Supporting information

Graft copolymer elastomers with polar polyacrylonitrile as semi-crystalline side chains: excellent toughness and healability

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1. Chemicals

Methyl acrylate (MA, purity \geq 99.7%), acrylonitrile (AN, purity \geq 99.5%), acrylic acid (AA, purity \geq 97%), N,N-dimethylformamide (DMF, analytical reagent), potassium hydroxide (KOH, purity \geq 95%), methanol (analytical reagent), sodium dodecylbenzene sulfonate (SDS, purity \geq 97%) and AgNO₃ (purity \geq 98%) were purchased from Sinopharm. 2-bromopropionitrile (CH₃CH(Br)CN), cuprous bromide (CuBr, purity \geq 97%), ascorbic acid (Vc, purity \geq 97%), hexadecane (HD, purity \geq 97%) and azobisisobutyronitrile (AIBN, purity \geq 99%) were purchased from Aladdin. N, N, N', N'', N''-pentamethyldiethylenetriamine (PMDETA, purity \geq 98%) was purchased from TCI. Methyl acrylate and acrylonitrile were purified by a basic alumina column to remove the stabilizer, and cuprous bromide was purified by glacial acetic acid to remove the oxidized copper oxide. AIBN was recrystallized from methanol. Deionized water (DI water) and other reagents were used as received.

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2. Experimental section

Table S1 Formulation and molecular characteristic of the polymerization for synthesis of PAN-Br ^a								
Samples	AN(g)	CH ₃ CH(Br)CN(g)	PMDETA(g)	CuBr(g)	n(AN):n(CH ₃ CH(Br)CN)	$M_{\rm n}({\rm g/mol})$	$M_{\rm w}({ m g/mol})$	Đ
PAN-Br-1	21.196	0.276	0.176	0.143	194:1	3300	4400	1.34
PAN-Br-2	21.215	0.626	0.173	0.143	86:1	5700	7200	1.26

^aThe reaction temperature was 80 °C and the reaction time was 8 h.

Samples	PAN-Br(g)	Potassium acrylate (g)	n(PAN):n(KA)	$M_{\rm n}({\rm g/mol})$	$M_{\rm w}({\rm g/mol})$	Đ
PAN macromonomer -1	1.006	0.082	1:4	4200	7000	1.65
PAN macromonomer -2	1.005	0.106	1:5	5800	8600	1.48

Table S2 The formulation and molecular characteristic for polyacrylonitrile macromonomers

Samples	PAN macromonomer	MA	AIBN	HD	SDS	DI H ₂ O
	(g)	(g)	(g)	(g)	(g)	(g)
PMA-g-PAN-1	0.403	4.03	0.062	0.065	0.403	20
PMA-g-PAN-2	0.403	4.0	0.06	0.06	0.402	20
PMA-g-PAN-3	0.602	3.025	0.036	0.036	0.242	24

Table S3 The polymerization formulation for PMA-g-PAN graft copolymers

Table S4 Formulation for the fabrication of Ag⁺/PMA-g-PAN-3 composite elastomers

Samples ^a	m(PMA-g-PAN-3)	m(AgNO ₃)	DMF
	(mg)	(mg)	(ml)
5 wt%	82.86	0.785	1
10 wt%	82.79	1.592	1
20 wt%	82.83	3.186	1

 a5 wt%, 10 wt% and 20 wt% mean the weight ratio of Ag^+ to PAN segments.

3. Results and discussion



Figure S1 The latex particles distribution of PMA-*g*-PAN-2. (**Laser Light Scattering** (**LLS**). The latex was measured at 25 °C using Zetasizer Nano ZS 3600. A laser of 633 nm wavelength was used as the light source.)



Figure S2 GPC profiles of PAN-Br-1, PAN macromonomer-1 and PMA-g-PAN-1.



Figure S3 FTIR spectra of different polymers.



Figure S4 ¹H NMR spectrum of PAN-Br-1 for calculation of molecular weight.



