Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Reversible Dual Crosslinking in Anthracenyl Functionalized Butyl Elastomer Based on Ionic and (4+4) Cycloaddition Approaches.

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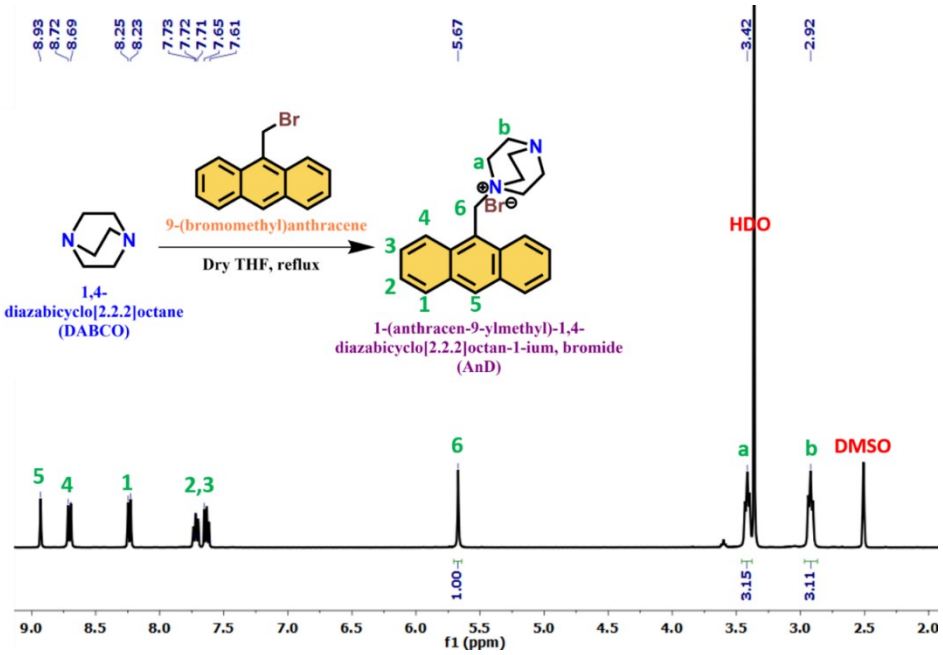

Fig. S1. ^{1}H NMR spectrum of AnD in DMSO-d_6.

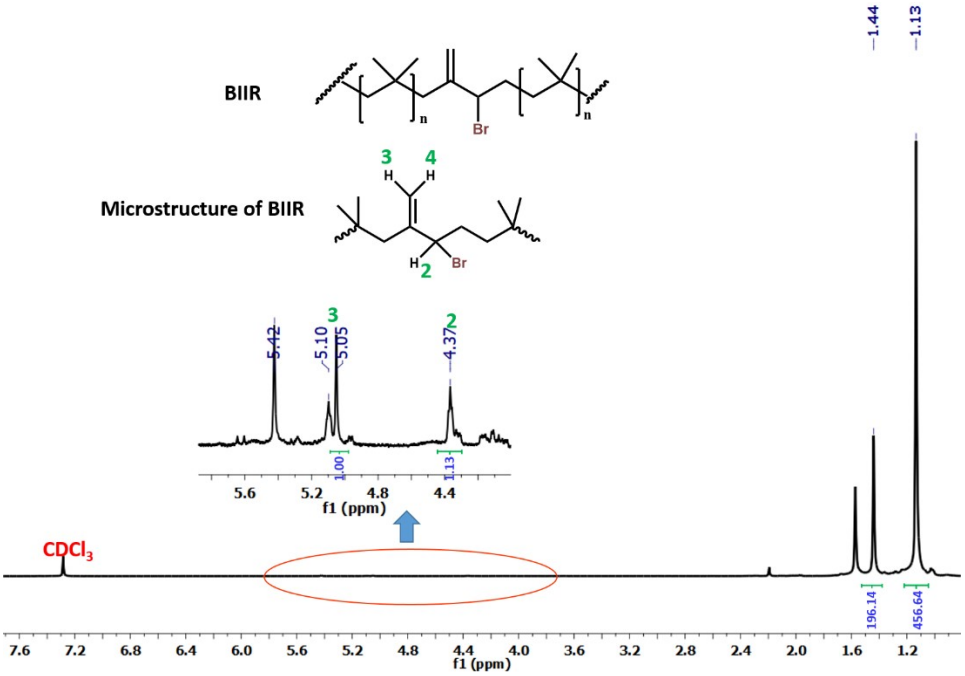

Fig. S2. ^{1}H NMR spectrum of BIIR in $CDCl_3$.

