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Polar poly(*n*-butyl acrylate)-*g*-polyacrylonitrile elastomer with high temperature elasticity and healability as flexible electronic substrate

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Abstract

In this work, graft copolymer poly (*n*-butyl acrylate)-*g*-polyacrylonitrile with poly (*n*-butyl acrylate) as backbones and polyacrylonitrile as side chains (PnBA-*g*-PAN) was synthesized by macromonomer method and emulsion polymerization. The macromonomer was synthesized by atom transfer radical polymerization and end-group modification. The chemical structures and thermal properties of macromonomer and graft copolymer were investigated by FTIR, GPC, NMR and TGA, etc. The mechanical properties of graft copolymer elastomer was also measured by uniaxial tensile test. Rheological properties at different temperature and mechanical property demonstrated that graft copolymer elastomer possessed elasticity until 180 °C because of cyclization of cyano groups. Ag nanowires@PnBA-*g*-PAN composite elastomer was developed, and the resulted material exhibited autonomic healing property on account of segments' flexibility and dynamic interaction between Ag nanowires (AgNWs) and cyano groups. This is a general method for generation of elastomer with high temperature elasticity and fast self-healing. The composite elastomer has potential application in flexible electronic conductor.

Keywords: Thermoplastic elastomers, Graft copolymer, High temperature elasticity, Healability

Introduction

With the development of smart textiles, flexible electrodes play an important role in wearable and functional textiles (Åkerfeldt et al. 2014). Elastomers can be used as flexible substrates, and they have obtained much attention in recent years (Cai et al. 2019; Cantarella et al. 2018). Thermoplastic elastomers (TPEs) which have unique property of being spontaneously and thermoreversibly cross-linked materials are widely used for a pyramid of important applications (Nian et al. 2019; Hu et al. 2019; Wang et al. 2019). For example, block copolymer thermoplastic elastomers such as SBS and SIS with double bonds in the backbones are commercial and used in broad fields. However, the oxidation resistance is poor owing to the double bonds and it limits the application in high temperature

environment. Moreover, developing elastomers with resistance to hydrocarbons and high temperature is significant for opening new applications in the automotive market (Dai et al. 2020; Gopalan and Naskar 2019). In addition, the construction of self-healing elastomer materials has been driven by developments in materials science and flexible electronics with long lifetime and environmental sustainability (Xun et al. 2020; Chen et al. 2019).

In the past decades, it was demonstrated that the absence of double bonds in fully acrylic TPEs was an important improvement in terms of light sensitivity and oxidation stability. Poly (*n*-butyl acrylate) (P*n*BA) with low *T*_g (glass transition temperature is about − 50 °C) and amorphous structure is a good choice for energy dissipation while loading under the ambient conditions, due to the flexibility of P*n*BA chains at room temperature (Wang and Zhang 2012). What's more, thermoplastic elastomers based on graft copolymers exhibited better properties in comparison with the conventional linear ABA triblock copolymers, such as larger elongation at break, lower residual strain, and high modulus (Jiang et al. 2019; Lu et al. 2018). Using grafting-from, grafting-onto and grafting-through methods by the aid of controlled/living radical polymerization (CRP) or living anionic polymerization techniques, it is possible to substitute traditional unsaturated middle segment by acrylates and hard segments by methacrylates in graft copolymer elastomers (Goodwin et al. 2015; Li et al. 2015; Lu et al. 2018). This would enable many benefits ranging from flexible glass transition temperatures to better oxidation resistance.

Polar polyacrylonitrile (PAN) is semi-crystalline despite being atactic. PAN's crystallinity is therefore driven by the highly dipolar nitrile groups that repel each other within one chain and form dipolar bonds between chains (Kopeć et al. 2019; Zhou et al. 2016). PAN segments could assemble to domains in block copolymers and organosilica materials (Kopeć et al. 2017; Zhang et al. 2018), and chemical cross-linking of the PAN segments occurred when the temperature was improved up to 280 °C (Karbownik et al. 2015a). The 3-arm star PBA-PAN block copolymers preserved their elastomeric properties until temperatures of more than 300 °C because of chemical cross-linking of the PAN segments, which had a much better thermal stability than the PMMA-based materials (Dufour et al. 2008).

