# Supporting Information

# **Using Coupling Motion of Connecting Ions in Designing Telechelic Ionomers**

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#### **S1** Materials

The monomer, isobutyl acrylate (iBA, Aladdin, 98%) was purified with basic alumina (Beijing Chemical Reagents Co.) to remove the inhibitor. 2,2'-Azobis (isobutyronitrile) (AIBN, Aladdin, 99%) was recrystallized from ethanol before use. Sodium 4-vinylbenzenesulfonate (SSNA, Fluorochem, 95%), carbon disulfide (CS<sub>2</sub>, Aladdin, 98%), 1-dodecanthiol (Aladdin, 98%), Aliquat 336 (Aladdin, 98%), o-xylylene dibromide (Aladdin, 98%), sodium hydroxide (NaOH, Beijing Chemical Reagents Co.) were used as received. The solvents, including absolute ethyl alcohol (analytical purity, Beijing Chemical Reagents Co.), acetone (analytical purity, Beijing Chemical Reagents Co.), chloroform (analytical purity, Beijing Chemical Reagents Co.), mineral ether (analytical purity, Beijing Chemical Reagents Co.), were used as received. The solvents and dioxane (99.8%, extra dry over molecular sieves, Energy) were used as received. A 1000 molecular weight cutoff membrane (Shanghai Yuanye Biotechnology Co.) was used as received.

#### S2 Synthesis of Samples

S2.1 Synthesis of Didodecyl-1,2-phenylene-bis(methylene) bistrithiocarbonate



Scheme S1. The synthesis route of Didodecyl-1,2-phenylene-bis(methylene) bistrithiocarbonate RAFT agent (bis-CTA)

The bis-trithiocarbonate RAFT agent (bis-CTA) was synthesized via two step phase transfer catalyzed reaction <sup>1</sup> as shown in Scheme S1. 1-dodecanthiol (9.05g, 0.045mol) and Aliquat 336 (0.72g, 0.0018mol) were mixed under nitrogen with 60mL toluene in a 500ml three-necked flask thermostated at 0°C, using ice-water bath. First, sodium hydroxide solution (50%wt) (3.63g, 0.046mol) was injected slowly and stirred for 15min. Second, carbon disulfide (3.44g,0.045mol) dissolved in 20mL toluene was injected and stirred for 15min. Third, o-xylylene dibromide (5.94g, 0.023mol) dissolved in 30mL toluene was added to the reactor. The mixed solution was stirred at room temperature under nitrogen for 12h, and the reaction was terminated by adding 100mL deionized water and stirring for 30min. The final

mixture solution was poured into a separation funnel, and the yellow toluene layer was collected and washed with deionized water for three times. The final product (yellow solid) was recovered by rotavap, and further purified in hexane by recrystallization for three times (yellow powder). The chemical structure of bis-CTA was confirmed with the <sup>1</sup>H-NMR as shown in Figure S1.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>): δ 7.38-7.28ppm (a, 4H), 4.71ppm (b, 4H), 3.3-3.39ppm (c, 4H), 1.72ppm (d, 4H), 1.28-1.39 ppm (e, 36H), 0.85-0.90ppm (f, 6H).



Figure S1. <sup>1</sup>H NMR spectra of Didodecyl-1,2-phenylene-bis(methylene)bistrithiocarbonate RAFT