Calculation of bromine contain in BIIR:

$$BXi = \frac{I_{H3} + I_{H2}}{I_{CH3} + I_{CH2}} \text{X } 100 = 0.8 \text{ mol\%} \text{.....(S1)}$$

The weight percentage (wt%) was measured by the following Eqn 2.

$$W_{Br} = \frac{M_{Br}}{M_{But}\, X\, {}^{1}/_{2}(I_{CH3} + I_{CH2})} \text{ X } 100 = 1.14 \text{ wt\%} \text{..... (S2)}$$

Where the weight of the butyl group [M_{But}] = 56 g and the molar mass of the bromine group [M_{Br}] = 80 a.m.u**.**

Table S1. The integral value of the ^{1}H NMR spectrum of BIIR

Nmr signal	Signal integral	Integral value for each proton
H-3 (δ = 5.05 ppm)	1.00	1.00
H-2 (δ = 4.37 ppm)	1.13	1.13
CH_2 (δ =1.13 ppm)	196.14	98.02
CH_3 (δ =1.44 ppm)	456.64	152.21

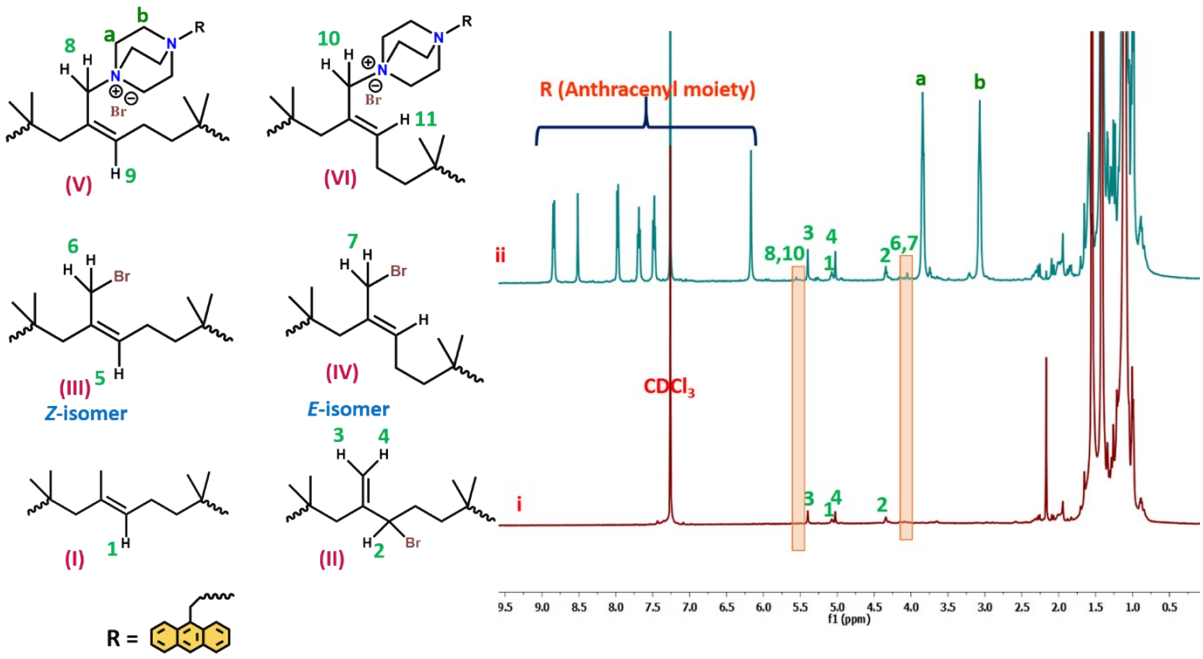

Fig. S3. ^{1}H NMR spectra of the pure BIIR (i) and BIIR_AnD (ii) in $CDCl_3$, along with chemical structures.

The signal at around 5.1 ppm representing the non-brominated isoprene units remains consistent in all samples due to their lack of reactivity. The distinctive peaks of H8 and H10 about 5.6 ppm, associated with the methylene group linked to AnD post-reaction, originate from the signals of isomerized protons H5 and H6 at 4.1 ppm. The distinctive signals of H8 and H10 in pure BIIR are downfield displaced compared to H3 and H4 due to the influence of AnD. The degree of grafting[1,2] was estimated 18%, using the signal intensities of proton H3, H4 (unconverted isomers), and H8 and H10 (AnD replaced sites).