In this work, to simultaneously address the requirements of resistance to hydrocarbons and high temperature as well as self-healing for elastomers, PAN macromonomer was synthesized firstly for the branch chains, and graft copolymer with P*n*BA as backbones (P*n*BA-*g*-PAN) was synthesized by emulsion polymerization. The chemical structures and thermal properties of macromonomer and graft copolymer were investigated. Mechanical properties and rheological property at different temperature of graft copolymer elastomer were also demonstrated. Furthermore, Ag nanowires (AgNWs) were generally used to fabricate electronic conductor, thermal management materials and (Liang et al. 2019, 2020). Finally, Ag nanowires@P*n*BA-*g*-PAN (AgNWs@P*n*BA-*g*-PAN) composite elastomer was prepared, and the healability of composite elastomer was studied.

Methods

Synthesis of polyacrylonitrile with bromine end-group (PAN-Br)

Polyacrylonitrile with bromine end-group (PAN-Br) was synthesized by atom transfer radical polymerization (ATRP), and the typical procedure was as below. Acrylonitrile (AN, 21.196 g, 400 mmol), 2-bromopropionitrile (CH₃CH(Br)CN, 0.276 g, 2 mmol), N, N, N', N''-pentamethyldiethylenetriamine (PMDETA, 0.176 g, 1 mmol), and solvent

(DMF, 50 ml) were separately added to 100 ml two-necked flask. The mixture was carried out with magnetic stirring for 30 min in a flow of high-purity nitrogen at a rate of 200 r/min. After two cycles of freezing-pump-thawing on vacuum line, catalyst (CuBr, 0.143 g, 1 mmol) were then added in a high-purity nitrogen atmosphere. The flask was immersed into the oil bath at 80 °C to start the polymerization. The mixture was purified through a neutral alumina column after 8 h, and the polymer was obtained by precipitation into methanol. Then the product was filtered and dried for 24 h at 40 °C in vacuum oven.

Synthesis of PAN macromonomer

Polyacrylonitrile with bromine end-group (PAN-Br, 1.006 g) was dissolved in DMF and the mixture was kept in an ice bath under an ultra-high concentration of nitrogen. Then potassium acrylate, which was obtained from acrylic acid with potassium hydroxide, was added to the above mixture. After 2 h, PAN macromonomer was obtained by precipitation in methanol. Then the product was filtered and dried in vacuum oven at 40 °C for 24 h.

Synthesis of PnBA-*g*-PAN

PnBA-*g*-PAN graft copolymer elastomer was prepared by miniemulsion polymerization. In a typical miniemulsion copolymerization, DMF (5 ml), *n*-hexadecane (HD, 0.06 g), AIBN (0.06 g, 0.36 mmol), *n*-butyl acrylate (nBA, 4.0 g, 31 mmol) and polyacrylonitrile macromonomer (0.5 g) was uniformly mixed to be the organic phase. Sodium dodecylbenzene sulfonate (SDS, 0.4 g) and deionized water were mixed to be aqueous phase. Then the organic phase was added dropwise to the aqueous solution under magnetic stirring. The mixture was sonicated in ice bath for 10 min and then the polymerization was carried out for 8 h at 70 °C. The reaction mixture was demulsified by saturated sodium chloride aqueous solution and the product was washed three times with deionized water to remove the surfactant. The product was purified by fractional precipitation to remove unreacted macromonomer. The obtained graft copolymer was dried in vacuum oven at 40 °C for 24 h.

Preparation of Ag nanowires@PnBA-*g*-PAN composite elastomer

PnBA-*g*-PAN spline (1.5 cm*0.5 cm*0.5 cm) was prepared, and AgNWs solution (1 ml, diameter: 50 nm, L: 50 μm, anhydrous ethanol, concentration: 10 mg/mL) was deposited on the spline three times by drop-coating. The composite elastomer was dried completely in a vacuum oven.

