Supplementary information

Triazolinedione-functionalized isoprene rubber composites with self-adhesion *via* cross-linking with zinc dimethacrylate

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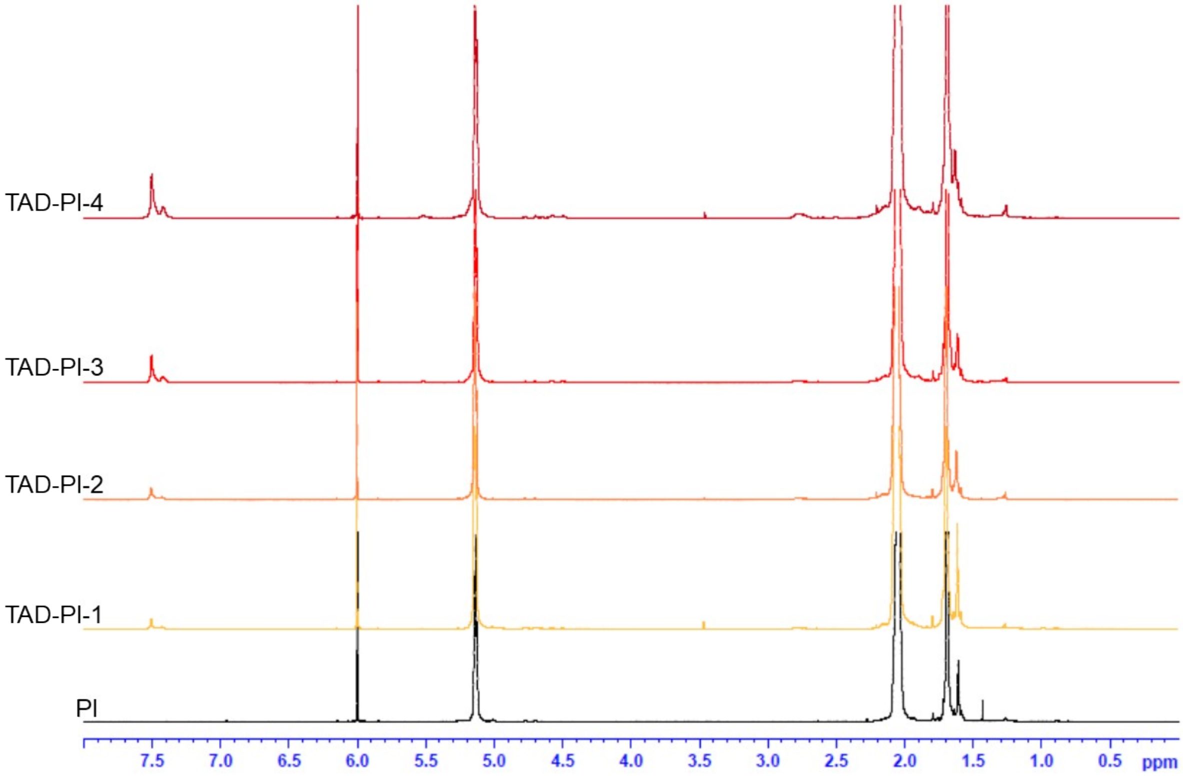

Fig. S1 ^{1}H NMR spectra of PI (black line), TAD-PI-1 (yellow line), TAD-PI-2 (orange line), TAD-PI-3 (red line) and TAD-PI-4 (dark red line) ($C_2D_2Cl_4$, 600 MHz).

The ratio of isoprene unit and TAD unit were calculated by the following equations respectively. Here, *I (A)* and *I (B)* represent the integral ratio of δ 7.63–7.30 ppm (aromatic 5H of phenyl group in TAD unit), 5.14 ppm (1H of *cis*-1,4-isoprene olefinic unit), respectively.

$$Isoprene\ unit\ (mol\%) = \frac{I(B)}{I(A)/5 + I(B)} \times 100\ (mol\%) \tag{S1}$$

$$TAD\ unit\ (mol\%) = \frac{I\ (A)/5}{I(A)/5 + I\ (B)} \times 100\ (mol\%) \tag{S2}$$

Modification efficiency is determined by following equation.

$$Modification\ efficiency\ (\%) = \frac{TAD\ unit}{Loading\ PhTAD\ ratio\ to\ isoprene\ monomer\ unit} \times 100\ (\%)$$

