

Supporting information

Relationship between the Relative Dielectric Constant and the Monomer Sequence of Acrylonitrile in Rubber

Ryosuke Matsuno,^{1,2} Yuusaku Takagaki³, Takamasa Ito³, Hitoshi Yoshikawa³, Shigeaki Takamatsu³ and Atsushi Takahara^{2}*

¹*KOINE project Division Global Innovation Center, Kyushu University, 6-1 Kasuga-koen, Kasuga-city, Fukuoka 816-8580, Japan.*

²*Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan.*

³*Sumitomo Riko Company, 1 Higashi 3-chome, Komaki, Aichi 485-8550, Japan.*

Figure S1. Sample preparation for measurement of relative dielectric constants

Figure S2. Time dependence of the residual monomer ratio of AN and VBE.

Figure S3. Plot of in feed ratio and in polymer ratio in each composition of VBE: AN.

Figure S4. Dimer model for calculation of C-N bond length.

Table1-4. The weight average molecular weight of copolymers.

Sample preparation for measurement of relative dielectric constants

The dielectric film was cut into 50 mm × 25 mm sheets. Electrode films (40 mm × 15 mm), consisting of acrylic rubber with carbon black, was placed on a 50 mm × 25 mm PET film. Copper foil was attached to the upper end of the electrode. The dielectric film was then applied on the PET film containing the electrode; the peelable PET film on the dielectric film was then peeled off. Copper foil was attached to the bottom of the dielectric film. Another electrode was attached to the lower end of the dielectric film. Finally, the film was laminated. The electrodes are vertically offset from each other by 10 mm. Overlap area of the electrodes was 15 mm x 30 mm.

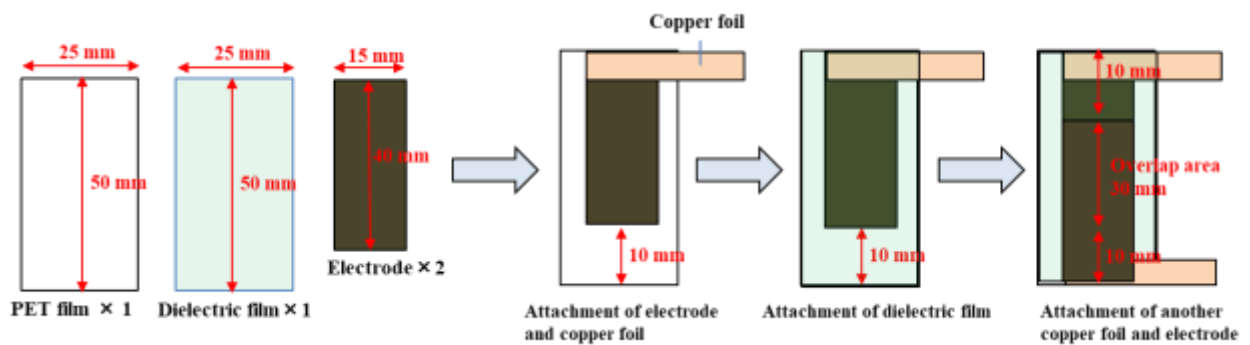


Figure S1. Scheme of sample preparation for measurement of relative dielectric constants.

Alternating evaluation of p(VBE-AN)

Time dependence of monomer ratio was evaluated. Polymerization was carried out under the conditions of AN:VBE=50:50, THF solvent, and AIBN initiator. After reaching 65 °C, sampling was performed, and the residual monomer ratio was calculated by $^1\text{H-NMR}$ measurement. Figure S2 shows the time dependence of the residual monomer ratio. From the result, the residual monomer ratio was independent of time. Therefore, AN and VBE reacted at a similar rate, indicating alternating polymerization.

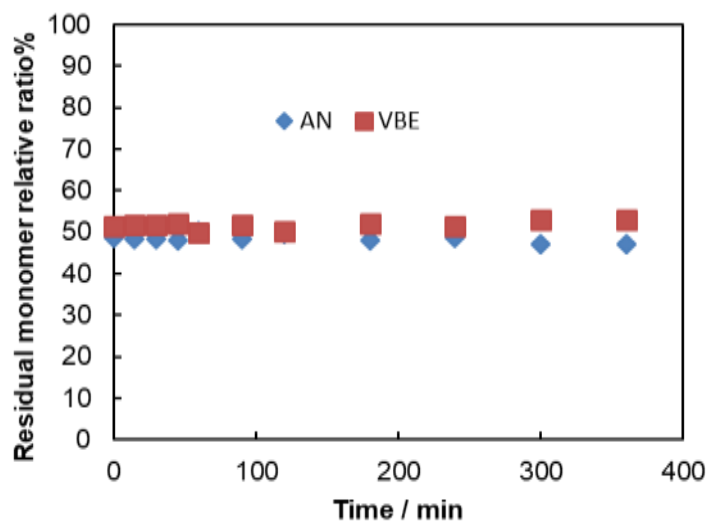


Figure S2. Time dependence of the residual monomer ratio of AN and VBE.