Characterization

GPC (Gel Permeation Chromatography)

The molecular weight and polydispersity index of the PAN-Br, PAN macromonomers and PMA-*g*-PAN graft copolymers were measured by a GPC instrument (TOSOH HLC-8320 GPC). A calibration curve was obtained using linear polystyrene as a standard and chromatographic grade N,N-dimethylformamide (DMF) as the mobile phase at an elution rate of 0.6 mL/min at a column temperature of 40 °C.

Fourier Transform Infrared spectroscopy (FTIR)

FTIR spectra were collected at room temperature on a BRUKER TENSOR 27 FT-IR spectrometer.

¹H Nuclear Magnetic Resonance Spectroscopy (¹H NMR)

¹H NMR spectra were obtained on a Bruker AVANCE NEO 600 instrument. Samples were dissolved in deuterated N,N-dimethylformamide (DMF-d₇).

Thermogravimetric Analysis (TGA)

Thermal stability of polymers was examined using TGA instrument (NETZSCH 209 F3 Tarsus). Briefly, 5–10 mg of the sample was placed on a platinum pan, and then equilibrated at a temperature of 30 °C. The temperature was then raised to 800 °C at 10 °C/min. All TGA tests were performed under a nitrogen atmosphere.

Differential Scanning Calorimetry (DSC)