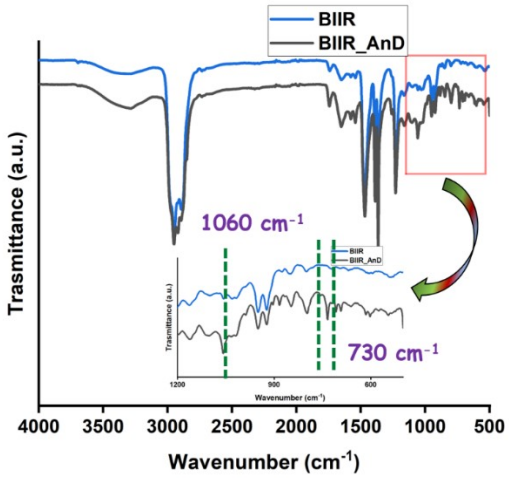

Fig. S4. FTIR spectra of BIIR and BIIR_AnD with inset image of 1200-500 cm^{-1} wavenumber.

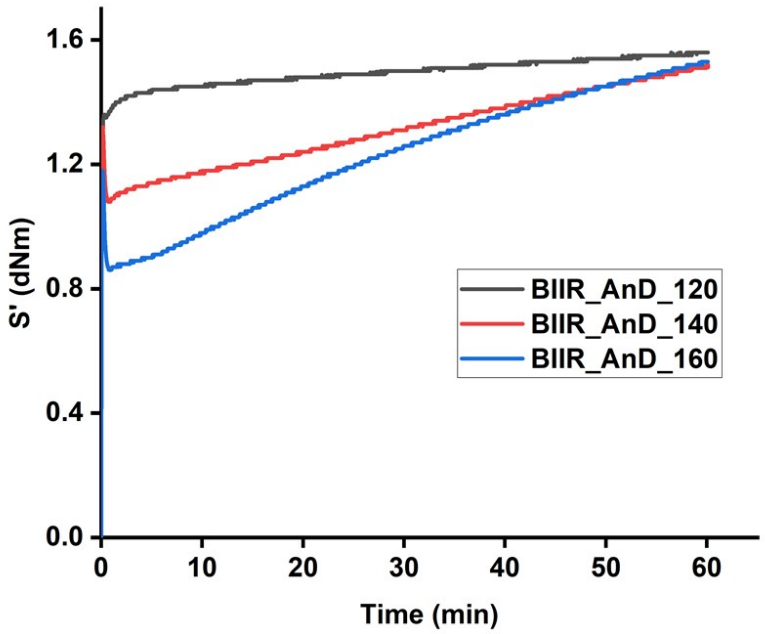

Fig. S5. Curing behaviour of the AnD crosslinked BIIR at different temperatures.