(S3)

Table S1 Loading TAD ratio to isoprene monomer unit, integral ratio, and modification-efficiency

Polymer	Loading PhTAD ratio to isoprene monomer unit (mol%)	*I (A)*	*I (B)*	Modification efficiency (%)
PI	0	0	1.00	0
TAD-PI-1	1.0	0.042	1.00	83.3
TAD-PI-2	2.0	0.087	1.00	85.5
TAD-PI-3	3.5	0.160	1.00	88.8
TAD-PI-4	5.0	0.226	1.00	86.5

Table S2 Comparison of M_n values measured by GPC and MALS

Polymer	M_n (10^3g/mol) measured by GPC	M_n (10^3g/mol) measured by MALS
PI	496	911
TAD-PI-1	365	368
TAD-PI-2	266	353
TAD-PI-3	122	348
TAD-PI-4	80	339

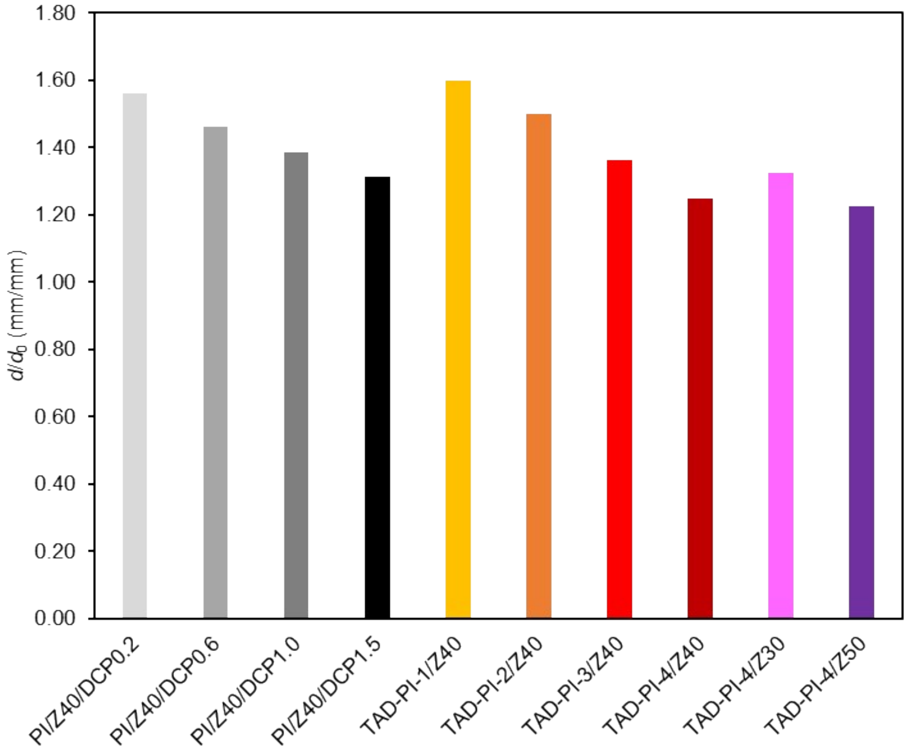

Fig. S2 Swelling degree of each sample after immersion in *n*-heptane for 4 days. Disc-shaped cross-linked specimens of 8.0 mm diameter were immersed in *n*-heptane for 4 days at r.t. and the swelling degree of specimens is defined as the length swelling ratio ($\lambda_s=d/d_0$; d_0 and d represent the diameter of a disc-shaped specimen before and after swelling, respectively).