Calculation of monomer reactivity ratios

Reactivity ratios (r_{VBE} , r_{AN}) were calculated by Fineman-Ross method¹⁾. Figure S3 shows plot in feed ratio and in polymer ratio in each composition of VBE: AN. The copolymerization reactivity ratios of VBE and AN in NBR were estimated to be $r_{\text{VBE}} = 0.031$ and $r_{\text{AN}} = 0.57$, respectively. When $r_{\text{VBE}} \approx 0$, $r_{\text{AN}} < 1$, VBE is not continuously incorporated into the polymer, and when AN in feed ratio is low, VBE and AN are alternately arranged.

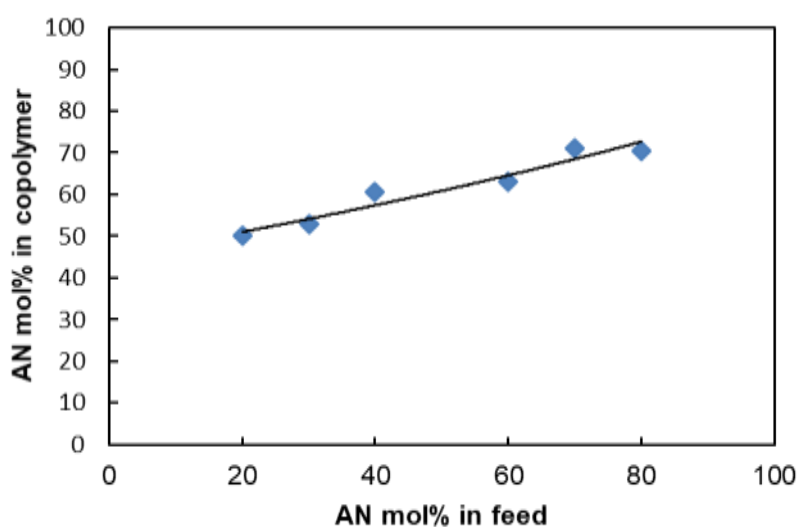


Figure S3. Plot of in feed ratio and in polymer ratio in each composition of VBE: AN.