agent

S2.2 Synthesis of Macro-CTA and TPiBA-m Samples



Scheme S2. The synthesis route of macro-CTA precursor and TPiBA-m samples

Macro-CTA poly isobutyl acrylate precursor was synthesized via Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization. A fixed molar ratio of iBA: bis-CTA: AIBN = 30:1:0.2 was chosen. Predetermined amounts of purified isobutyl acrylate (5g, 0.039 mol, 99.5%), bis-CTA (0.855g, 1.33 mmol) and AIBN (0.0426g, 0.26 mmol) were dissolved in 10 ml anhydrous dioxane and added into a glass tube. Three freeze-pump-thaw cycles were applied to remove oxygen and moisture before the reaction. This reaction solution under protection of nitrogen was then placed in an oil bath thermostated at 70 °C for 24 h, to allow the polymerization. After the reaction, the mixture was dialyzed to remove the unreacted monomers using a 1000 Da cutoff membrane (dialysis bag). The solvent was eliminated via rotavap and the sample was vacuum-dried at 60 °C for more than 48h. Chemical structure of the intermediate macro-CTA (TPiBA) was confirmed with the <sup>1</sup>H-NMR analysis, as shown in Figure S2.



Figure S2. <sup>1</sup>H NMR spectra of the precursor macro-CTA and TPiBA-*m* ionomer samples.

The telechelic ionomers (TPiBA-*m*) samples were synthesized with reversible additionfragmentation chain transfer (RAFT) polymerization, using anhydrous DMF as reaction solvent. Seven molar ratios of SSNA, macro-CTA and AIBN were chosen, i.e., SSNA: macro-CTA: AIBN = 8.0:1:0.2, 6.4:1:0.2, 4.4:1:0.2, 4.0:1: 0.2, 3.2:1:0.2, 2.0:1:0.2, 1.2:1:0.2, to synthesize the seven target samples. Three freeze–pump–thaw cycles were applied to remove oxygen and moisture before the reaction. The glass tube was immersed in an oil bath thermostated at 70 °C for 24 h under nitrogen for reaction. The reaction was quenched by dipping the tube into a liquid nitrogen bath. The reaction mixture was then dissolved in methyl alcohol and ethyl alcohol (v/v 1/1) and dialyzed thoroughly for 5 days to remove the unreacted reactants using a 1000 Da cutoff membrane (dialysis bag). Finally, the solvent was eliminated via rotavap and the sample was vacuum-dried at 80 °C for more than 72h before the measurements. Chemical structures of TPiBA-*m* were confirmed with the <sup>1</sup>H-NMR analysis, as shown in Figure S2.

S2.3 Synthesis of Reference rTPiBA Sample.



Scheme S3: The synthesis route of the reference rTPiBA sample

The reference telechelic ionomer sample rTPiBA(NaO<sub>3</sub>S-PiBA-SO<sub>3</sub>Na) was synthesized via three steps as illustrated in Scheme S3, using the same macro-CTA for synthesizing TPiBAm. First, macro-CTA was dissolved in 10 mL anhydrous toluene. The solution was purged with dry nitrogen for 30 min, and a 20-fold molar excess of *n*-butylamine was added. The mixture was stirred for 4h at room temperature for the reaction. The solution was dialyzed using a 1000 Da cutoff membrane (dialysis bag) with ethanol as the solvent. The solution of thiolterminated PiBA (HS-PiBA-SH) prepolymer after the dialysis was subjected to rotavap and further dried in vacuum at room temperature for 24h. Second, the thiol-terminated PiBA (HS-PiBA-SH) (0.5g, 0.06 mmol) was dissolved together with vinylsulfonic acid (35.1 mg, 0.325 mmol) and Irgacure®2959 photo-initiator (1 mg, 0.004 mmol) in a quartz bottle, using anhydrous DMF (5.0 ml) as the solvent. The mixture was subjected to irradiation with a 365 nm UV lamp for 40 min to complete the thiol-ene click reaction. The final crude product was dialyzed with ethanol as the solvent for 2-3 days, to remove the unreacted reactants. Third, the product was subjected to the acid-base titration with phenolphthalein as indicator, which indicated that 96% of the chain ends were successfully attached with the SO<sub>3</sub>H groups. rTPiBA was obtained from adding dropwisely the equivalent amount of sodium hydroxide (also dissolved in ethanol) into the telechelic sulfonated precursor (HO<sub>3</sub>S-PiBA-SO<sub>3</sub>H) and the solution was stirred for 12h. The solvent was removed by rotavap and the product was dried at 60 °C in a vacuum oven for three days. <sup>1</sup>H–NMR analysis was performed for rTPiBA, and the spectra is shown in Figure S3.



