC and DMA, the variation tendency for the same sample was similar. As shown in Fig. 5 and Table 4, it could be concluded that \(T_g\) increased with the increasing content of LCDM, and achieved a value of 310 °C in SPMIA-25 using DSC analysis, corresponding to 31 °C improvement as compared with pristine PMIA (279 °C), indicating the increased molecular chains interactions contributed to the rigidity. In addition, \(T_g\) could be tailored to the practical production by adjusting the

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**Table 3** Curve-fitting results of the FTIR spectra in the range of 1620–1720 cm\(^{-1}\).

| Sample   | Band 1 (cm\(^{-1}\)) | Band 2 (cm\(^{-1}\)) | Band 3 (cm\(^{-1}\)) | Band 4 (cm\(^{-1}\)) | Band 5 (cm\(^{-1}\)) |
|----------|----------------------|----------------------|----------------------|----------------------|----------------------|
| PMIA     | 1647.9               | 1655.5               | 1663.9               | 1673.4               | 1684.0               |
| SPMIA-5  | 1646.9               | 1655.4               | 1662.8               | 1672.9               | 1683.9               |
| SPMIA-10 | 1645.5               | 1655.4               | 1662.0               | 1671.9               | 1682.2               |
| SPMIA-15 | 1645.3               | 1655.3               | 1661.9               | 1670.7               | 1681.1               |
| SPMIA-20 | 1643.1               | 1653.2               | 1661.5               | 1670.3               | 1680.7               |
| SPMIA-25 | 1642.0               | 1652.7               | 1660.5               | 1669.0               | 1678.0               |

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**Table 4** \(T_p\) degradation temperature of SPMIA copolymers and corresponding weight losses.

| Sample   | \(T_{DSC}^a\) (°C) | \(T_{DMA}^b\) (°C) | \(T_{5\%}^c\) (°C) | \(T_{10\%}^c\) (°C) | CR \(^d\) (%) | LOI \(^d\) |
|----------|--------------------|--------------------|-------------------|-------------------|--------------|------------|
| PMIA     | 279                | 441                | 467               | 58.2              | 40.8         |
| SPMIA-5  | 294                | 438                | 479               | 58.7              | 41.0         |
| SPMIA-10 | 302                | 437                | 483               | 60.7              | 41.8         |
| SPMIA-15 | 304                | 436                | 485               | 62.5              | 42.5         |
| SPMIA-20 | 307                | 429                | 486               | 62.7              | 42.6         |
| SPMIA-25 | 310                | 427                | 487               | 63.3              | 42.7         |

\(^a\) Measured by DSC, with a heating rate of 20 °C/min under nitrogen atmosphere; \(^b\) Measured by DMA, with a heating rate of 5 °C/min and the frequency of 1.0 Hz; \(^c\) Char yield at 900 °C; \(^d\) Limited oxygen index determined by TGA, LOI = 17.5 + 0.4CR.
molar ratio of LCDM.

Apparently, all SPMIA copolymers presented high thermal stability without thermal degradation until 350 °C, as shown in Fig. 6 and Table 4. The 5%-weight-loss temperature ($T_{5\%}$) values of SPMIA copolymers under nitrogen were in the range of 438–427 °C, which were slightly lower than that of homopolymers (441 °C), demonstrating the decomposition of extra free sulfonic acid group.[40] However, the result showed that the 10%-weight-loss decomposition temperatures ($T_{10\%}$) of SPMIA copolymers were remarkably higher than that of neat PMIA sample. The reasons could be explained as follows. Firstly, the existence of sulfonic acid group in the SPMIA copolymers structure can increase the chain rigidity and decrease the chain mobility, thus leading to a higher thermal stability. Secondly, the existence of strong hydrogen bonding interaction in the molecular chains could prevent the thermal motion of pyrolysis free radicals and thus retard thermal degradation of SPMIA copolymers. Finally, it has been reported that polar functional groups can increase the degradation activation energy and the transition temperature.[41] The limited oxygen index (LOI) was calculated from the experimental van Krevelen equation, which was related to the flame resistance properties of polymer materials.[42] Char yields of the copolymers at 900 °C in nitrogen were in the range of 58.7%–63.1%, with PMIA having the lowest char yield of 58.2%. The higher the char yield at 900 °C, the higher the value of LOI, and the better the flame resistance. Due to the satisfactory LOI values (higher than 41.0) calculated from the mentioned equation, as-prepared SPMIA copolymers with very good fireproof characteristics would have great potential for use in self-extinguishing materials.

Dynamic Mechanical Properties

To further investigate the impacts of LCDM on the mechanical properties of SPMIA copolymers, the prepared samples were measured by DMA, as depicted in Fig. 7. As observed, the tanδ curves of SPMIAs shifted to higher temperatures with the increasing molar ratios of LCDM, which was consistent with the increased hydrogen bonds after the introduction of sulfonic acid groups. Fig. 7 shows that the relaxation temperature shifted to high temperature remarkably with a decreased peak intensity. Furthermore, the curves of glass transition gradually became wider compared with that of neat PMIA. It should be known that the mentioned relaxation process (i.e., the glass transition) must correspond to segment motion which is ascribed to a mobile amorphous region of polymers. Hence, the relaxation temperature shifted to higher temperature range with the decreased intensity, suggesting the chain movement might be governed by the intermolecular hydrogen bonding interactions resulting from the sulfonic acid groups, as revealed by the ATR-FTIR spectra in Fig. 4.