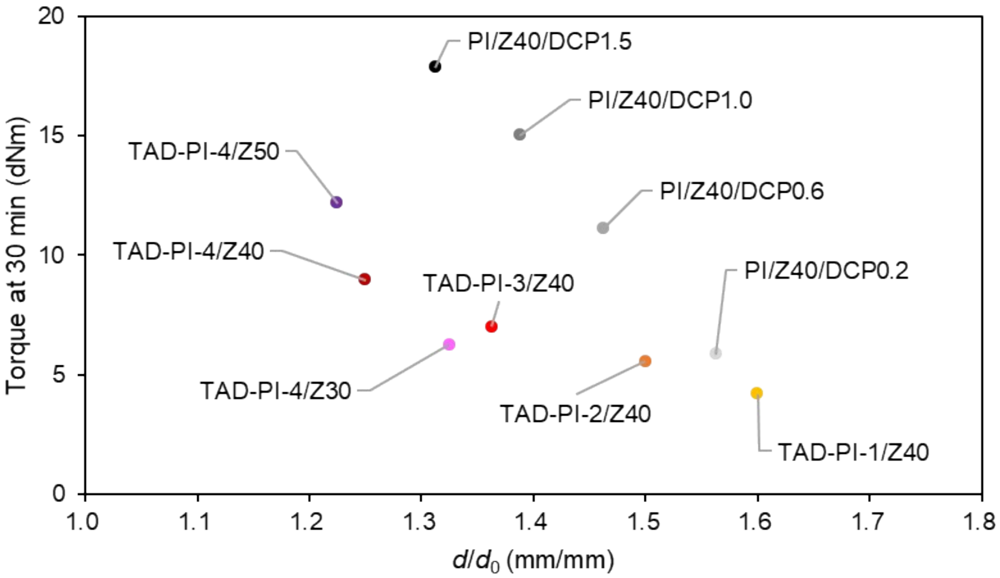

Fig. S3 Relationship between torque at 30 min measured at 145 °C on the moving die rheometer and swelling rate with *n*-heptane.