1) Fineman, M.; Ross, S. D. J. Polymer Sci. 1950, 5, 259

Dimer model for calculation of C-N bond length

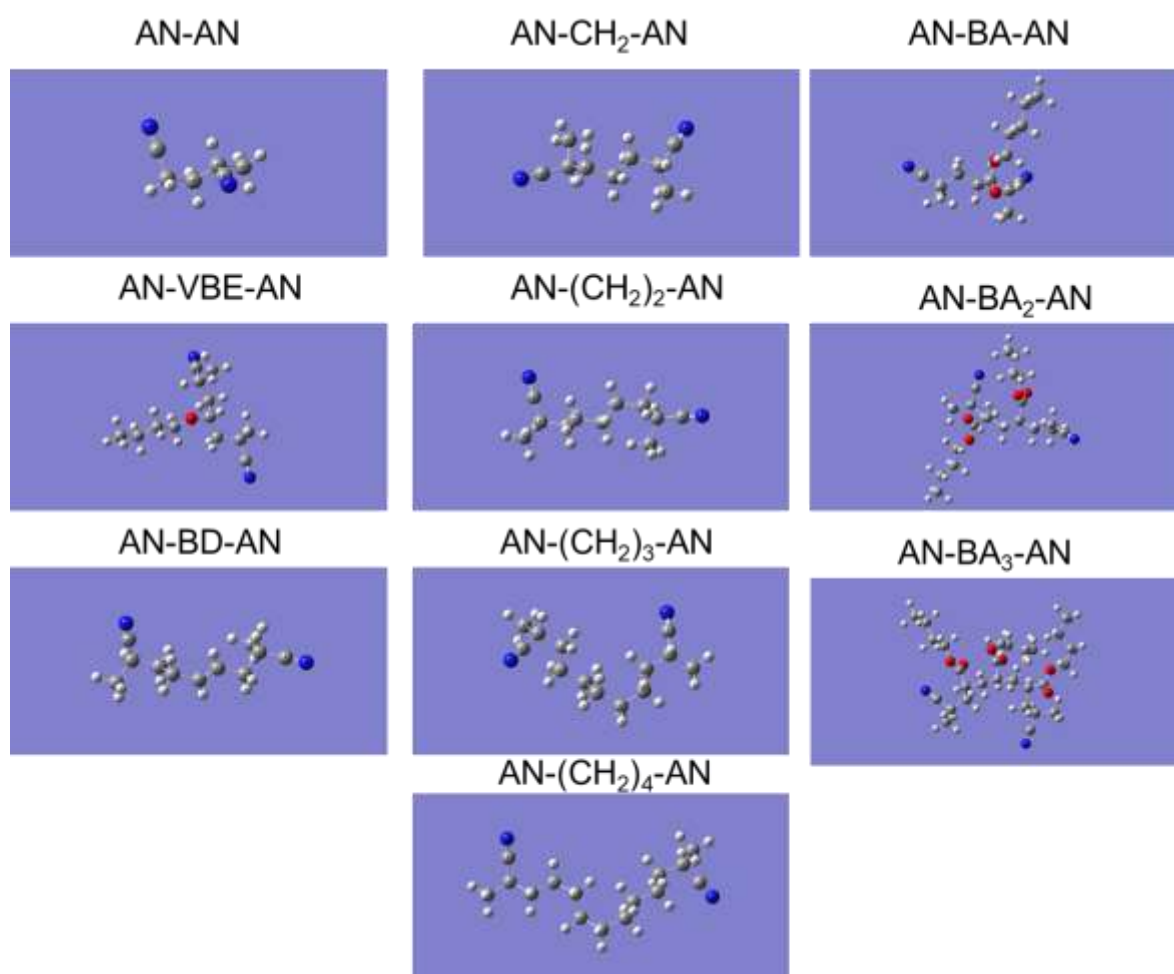


Figure S4. Dimer model for calculation of C-N bond length.

The weight average molecular weight of copolymers

As another characteristic of the polymers, the weight average molecular weight is summarized in Table S1-4. Gel permeation chromatography (GPC) for THF soluble sample was performed using HLC-8220GPC (Tosoh Corp. Japan) equipped with a refractive index detector. Molecular weights were calibrated by Polystyrene standard sample. GPC for DMF soluble sample was performed using a CO-2065 plus (Jasco corporation, Japan). Molecular weights were calibrated by Polyethylene oxide standard sample.

Table S1. Properties of P(VBE-AN) copolymers.

sample	Monomer ratio VBE:AN		Molecular weight(Mw)	Mw/Mn
	In feed	In polymer		
P(VBE49-AN51) Emulsion	90:10	49:51	3.72×10^4	2.27
P(VBE39-AN61) Emulsion	70:30	39:61	5.97×10^4	1.81
P(VBE42-AN58) Solution	70:30	42:58	2.25×10^4	1.39
P(VBE33-AN67) Bulk	50:50	33:67	1.30×10^6	2.97

Table S2. Properties of P(VBE-AN-BA) copolymers.

sample	Monomer ratio VBE:AN:BA		Molecular weight (Mw)	Mw/Mn
	In feed	In polymer		
P(VBE32-AN63-BA5)	50:45:5	32:63:5	4.66×10^5	2.89
P(VBE29-AN61-BA10)	50:40:10	29:61:10	5.73×10^5	2.95
P(VBE22-AN58-BA20)	50:30:20	22:58:20	4.78×10^5	2.63
P(VBE30-AN55-BA15)	67:20:13	30:55:15	5.65×10^5	3.03

Table S3. Properties of P(BA or OA-AN) copolymers.

sample	Monomer ratio BA or OA:AN		Molecular weight (Mw)	Mw/Mn
	In feed	In polymer		
P(BA62-AN38)	70:30	62:38	4.13×10^5	4.36
P(BA45-AN55)	60:40	45:55	3.96×10^5	4.22
P(BA39-AN61)	50:50	39:61	4.21×10^5	4.10
P(BA84-AN16)	73:27	84:16	1.73×10^5	2.21
P(BA94-AN6)	85:15	94:6	2.09×10^5	2.13
P(BA98-AN2)	95:5	98:2	2.66×10^5	2.20
P(OA55-AN45)	60:40	55:45	7.84×10^5	1.49
			7.60×10^4	1.90
P(OA47-AN53)	50:50	47:53	6.95×10^5	1.71
			5.83×10^4	1.78
P(OA99-AN1)	95:5	99:1	3.55×10^5	3.45

Table S4. Properties of HNBR and NBRs

Sample	Product name	AN mol%	Molecular weight (Mw)	Mw/Mn
HXNBR	Therban XT 8889	33.8	2.28×10^5	3.51
NBR1	Nipol® DN302	27.5	4.00×10^5	3.49
NBR2	Nipol® DN2850	28.0	3.34×10^5	3.04
NBR3	Nipol® DN3350	33.0	3.09×10^5	2.63