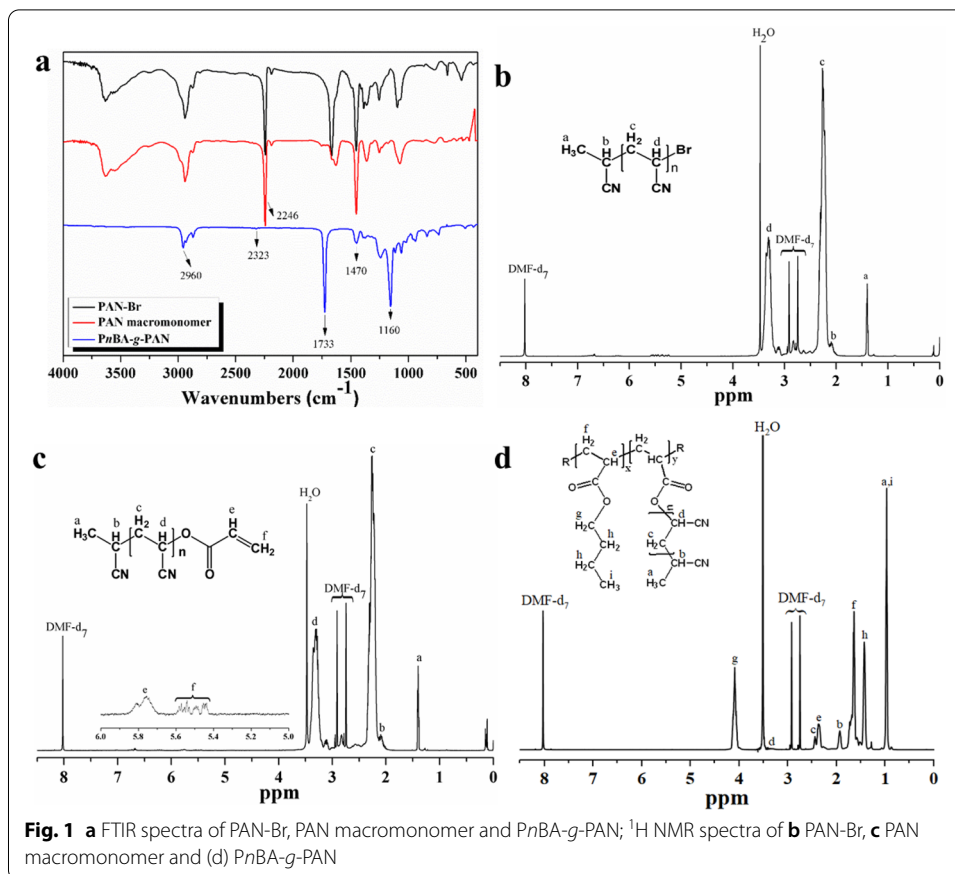
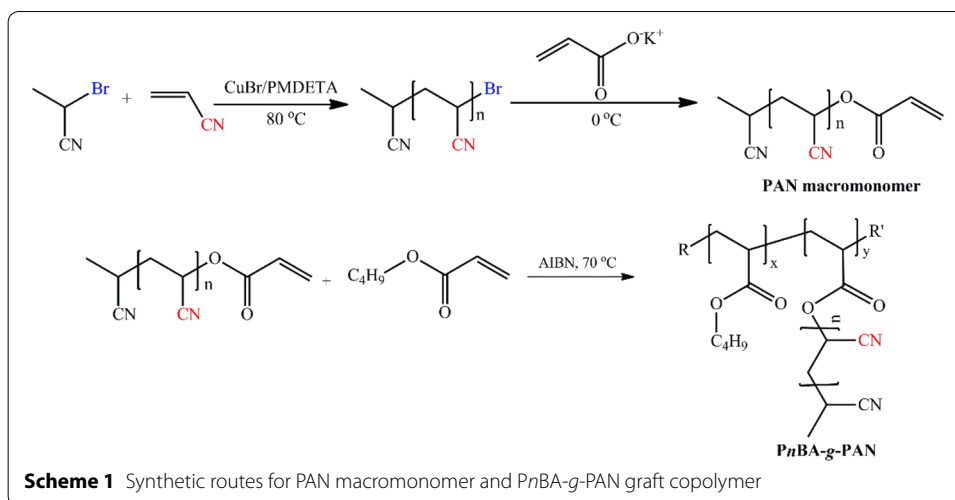
NETZSCH DSC 204F1 was used to evaluate thermal transitions of PAN-Br and P η BA-*g*-PAN copolymer under nitrogen purge. The samples were heated from 20 to 200 °C at heating rate of 10 °C/min for eliminating thermal history. Then the P η BA-*g*-PAN graft copolymer was measured at heating rate of 10 °C/min from – 70 to 350 °C, and PAN-Br was measured at heating rate of 10 °C/min from 20 to 350 °C. The glass transition temperature (T_g) was determined from the second heating in order to erase the thermal history. T_g was reported as the temperature at the midpoint of the heat capacity using the software.

Rheological properties

Solid samples were analyzed for oscillating mode on a parallel plate rheometer (HAKKE). A polymer disc having a diameter of 2 cm and a thickness of 2–5 mm was selected for analysis. The strain was subjected to strain-fixed dynamic rheological analysis at room temperature with a frequency sweep of 0.1–10 Hz at different temperatures up to 200 °C.

Mechanical properties

The samples for testing were prepared as follows: a solution of 2.0 g of polymer in 20 ml of DMF was stirred overnight at room temperature and cast into a 50 × 50 mm PTFE mold and evaporated slowly over 7 days, resulting in films with the thicknesses of around 0.5 mm. Then the samples were dried for 2 days in a vacuum oven at around 50 °C. Then the national standard dumbbell-shaped polymer samples (GB/T 528-2009) were prepared and measured at tensile rate of 15 mm/min on INSTRON 5965 at room temperature.



Scanning Electron Microscope (SEM)

The surface of Ag nanowires@PnBA-*g*-PAN composite elastomer was characterized by using a field emission scanning electron microscope (SEM) (JEOL, JSM-IT300A) with an acceleration of 20 kV after being coated with Au–Pt of 5 min.