Figure S3. <sup>1</sup>H NMR spectra of the reference rTPiBA sample

#### **S3** Sample Characterization

#### S3.1 NMR Measurement

<sup>1</sup>H-NMR spectra of the precursor, ionomer and reference samples (TPiBA, TPiBA-*m*, and rTPiBA) were recorded with a Brucker AV 400-MHz spectrometer using CDCl<sub>3</sub> and DMSO-D6 as solvents and trimethylsilane as an internal standard. Chemistry shift was reported in ppm relative to the internal standard peak. The TPiBA and rTPiBA samples were dissolved in CDCl<sub>3</sub>, while the TPiBA-*m* samples were dissolved in DMSO-D6. <sup>1</sup>H-NMR spectra of all samples are shown in Figures S1-S3.

#### S3.2 GPC Measurement

Gel permeation chromatography (GPC) measurement of TPiBA was performed at room temperature with Wyatt Optilab equipped with an index indicator and a low-angle light scattering monitor. Tetrahydrofuran (THF) was used as an eluent at a flow rate of 1 ml/min. The weight average molecular weight  $M_w$  and and polydispersity index ( $M_w/M_n$ ) were evaluated from the LS and RI signals as shown in Figure S4, which are summarized in Table 1.



Figure S4. GPC trace (RI and LS signals) of telechelic precursor sample TPiBA. The eluent was THF. S3.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The mass fraction of sodium ion in the sample,  $w_{ion}$ , was determined from inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis using the Thermo iCAP 6300 spectrometer. The spectrometer was calibrated with a standard NaCl aqueous solution (with name code GSB 04-1738-2004) purchased from Guobiao (Beijing) Testing & Certification Co., Ltd. A considerably large amount of each sample (~0.05 g) was consumed to ensure the precise measurement. The actual average number *m* of ion-containing monomer(s) per chain end was determined from  $w_{ion}$  and  $M_n$  (=4800 g/mol) of the precursor through a relationship  $w_{ion} = 2mM_{ion} / (M_n + 2mM_{SS})$ , with  $M_{ion}$  (= 23g/mol) and  $M_{SS}$  (= 206 g/mol) being the molecular weights of sodium ion and sodium styrene sulfonate, respectively, and a prefactor 2 corresponds to two ends per chain. The actual and targeted values of *m* and *n* are listed in Table 1.

#### S3.4 DSC Measurement

Differential scanning calorimetry (DSC) analysis was performed using DSC Q20 (TA Instruments, USA). All TPiBA-*m* and rTPiBA samples were dried in vacuum at higher  $T \ge T_g + 60$  °C for one week or more before the measurements to remove the solvent and moisture. All samples were examined in three heating runs in the temperature range of -80 to 150 °C, at heating and cooling rates of 10 °C/min and -10°C/min, respectively. The glass transition temperature of all samples was determined from the third heating runs using the commercially available Universal Analysis software. The DSC traces for all samples are shown in Figure S5, and the DSC  $T_g$  are summarized in Table 1.

#### S3.5 X-ray Scattering Measurement

Before the X-ray scattering experiments, all samples were annealed in a vacuum oven at  $T \ge T_g + 60$  °C for one week. The wide-angle X-ray diffraction (WAXD) (SmartLab, Rigaku) was performed on all samples packed with thin tin foil. This process was performed in the transmission mode at room temperature. Ni-filtered Cu K $\alpha$  radiation (1.54° A) operated at 40 kV and 40 mA was acquired for 1 h for each sample. The patterns of both meridian and equator directions of the samples were recorded. Data were collected in a scattering angle (2 $\theta$ ) range of 0.5° to 30° with each step of 0.03°, and the scattering vector is thus  $q = (4\pi/\lambda)sin\theta = 0.35-21.09$  nm<sup>-1</sup>.