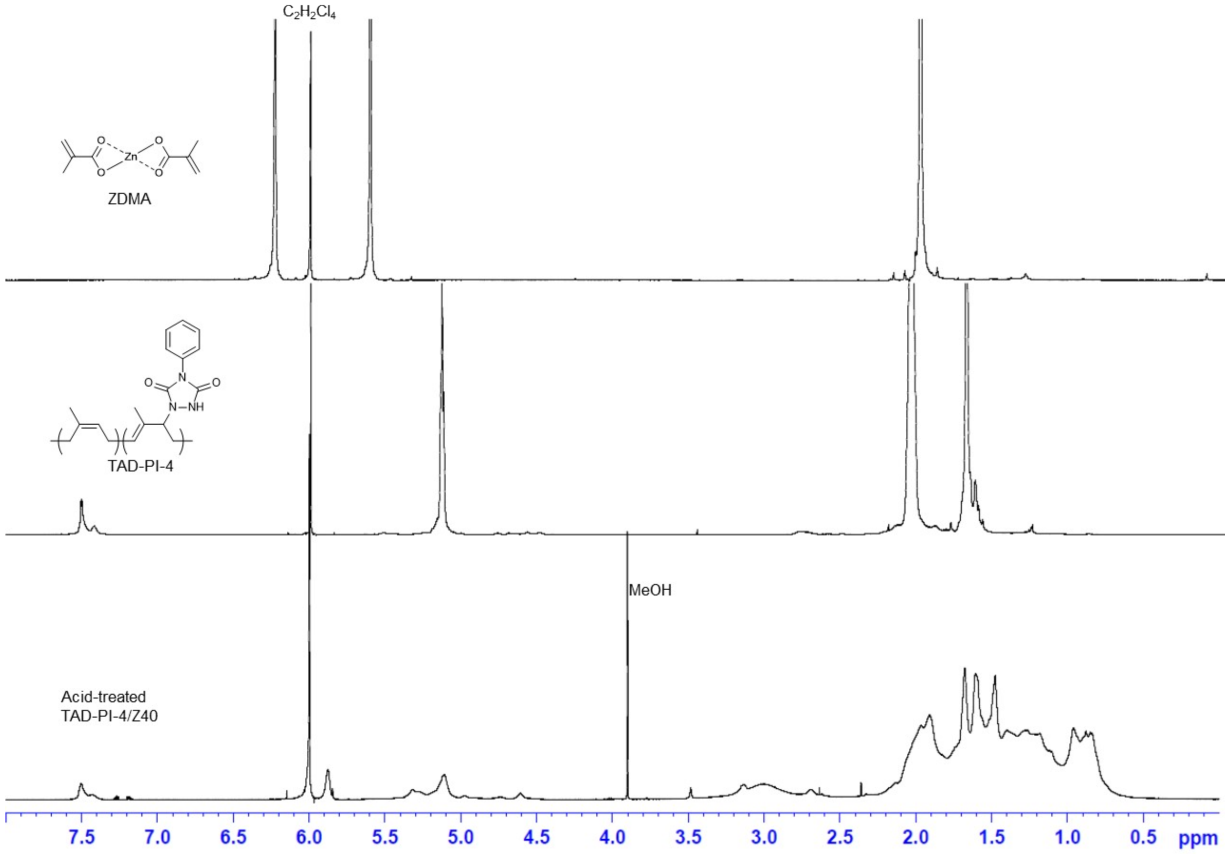

Fig. S4 ^{1}H NMR spectra of ZDMA (top), TAD-PI-4 (middle) and acid-treated TAD-PI-4/Z40 (bottom) ($C_2D_2Cl_4$, 600 MHz).

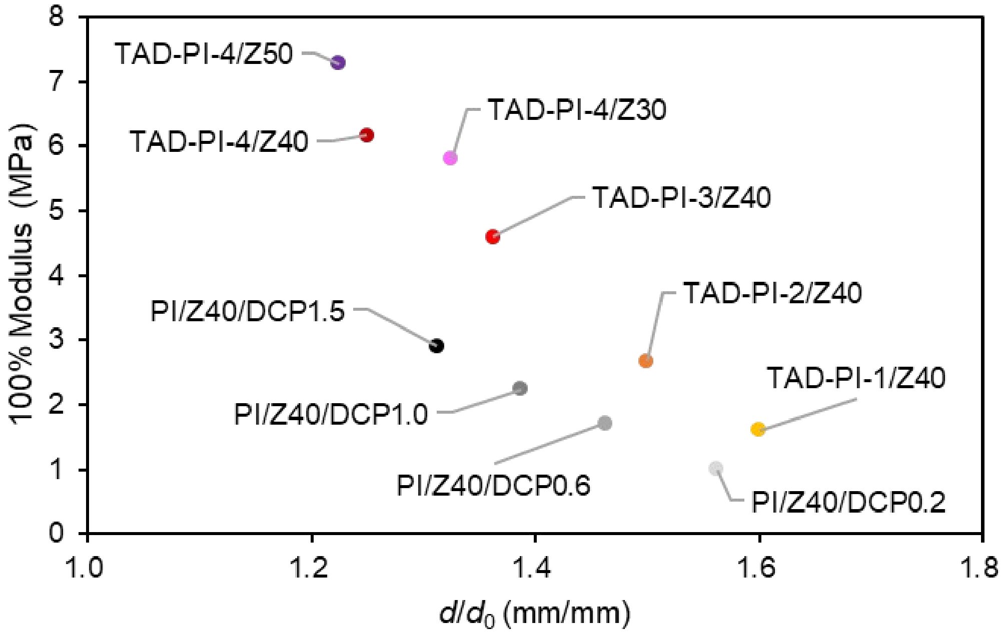

Fig. S5 Relationship between 100% modulus and swelling rate with *n*-heptane.