Results and discussion

Chemical structures of polymers

The synthetic routes for PAN macromonomer and graft copolymer are shown in Scheme 1. The chemical structures of PAN-Br, PAN macromonomer and graft copolymer were characterized by FTIR and ^1H NMR, which can be seen in Fig. 1. In Fig. 1a, the absorption bands of the stretching vibration and bending vibration of CH_2 are observed at 2960 and 1470 cm^{-1} , respectively (Ouyang et al. 2009). The peak at 2246 cm^{-1} is assigned to stretching vibration of nitrile groups in PAN-Br and PAN macromonomer (Shimada et al. 1986). Peaks at 1733 and 1160 cm^{-1} correspond to the $\text{C}=\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibration of *PnBA-g-PAN* graft copolymer, respectively (Ouyang et al. 2009). In the spectrum of graft copolymer, the peak of stretching vibration of nitrile groups modified to 2323 cm^{-1} . In Fig. 1b, c, chemical shifts at 1.37–1.42 ppm can be assigned to methyl protons (H_a) from the initiator, and peaks at 3.2–3.43 ppm correspond to methenyl protons (H_d) in PAN segments (Kopeć et al. 2017; Matyjaszewski et al. 1997). In Fig. 1d, signals at 3.2–3.43 ppm can also be seen, which implies that PAN segments existed in the copolymer. With combination of FTIR spectra and GPC traces in Additional file 1: Fig. S1, graft copolymer *PnBA-g-PAN* was successfully synthesized by emulsion copolymerization in this work. The chemical composition of graft copolymer was calculated by ^1H NMR spectra according to M_n of graft copolymer and the integral area of protons (H_d and H_g) in PAN and *PnBA* segments in Fig. 1d. Molecular weight of polymers and PAN content in graft copolymer can be seen in Table 1. In addition, it can be seen from Additional file 1: Figs. S2 and S3 that ^{13}C NMR spectra of PAN-Br and PAN macromonomer are similar, which is because of overlapping of chemical shifts of carbons in carbon–carbon double bonds and cyano groups at 120–121 ppm (Karbownik et al. 2015a).

Thermal properties of polymers

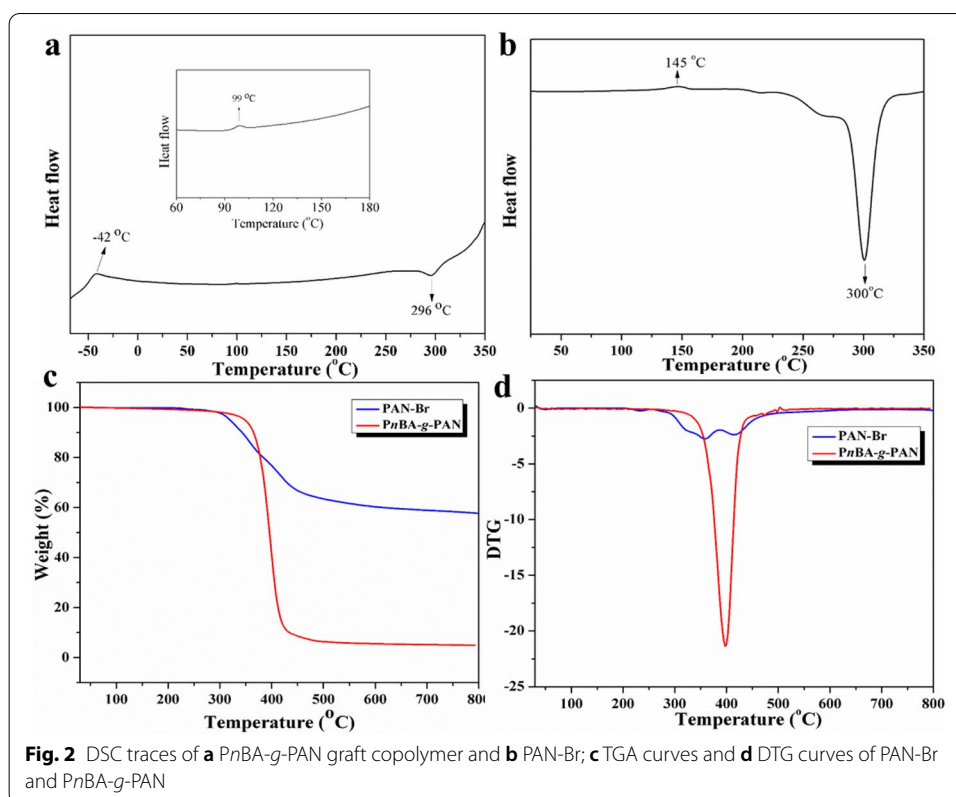
Glass transition temperature (T_g) and thermal transition of graft copolymer were investigated by DSC, which is shown in Fig. 2a. PAN-Br was also measured for comparison. It can be seen from Fig. 2a that -42°C is assigned to T_g of *PnBA* segments (Wang et al. 2014). Melting peak of PAN segments in graft copolymer decreases to 99°C , which is lower than that of pure PAN (PAN-Br) (145°C) in Fig. 2b. Moreover, at higher temperatures ($\sim 300^\circ\text{C}$), an exothermal process is observed in DSC profiles of graft copolymer and PAN-Br. These processes are related to chemical cross-linking