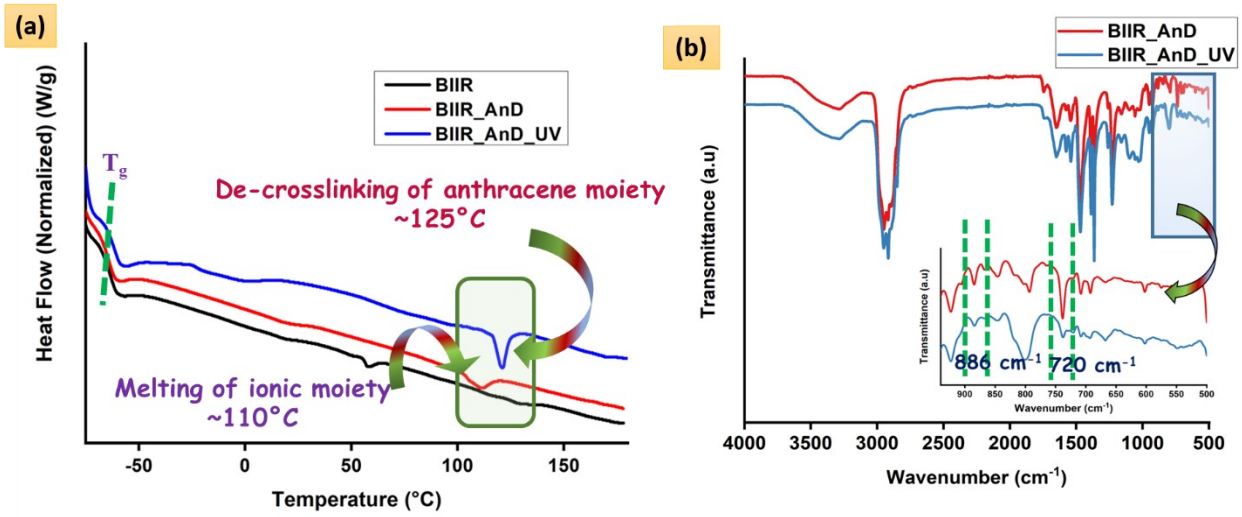

Fig. S6. (a) DSC curves of virgin BIIR, BIIR_AnD (2nd heating curve) and BIIR_AnD_UV (1st heating curve); (b) FTIR spectra of BIIR_AnD and BIIR_AnD_UV with inset image of 950-500 cm^{-1} wavenumber.

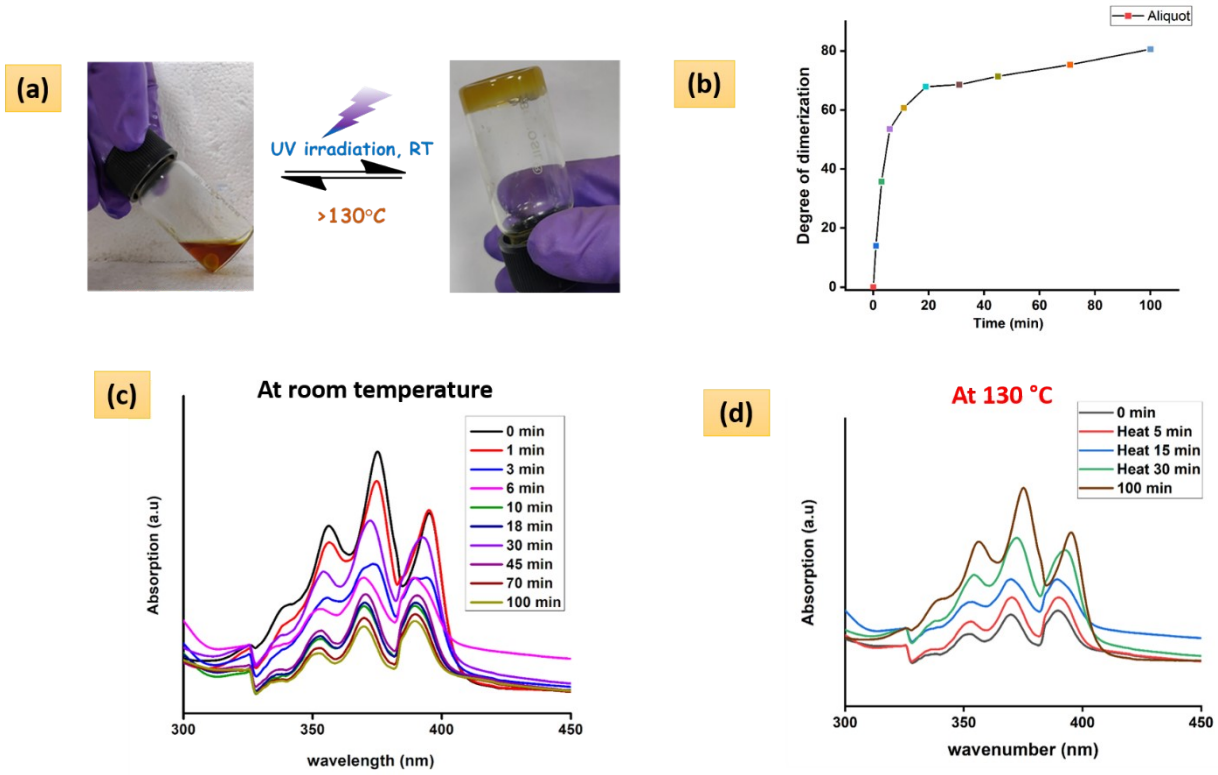

Fig. S7. (a) Inverted Vial Tests for rubber solution before and after UV Light Irradiation; (b) The dimerization degree (D) of AnD solution after irradiation w.r.t time; UV spectrum of (c) dimerization and (d) de-dimerization of AnD solution w.r.t time at RT and 130 °C, respectively.

