Electronic Supporting Information (ESI) for

Interpenetrating Covalent Adaptable Networks with Enhanced Mechanical Properties and Facile Reprocessability and Recyclability

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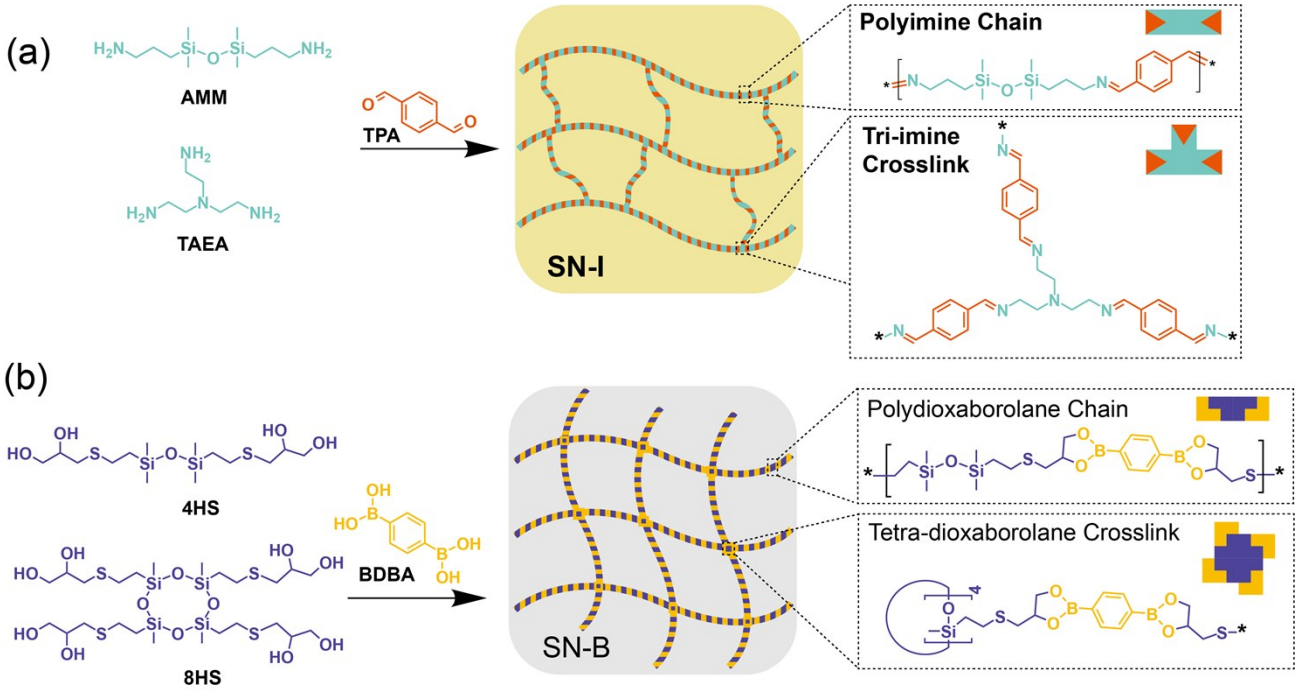
PART S1. Synthesis of Covalent Adaptable Single Network



Scheme S1. Synthesis of covalent adaptable single network: (a) imine-based single network (SN-I), (b) boronic-acid based single network (SN-B).

Imine-based single network (SN-I): As is illustrated in **Scheme S1a**, SN-I was synthesized *via* imine condensation of small-molecular amines and aldehydes according to our previous report[1]. Briefly, TAEA (0.97 g, 6.7 mmol), AMM (2.48 g, 10 mmol) and TPA (2.68 g, 20 mmol) were dissolved in THF separately and then mixed. After 1 h stirring at ambient conditions, the solvents were evaporated at 80 ^{o}C for 6 h. The resultant orange transparent film was further heated in a vacuum oven at 80 ^{o}C for 12 h for the complete curing of polyimine network.

Boronic-ester-based single network (SN-B): As is illustrated in **Scheme S1b**, SN-B was synthesized *via* esterification of small-molecular diols and boronic-acids according to our previous report[2]. Briefly, **4HS** (4.02 g, 10 mmol), **8HS** (3.88 g, 5 mmol) and BDBA (2.68 g, 20 mmol) were dissolved in THF separately and then mixed. After 1 h stirring at ambient conditions, the solvents were evaporated at 80 ^{o}C for 6 h. The resultant colorless transparent

film was further heated in a vacuum oven at 80 ^{o}C for 12 h for the complete curing of polydioxaborolane network.