Table 1 Molecular weight characteristic and weight content of PAN-Br, PAN macromonomer and *PnBA-g-PAN* graft copolymer

Samples	M_n^a (g/mol)	M_w^a (g/mol)	\bar{D}^b	PAN content (wt%)
PAN-Br	3400	4400	1.3	100
PAN macromonomer	4300	7000	1.6	100
<i>PnBA-g-PAN</i>	149,400	459,600	3.1	3.6

^a The molecular weight was measured by GPC

^b The polydispersity of molecular weight of polymer

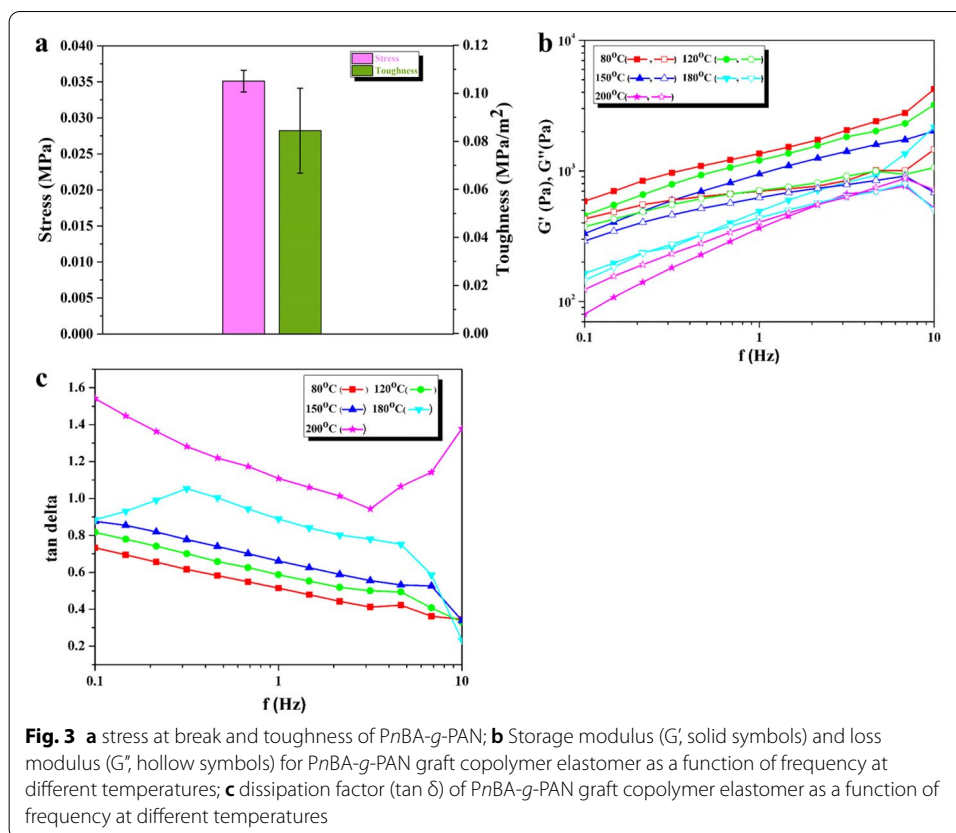


of PAN segments (Karbownik et al. 2015a). In Fig. 2c, d, TGA measurements were conducted to investigate the weight retention of PAN-Br and graft copolymer during thermal treatment. Weight loss curves show that PnBA-g-PAN experienced virtually no weight loss up to ~ 290 °C. The slight weight loss between 290 and 310 °C was attributed to the cyclization of PAN while the significant weight loss between 320 and 460 °C is associated with decomposition of PnBA segments.

Mechanical and rheological properties of graft copolymer