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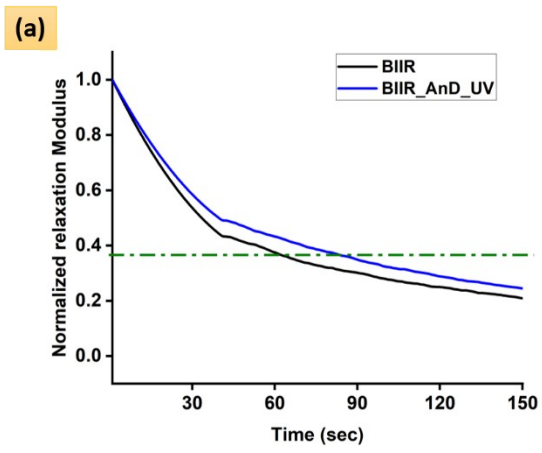
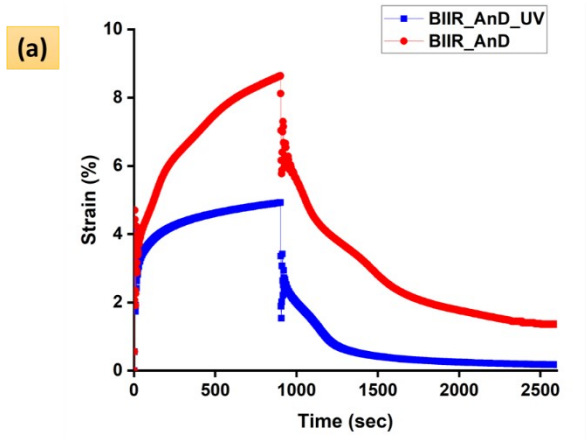


(b)

Sample name	Normalized relaxation modulus	Time (sec)
Pristine BIIR	0.367	62
BIIR_AnD_UV	0.367	85

Fig. S8. (a) Stress relaxation curve of pristine and dual crosslinked BIIR. (d) The stress relaxation time w.r.t. normalized relaxation modulus.



(b)

Sample name	Recovered extension (%)	Permanent extension (%)
BIIR_AnD	65.4	1.3
BIIR_AnD_UV	93.2	0.2

Fig. S9. (a) Torsional creep-recovery curve of BIIR_AnD and BIIR_AnD_UV. (b) The properties of creep of two samples.

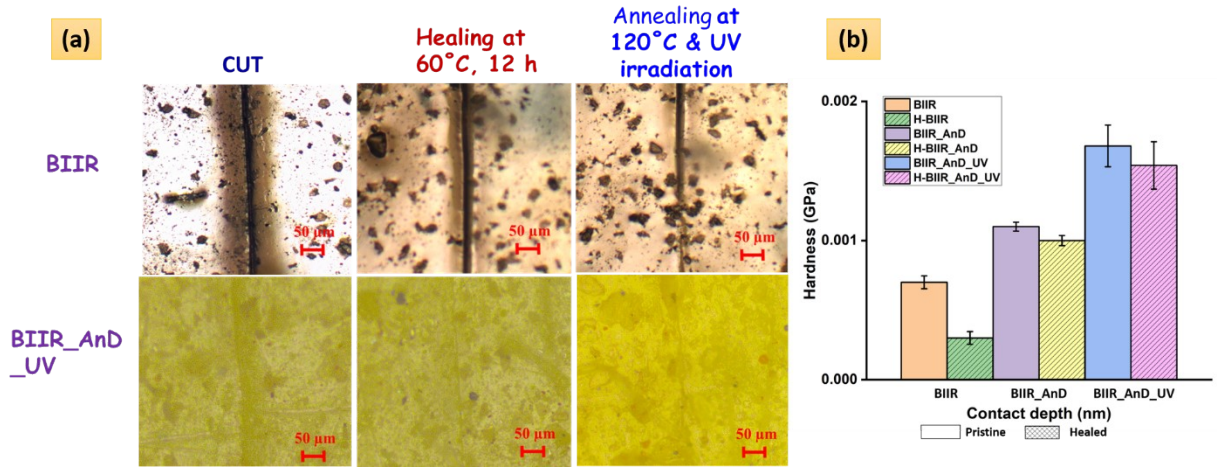


Fig. S10.(a) Optical microscopic images of scratched and healed films of BIIR (b)The hardness of pristine, modified and repaired BIIR.

References:

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