References

[1]. Lei, Y.; Shan, S.; Lin, Y.; Zhang, A. Network Reconfiguration and Unusual Stress Intensification of a Dynamic Reversible Polyimine Elastomer. *Polymer* **2020**, *186*, 122031.

[2]. Lei, Y.; Zhang, A.; Lin, Y. Reprocessability of Dynamic Polydioxaborolane Networks Activated by Heat, Moisture and Mechanical Force. *Polymer* **2020**, *209*, 123037.

PART S2. Supporting Figures

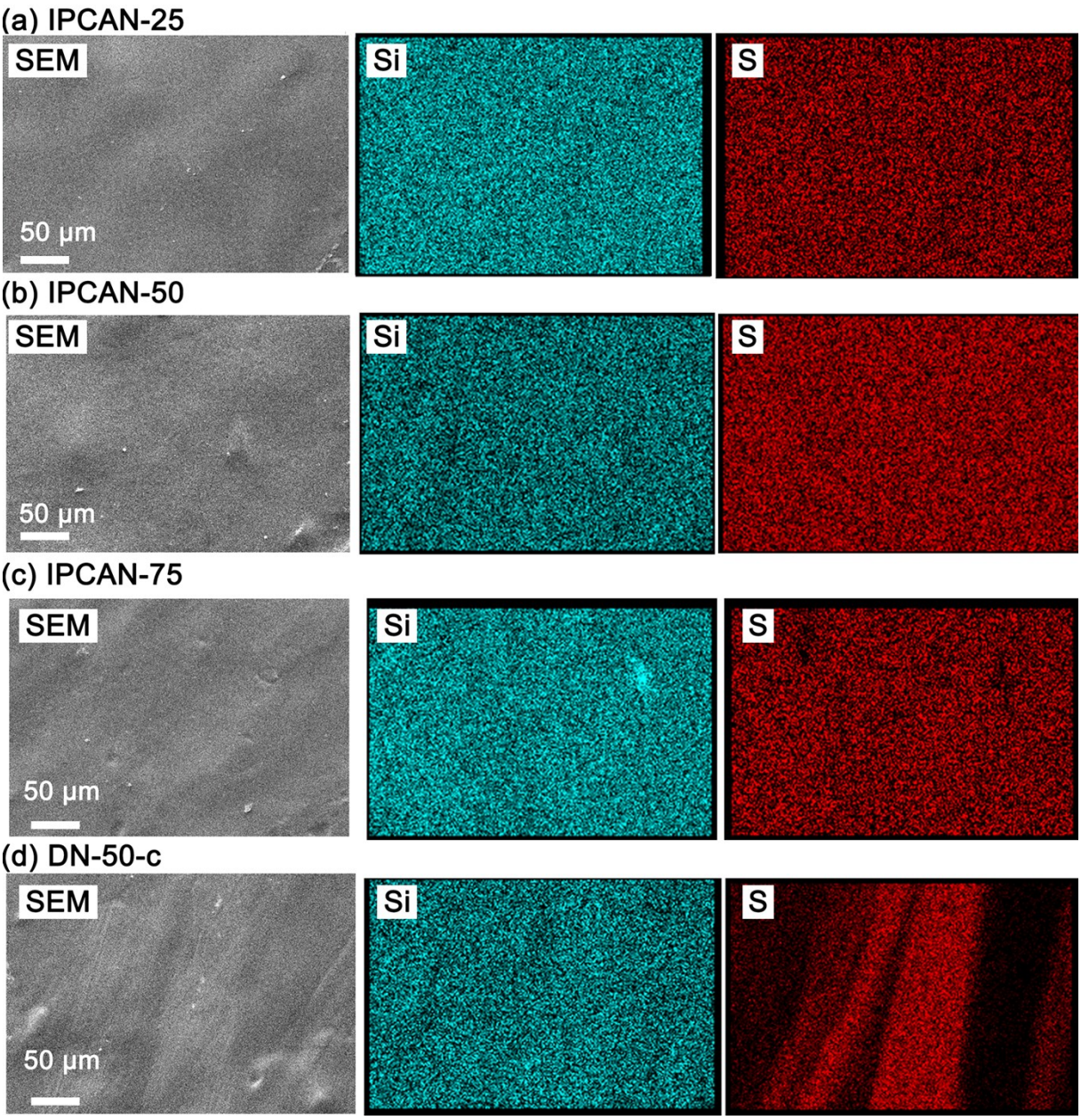


Fig. S1. SEM photos and elemental mapping of IPCANs and DN-50-c.