Mechanical properties of graft copolymer were investigated by uniaxial tensile test. The stress–strain curves for three times are shown in Additional file 1: Fig. S2, and the stress at break and toughness are shown in Fig. 3a. It can be seen that stress at break of graft copolymer is about 0.035 MPa and the graft copolymer can be stretched up to more than 450% strain. The toughness is about 0.85 MPa/m². The low stress at break and toughness are ascribed to the low content of PAN segments in the graft copolymer and we will try to increase PAN content in order to improve the physical cross-linking domains for high strength.

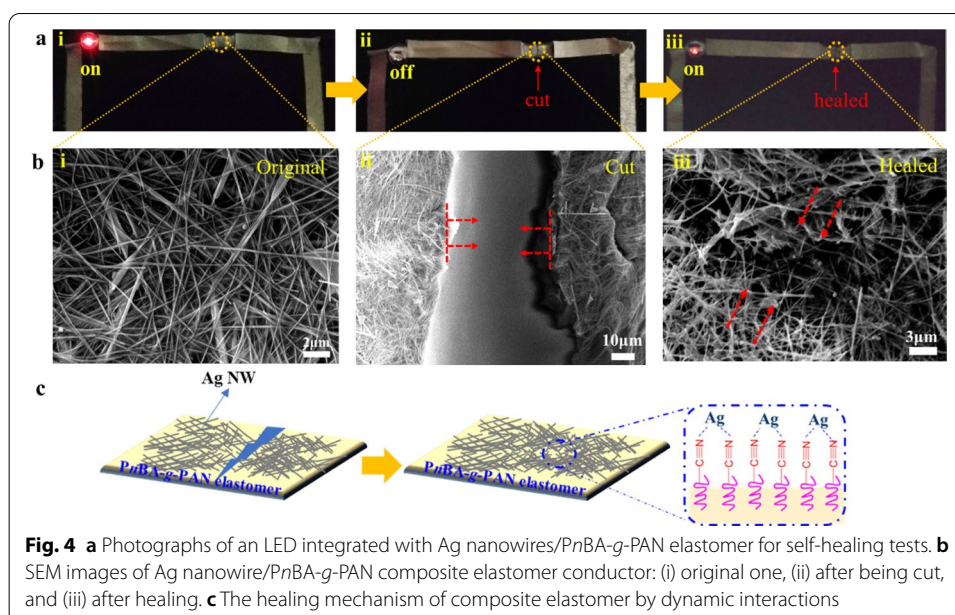
To further quantify the thermally induced rheological changes of the graft copolymer, its rheological behavior was studied by comparing their storage (G') and loss (G'') moduli as a function of frequency at different temperatures (Fig. 3b). We can see from Fig. 3b that G' was larger than G'' over the frequency range (0.1–10 Hz) at 80, 120 and 150 °C, and therefore the graft copolymer exhibited elastic property at high temperature even up to 150 °C (Singh et al. 2007). G' increased with the increment of frequency,