#### S3.6 Rheology

All frequency sweep measurements were conducted with a strain/stress-controlled rheometer (ARES-G2 from TA Instruments or MCR302 from Anton Paar). The TPiBA, TPiBA-*m* with  $m \le 0.73$  and rTPiBA samples were annealed in vacuum oven at higher  $T \ge T_g + 60$  °C for one week or more before the measurements, and loaded directly in the rheometer. The TPiBA-*m* samples with high  $m \ge 0.98$  did not flow easily at  $T \ge T_g + 60$  °C, so these samples were annealed in vacuum at 80 °C for a week and then molded into pills at 180 °C with a homemade mold. These pills were further annealed in vacuum at 150 °C for one day before the frequency sweep measurements.

All measurements were performed in dry  $N_2$  environment to prevent humidity and suppress sample degradation. For the small-angle oscillation shear (SAOS) measurement, two sets of parallel-plate fixtures with the diameter of 8 and 25 mm were utilized, and the strain amplitude was kept in the linear regime as verified from strain amplitude sweep measurements.

#### S4 DSC traces



Figure S5: DSC traces of PiBA precursor and TPiBA-*m* ionomers. Glass transition temperature  $T_g$  was determined from the traces and shown in arrow.

#### **S5** Linear Viscoelasticity

The shift factors of the (pseudo-) master curves in Figure 3 of the main text is summarized in Figure S6 (a). In Figure 3, tTs holds for the precursor and sol samples, where the master curves can be easily constructed. However, tTs does not hold for the gel samples, and thus the shift factor was chosen under the guidance the Rouse part of modulus for  $T < T_r$ , where the shift factor exhibits the WLF-type *T* dependence. In contrast, the shift factor was chosen under the guidance of the plateau relaxation for  $T > T_r$ , while the shift factor exhibits the Arrhenius-type *T* dependence. As a result, the shift factor shows a transition from WLF-type to Arrhenius-type *T* dependence with increasing *T*. To show clearly this transition, we plot in Figure S6(b) a corrected shift factor log  $a_{T,iso}$  against  $T - T_{iso}$ , where  $T_{iso}$  is an iso-frictional temperature that has the same distance to  $T_g$ , i.e.,  $T_{iso} - T_g = 31^{\circ}$ C. The solid curve in Figure S6 is the WLF

curve, which exhibit the Arrhenius-type behavior. Similar trend was observed in our previous study.<sup>2</sup>



Figure S6. (a) Plots of viscoelastic shift factor,  $a_T$ , against  $T - T_r$  for all LVE curves of PiBA, TPiBA-*m*, and rTPiBA shown in Figure 3. (b) Plots of corrected shift factor,  $a_{T,iso}$ , against  $T - T_{iso}$ , where  $T_{iso} = T_g + 31^{\circ}$ C the iso-frictional temperature. The solid curve is a prediction of the WLF equation of the precursor,

$$\log a_{\rm T} = -10.4(T - T_{\rm r})/(104 + T - T_{\rm r})$$
 with  $T_{\rm r} = 0^{\circ}{\rm C}$ .

In Figure S7, we present the LVE data in another way; we plot G' and G'' obtained at  $\omega = 1$ rad/s against temperature T. It is clear that the crossover from G' > G'' to G' < G'', representing a transition from solid-like to liquid-like behavior, occurs at higher T with an increase of m.

Figure S8 shows the van Gurp-Palmen plots of the TPiBA-2.2 and TPiBA-3.0 samples, which demonstrate, respectively, two and three relaxation processes.



Figure S7. Plots of G' (diamonds) and G'' (squares) obtained at  $\omega = 1$  rad/s against temperature T.



Figure S8. The van Gurp-Palmen Plots of the TPiBA-2.2 and TPiBA-3.0 samples.