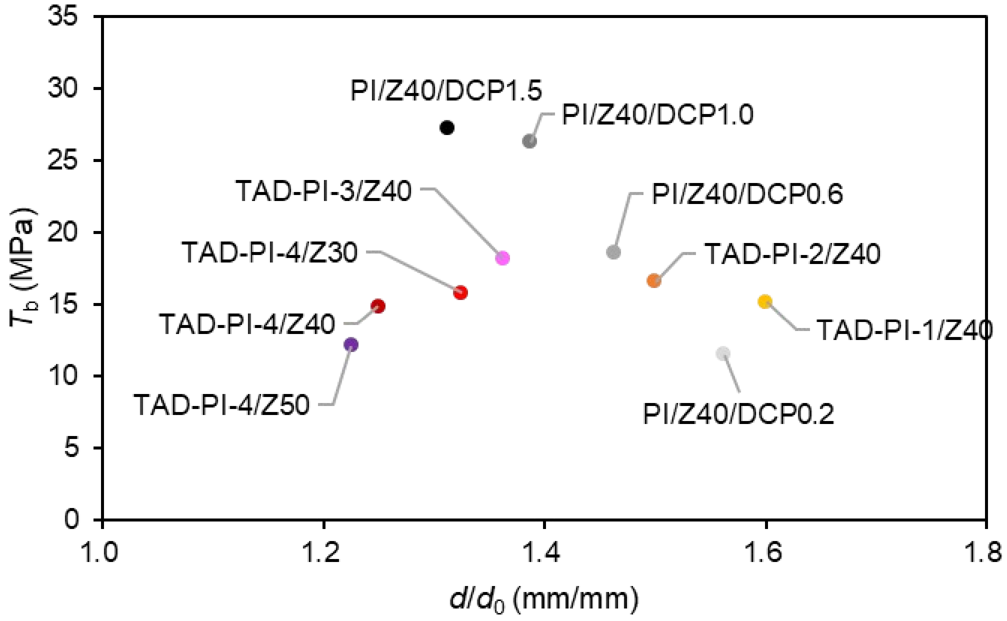

Fig. S6 Relationship between T_b and swelling rate with *n*-heptane.

To measure the degree of strain induced crystallization for each sample, two-dimensional wide-angle X-ray scattering (2D-WAXS) images were obtained while stretching the samples. The 2D-WAXS images were obtained using NANO-Viewer (Rigaku), and Cu-Kα ray (wavelength: 0.1541 nm) was used with operating at 40 kV and 30 mA. Dumbbell-shaped ISO 37–4 specimens of each cured rubber sample were elongated horizontally in a symmetrical manner with a self-made device. The elongation speed was 0.05 mm/s, and 2D-WAXS images were continuously acquired at every 2.74% strain. The obtained 2D-WAXS images were integrated in the equatorial direction using an analysis software (Rigaku 2DP), and the scattering intensity was converted into a one-dimensional profile for the scattering vector q. The obtained one-dimensional profiles were separated into amorphous scattering and crystalline reflections using a fitting software (Fityk). The degree of crystallinity was determined by integrating the amorphous and crystalline scattering intensities in the range $0 < q < 20.4$ nm^{-1}, and the total crystalline scattering intensity was calculated. The degree of strain induced crystallization at 170% strain as a representative value of strain induced crystallinity is summarized in Fig. S7. The results using samples containing TAD-PI-3 and TAD-PI-4 were not described because these samples were broken before the crystallization.

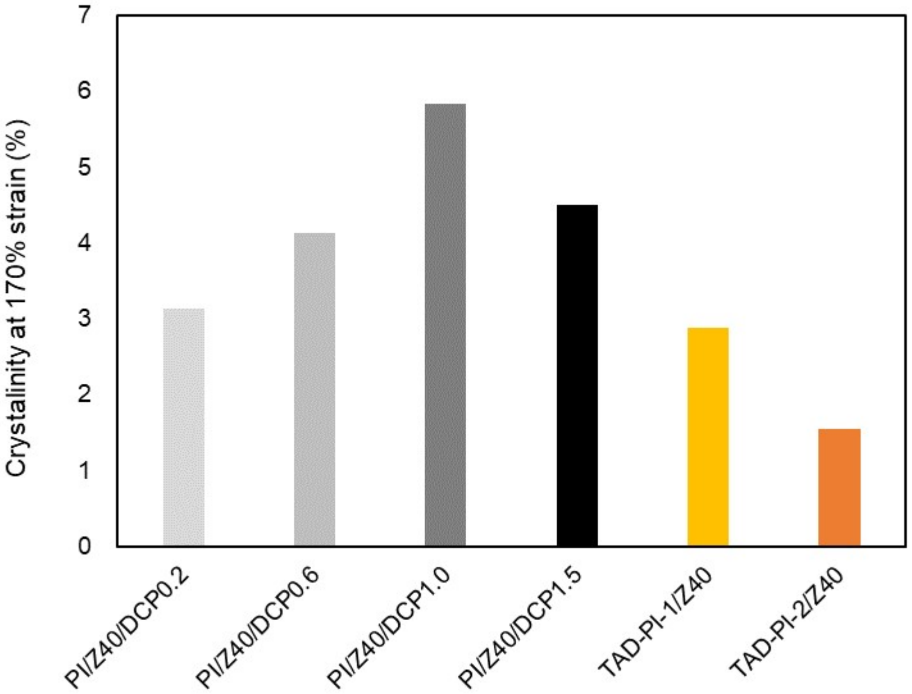

Fig. S7□The degree of strain induced crystallization at 170% strain.