which was attributed to the time scale being inadequate for entangled chains to relax and reorientate at higher frequency (Wang et al. 2014). G' decreased with temperature increasing from 80 to 150 °C at 0.1–10 Hz and decreased dramatically when the temperature increased to 180 and 200 °C. Furthermore, a solid-to-liquid transition occurred, as shown in Fig. 3b, with $G'' > G'$ at 0.1–10 Hz when the temperature was increased up to 200 °C, indicating the loss of elasticity. While 180 °C, G' was larger than G'' at high frequency from 1 to 10 Hz, which demonstrated that graft copolymer was elastic. It indicates that PnBA-g-PAN elastomer softened when the temperature was increased from 80 to 180 °C, but the cyclization temperature of PAN segments decreased to 180 °C when the elastomer was in air environment and the oxidation of PAN segments existed meantime. In addition, evolution of dissipation factor ($\tan \delta$) of PnBA-g-PAN as a function of frequency at different temperatures also showed the similar results. Dissipation factor ($\tan \delta$) increased sharply and it illustrated the loss of elasticity at 200 °C.

Healability of graft copolymer composite elastomer

The graft copolymer was elastic and flexible at ambient temperature, and its utility was demonstrated for self-healable and flexible electronic conductors. This was motivated by the requirement to reduce the failure of electronic devices that is due to mechanical fracture, thereby increasing their lifetime and reliability (Yu et al. 2018; Mao et al. 2020; Yang et al. 2018). While considerable effort has been invested in covering a conductive nanowire



layer (silver nanowires or nanotubes) with self-healing materials (Li et al. 2014; Zhou et al. 2019), the direct application of *PnBA-g-PAN* was carried out with coating silver nanowires (AgNWs) onto its surface to obtain a healable conductor.

As illustrated in Fig. 4a, AgNWs@*PnBA-g-PAN* composite elastomer was connected to a light-emitting diode (LED) and a power source. The LED was powered with a DC voltage of 5 V because of the electrical conductivity of the silver nanowires (Fig. 4a, i). When the Ag nanowires@*PnBA-g-PAN* composite elastomer was cut, the LED went off (Fig. 4a, ii). It then re-lit after the cut self-healed for 16 h at 50 °C (Fig. 4a, iii). The restoration of conductivity was attributed to the reconnection of the silver nanowires. SEM images in Fig. 4b were taken to investigate the healing process. Before cutting, a high density of wire-wire junctions between AgNWs were bonded by the composite elastomer, yielding electrical conductivity (Fig. 4b, i). When a cut was made across the surface layer, AgNWs were broken (Fig. 4b, ii). Under 50 °C for several hours, segments of *PnBA-g-PAN* moved to connect with each other and Ag NWs coordinated with cyano groups (Fig. 4c) (Karbownik et al. 2015b), resulting in the re-contact of AgNWs and self-healing of the cut (Fig. 4b, iii).

Conclusions

In summary, we have demonstrated a strategy for synthesis of polar graft copolymer with *PnBA* as backbones and PAN as side chains. The chemical structure and mechanical properties were investigated, and the graft copolymer possessed elasticity until 180 °C because of cyclization of cyano groups. The Ag nanowires@*PnBA-g-PAN* composite elastomer was developed, and the resulting material exhibited autonomic healing property on account of segments' flexibility and dynamic interaction between AgNWs and cyano groups. This is a general method for the generation of elastomer capable of high temperature elasticity and fast self-healing. The composite elastomer has potential application in flexible electronic conductor.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40691-020-00235-4>.

Additional file 1. The supplementary information includes: GPC traces of PAN-Br, PAN macromonomer and PnBA-g-PAN graft copolymer; ^{13}C NMR spectra of PAN-Br and PnBA-g-PAN; Stress-strain curves of PnBA-g-PAN graft copolymer.

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Authors' contributions

YZ: Methodology, Writing-original draft. DX: Investigation. ST: Methodology, Visualization. ML: Investigation. WW: Conceptualization, Supervision, Writing-review & editing. KL: Methodology, Funding acquisition. All authors read and approved the final manuscript.

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Availability of data and material

All data generated or analyzed during this study are included in this published article and its supplementary information files.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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