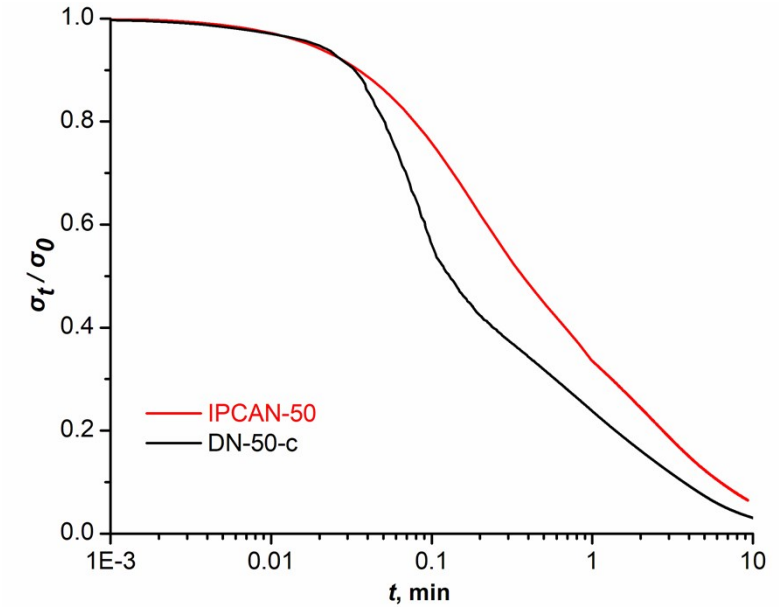


Fig. S2. Tensile stress relaxation curves of IPCAN-50 and DN-50-c.

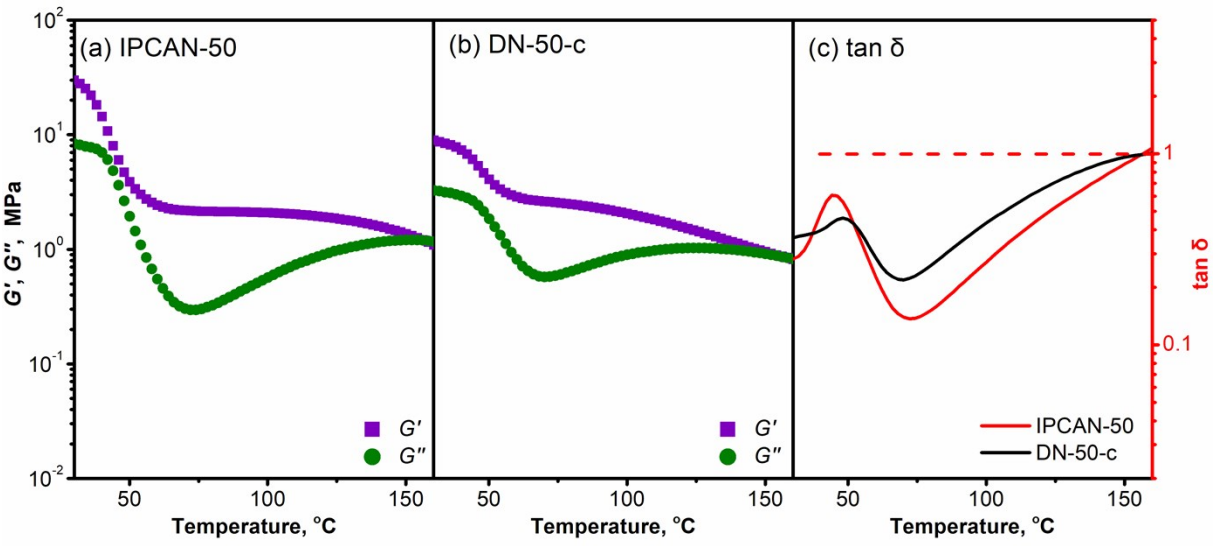


Fig. S3. Temperature dependency of storage modulus (*G'*), loss modulus (*G''*) for (a) IPCAN-50, (b) DN-50-c and (c) plot of tan δ against temperature for IPCAN-50 and DN-50-c.