For all samples in this study, we can see clearly the  $G' \sim \omega^2$  and  $G'' \sim \omega$  terminal tails. From these tails, we can estimate the second-moment terminal relaxation time  $\tau$  and the recoverable compliance  $J_{r,r}$ 

$$\tau = [G'/\omega G'']_{\omega_{n,0}} \tag{S1}$$

$$J_{\rm r} = [G'/G''^2]_{\omega_{\to}0}$$
(S2)

In Figure S9a and S9b,  $\tau$  and  $J_r$  are plotted against m.



Figure S9. Dependences of terminal relaxation time,  $\tau$ , and recoverable compliance,  $J_r$  on m.

### **S6 X-Ray Scattering**

Considering that the scattering profile of the precursor shows two q peaks, reflecting backbone-backbone correlation and amorphous scattering of the side chains, and a power law-

like behavior at low q, we use two Lorentzian functions and one power law term to fit the scattering profile,

$$I(q) = L_{a}(q) + L_{b}(q) + Bq^{-2}$$
(S3)

where  $L_X(q) = MK^2/[(q - q_X)^2 + K^2]$ , with X = a and b representing the side chain and backbone correlations, respectively, and the  $Bq^{-2}$  term representing the upturn at the lowest q. Three parameters are adjusted in the fitting, i.e., the peak position,  $q_X$ , the half-width at half-maximum, K, and an intensity factor M. The peak area is given as  $A_X = \pi MK$ .

For the TPiBA-*m* ionomers, there is one ionic peak at low q, which is fit to the Percus-Yevick model, so the fitting equation becomes,

$$I(q) = L_{a}(q) + L_{b}(q) + I_{ion}(q)$$
(S4)

The Percus-Yevick model<sup>3</sup> was chosen according to literature, <sup>4, 5</sup> which showed that this model works well for the micellar structure formed by the telechelic associative polymers. The PY model considers a suspension of hard spheres with repulsive interaction. The scattering intensity function is given by a product of a structure factor and a form factor plus a flat background.

$$I_{\rm ion}(q) = KS(qR_2) \int_{R_1}^{\infty} \phi(qR_1) f_p(R_1, \bar{R}_1, \sigma) dR_1 + C$$
(S5)

Here, *K* is a constant factor depending on the electron density difference between the particles and the matrix, *C* is the scattering background. The structure factor of a system of hard spheres is given by  $S(qR_2)$  that depends on the volume fraction *f* of the effective hard spheres of the radius  $R_2$ ,

$$S(qR_2) = \left(1 + \frac{24fG(x)}{x}\right)^{-1}$$
(S6)

where  $x = 2qR_2$ , and

$$G(x) = \frac{\alpha}{x^2} (sinx - xcosx) + \frac{\beta}{x^3} (2xsinx + (2 - x^2)cosx - 2)$$
(S7)  
+  $\frac{\gamma}{x^5} (-x^4 + 4[(3x^2 - 6)cosx + (x^3 - 6x)sinx + 6])$ 

Since there is no structural boundary at  $R_2$ , the only scattering contrast arises from the aggregated chain ends as the core, which is represented by the hard sphere of radius  $R_1$ . Hence, the form factor  $\phi(qR_1)$  in the scattering function depends on  $R_1$  of the aggregates. We

approximate a distribution of  $R_1$  using a lognormal distribution  $f_p$  with a width  $\sigma$  and a mean value of  $\overline{R}_1$ . All fitting parameters of the PY model and Lorentzian functions are summarized in Table S1.