UV-Vis Transmittance

The UV-Vis transmission spectra of SPMIA copolymer membranes with a thickness about 22 μm are presented in Fig. 8. All the membranes exhibited high transparency in the visible region. Nevertheless, the result showed that the transmittance was lower than 1% in the UV region. As we know, electron conjugation and/or intra- and intermolecular charge-transfer interactions (CTC) are two main factors that affect the shade of membranes.[23] In previous studies, large side groups, nonplanar structure and electron withdrawing groups were usually introduced into the polymer backbones so as to weaken the role of electron conjugation and CTC.[43–46] Compared with that of neat PMIA membrane, the light transmittance of SPMIA copolymer membranes was slightly increased, indicating that

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the sulfonic acid side group has small positive effect on improving the visible light transmittance.

**Mechanical Properties and Dyeability of High-performance SPMIA Fibers**

The high-performance fibers were obtained by wet-spinning process. Fig. 9 shows the typical stress-strain curves of SPMIA-10, PMIA, and commercial easily dyeable Nomex fibers under the same test condition. Table 5 shows that the tensile strength of SPMIA-10 fiber was higher than that of the pristine PMIA fiber. However, the elongation at break of the sulfonated PMIA fiber showed a slight decrease, which could be attributed to the increased molecular chain rigidity.

![Fig. 9](image-url)  
**Fig. 9** Typical stress-strain curves of high-performance fibers.

| Fiber  | Fineness (dtex) | Tensile strength (CN/dtex) | Elongation at break (%) |
|-------|----------------|---------------------------|-------------------------|
| PMIA  | 3.34           | 2.44                      | 27.45                   |
| SPMIA-10 | 3.37          | 2.74                      | 25.54                   |
| Nomex | 2.15           | 2.65                      | 42.00                   |

Table 5 Mechanical performances of SPMIA-10 fiber compared with neat PMIA fiber and Nomex.

To explore the dyeability of sulfonated copolymer fiber, dyeing experiments were carried out in aqueous solution. SPMIA fibers were found to exhibit very strong and effective affinity towards cationic dyes, which was expected to improve their dyeability to cationic dyes. Fig. 10 shows the color hue of several fibers as obtained upon dyeing experiments with different cationic dyes. Combined with color depth data (see Fig. 11), the SPMIA-10 fibers exhibited satisfactory dyeing evenness and a deep hue. Color fastness assessments of the SPMIA-10 fiber were carried out after dyeing and the results are shown in Table 6. The fastness ratings ranged from 4/5 to 5, which were generally acceptable. The fastness values to wash and rubbing demonstrated that the sulfonic acid groups on the copolymer imparted negative charges, which could strongly bond with the cationic dye molecules. In contrast, the hues of dyeing Nomex and pristine PMIA fiber were not deep enough to make color acceptable. Hence, the superior mechanical performance together with the enhanced dyeability suggests that SPMIA fibers had even more value added for use as easily colored high-performance protected apparels.

![Fig. 10](image-url)  
**Fig. 10** Color hue of high-performance fibers as obtained upon dyeing experiments with different cationic dyes after wet-spinning process.

![Fig. 11](image-url)  
**Fig. 11** Color depth ($K/S$) data of high-performance fibers with different cationic dyes.

| Cationic dyes | Wool | Polyamide | Cotton | Wash | Rubbing |
|---------------|------|-----------|--------|------|---------|
| Basic Red 46  | 4-5  | 4-5       | 4-5    | 4-5  | 4-5     |
| Basic Yellow 28 | 4-5 | 4-5       | 4-5    | 4-5  | 4-5     |
| Basic Blue 41 | 4-5  | 4-5       | 4-5    | 4-5  | 4-5     |

Table 6 Color fastness properties of the SPMIA-10 fiber dyed with different cationic dyes.

**CONCLUSIONS**

In summary, a series of SPMIA copolymers containing sulfonate moiety with different diamine molar ratios were synthesized via low temperature polycondensation method. Notably, all SPMIA membranes showed remarkably enhanced mechanical properties, and the highest tensile strength and tensile modulus realized were 119 MPa and 3.51 GPa, corresponding to the MPD/LCDM molar ratios were 90/10 and 75/25, respectively. Deconvoluted FTIR results indicated the occurrence of red-shift compared with neat PMIA, which was explained to be the formation of hydrogen bonding between CONH groups and the...
introduced sulfonic acid group. In addition, it was also suggested to account for the enhanced mechanical properties. The prepared SPMIA copolymers exhibited excellent thermal stabilities with the 10%-weight-loss decomposition temperatures of 479–487 °C under nitrogen environment. The glass transition temperatures of synthesized copolymers were much higher than that of homo-PMIA, which also could be tuned by changing the content of LCDM. As observed in DMA characterization, the peak intensities and glass transition were dependent on hydrogen bonding. Remarkably, the dyeability of resultant SPMIA fiber was significantly improved due to the electrostatic interaction with various cationic dyes. Based on these advantages, this work provides a promising high-performance sulfonated PMIA copolymer, which is expected to extend the materials to easily dyeable high performance membranes or fibers in the future.

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