Figure S5 ¹H NMR spectrum of PAN macromonomer-1 for calculation of molecular weight.



Figure S6 ¹H NMR spectrum of PAN-Br-2.



Figure S7 ¹H NMR spectrum of PAN macromonomer-2.



Figure S9 ¹H NMR spectrum of PAM-*g*-PAN-3.



Figure S10 ¹³C NMR spectrum of PAN-Br-1.



Figure S11 ¹³C NMR spectrum of PAN macromonomer-1.



Figure S12 ¹³C NMR spectrum of PAN-Br-2.



Figure S13 ¹³C NMR spectrum of PAN macromonomer-2.



Figure S14 (a) AFM height image of PMA-*g*-PAN-3 formed by spin-coating of dilute solution (0.002 mg/ml). (b) AFM height image of PMA-*g*-PAN-3 formed by spin-coating of dilute solution (0.001 mg/ml). (c) 3D AFM image of (a).



Figure S15 (a) Height image and (b) phase image of microphase separation morphology of PMA-*g*-PAN-2 membrane after being annealed for 12h at 150 °C.



Figure S16 Stress-strain curves of graft copolymer elastomers. Each sample was measured for three times.



Figure S17 The cyclic uniaxial stress-strain curves for PMA-*g*-PAN-2 stretched to (a) 300% and (b) 400% strain, respectively.



Figure S18 The pictures of PMA-g-PAN-3elastomers (a) before and (b) after being stretched.



Figure S19 Optical microscope photographs of damaged and healed samples. (a) The surface image of PMA-*g*-PAN-2 elastomer before being cut. (b) The top view image of cracks in PMA-*g*-PAN-2 elastomer after being cut. The top view images of cracks after being healed for (c) 5h, (d) 10h, (e) 15h and (f) 35h at 30 °C, respectively.



Figure S20 Optical microscope photographs of damaged and healed samples. (a) The surface image of PMA-g-PAN-2 elastomer before being cut. (b) The top view image of cracks in PMA-g-PAN-2 elastomer after being cut. The top view images of cracks after being healed for (c) 5h, (d) 10h, (e) 15h and (f) 35h at 70 °C, respectively.



Figure S21 Optical microscope photographs of damaged and healed samples. (a) The surface image of PMA-*g*-PAN-2 elastomer before being cut. (b) The top view image of cracks in PMA-*g*-PAN-2 elastomer after being cut. The top view images of cracks after being healed for (c) 5h, (d) 10h, (e) 15h and (f) 35h at 90 °C, respectively.



Figure S22 Fluorescence microscope photographs of cracks in PMA-g-PAN-2 elastomer after being healed for (a) 2h and (b) 4h at 50 °C, respectively.



Figure S23 Optical microscope photographs of damaged and healed samples. (a) The surface image of PMA-*g*-PAN-1 elastomer (PAN: 1.5 wt%) before being cut. (b) The top view image of cracks in PMA-*g*-PAN-1 elastomer after being cut. The top view images of cracks after being healed for (c) 5h, (d) 10h, (e) 15h and (f) 35h at 50 °C, respectively.



Figure S24 Optical microscope photographs of damaged and healed samples. (a) The surface image of PMA-*g*-PAN-3 elastomer (PAN: 18.8 wt%) before being cut. The top view image of cracks in PMA-*g*-PAN-3 elastomer after being healed for (b) 5 h, (c) 10 h, (d) 15 h, (e) 20 h and (f) 68 h at 50 °C, respectively.



Figure S25 (a, b) Photographs of PMA-*g*-PAN-3 elastomer captured (a) before and (b) after being cut into two pieces. (c) Photos of the 1 h healed PMA-*g*-PAN-2 sample when lifting object.

References

[1]Wang W; Wang W; Lu X, et al., Synthesis and Characterization of Comb and Centipede Multigraft Copolymers P*n*BA-*g*-PS with High Molecular Weight Using Miniemulsion Polymerization[J], Macromolecules, 2014, 47 (21), 7284-7295.