samples	La			L <sub>b</sub>			I <sub>PY</sub>		
	М	Κ	$q_{\mathrm{a}}$	М	Κ	$q_{ m b}$	f	$R_1$	$R_2$
TPiBA-0	2250	2.3	13.4	1450	2.2	5.1	-	-	-
TPiBA-0.12	1790	2	13.4	1000	1.8	5.1	0.051	1.1	2.35
TPiBA-0.54	1680	2	13.4	950	1.8	5.1	0.116	1.12	2.44
TPiBA-0.73	1700	2.3	13.4	1100	2	5.1	0.152	1.14	2.52
TPiBA-0.98	1900	2.4	13.4	1220	2	5.1	0.180	1.16	2.54
TPiBA-1.6	1050	2.2	13.4	540	2	5.1	0.216	1.18	2.71
TPiBA-2.2	1000	2.1	13.4	580	1.9	5.0	0.241	1.2	2.95
TPiBA-3.0	570	2.2	13.4	600	2.9	4.45	0.274	1.23	3.25
rTPiBA	780	2.2	13.4	800	2.1	5.1	0.027	0.76	3

 Table S1. Important parameters in Eqs S3-S5

The presence of hard cores as filler would increase the localized strain and accordingly reinforce the modulus. This filler effect is estimated using Guth-Gold equation as<sup>6</sup>

$$G^* = G_0^* (1 + 2.5f + 14.1f^2) \tag{S8}$$

Here, f is the volume fraction of the filler, which is obtained from fitting the ionic peak with the PY model (cf. Eqs S5-S7 and Table S1).



Figure S10. plots of a ratio of moduli of the system with and without filler,  $1 + 2.5f + 14.1f^2$ , estimated with the Guth-Gold equation, against an average number of ions per chain end *m* for the TPiBA-*m* 

ionomers.

The ratio between moduli before and after introducing the filler is  $1 + 2.5f + 14.1f^2$ , which is plotted against *m* in Figure S10. This parameter is not trivial, a factor of 2.7 at high m = 3.0would lead to a logarithmic shift of 0.43 of the plateau, which reasonably account for a difference between  $G_n = 10^{6.1}$ Pa observed in experiment and  $G_c = 10^{5.7}$ Pa obtained by assuming that all precursor chains are elastically active.

In Figure S11, the plots of I(q) against q for rTPiBA are fit with Eqs S4-S7. Since the ion peak is at low q is much broader than those of the TPiBA-m ionomers, larger  $\sigma$  is utilized in the fitting.



Figure S11. X-ray scattering intensity I(q) plotted against scattering vector q for the reference telechelic ionomer rTPiBA.

## S7 Analysis of the Gel Point

Here, we analyze the distribution of number of ions per chain  $n_s$  near the gel point. In our experiment, we find from Figure 3 of the main text that TPiBA-0.54 is very close to the gel point. The distribution of number of ions per chain end can be calculated by:

$$P(x) = e^{-m}m^x/x!$$
 (S9)

which is Eq 1 in the main text. Considering that each chain has two ends, the fraction of chains having a number of  $n_s$  ions per chain can be calculated as:

$$P(n_s) = \sum_{0}^{n_s} P(x) P(n_s - x)$$
(S10)

In comparison, the gel point is predicted by the mean-field theory as  $p_c = 1/(N-1)$  for random

ionomers, with N being a number of monomers per precursor chain. The probability that a precursor chain has  $n_s$  ionized monomers can be calculated using the binomial distribution function  $P(n_s)$ 

$$P(n_s; p, N) = \frac{N!}{(N-n_s)!n_s!} p^{n_s} (1-p)^{N-n_s}$$
(S11)

Here, we input the number fraction of ionized monomers  $p = p_c = 1/(N-1)$ , with N = 37 the number of monomers per chain in this study, to be compared with  $P(n_s)$  calculated for TPiBA-0.54 in Figure S12. The distribution function  $P(n_s)$  for TPiBA-0.54 calculated through a combination of Eqs S9 and S10 (sphere symbols) agrees well with that calculated for random ionomer at  $p_c$  given by Eq S11 (square symbols). In particular, most of the chains have two or less ions per chain on average for both cases. Probably, those chains have no ion, one ion, and two or more ions serve as the diluent, the dangling chains, and the chains for constructing the sol and gel structures, respectively. The factions of these chains are similar for the special telechelic ionomer and the random ionomer near their gel points.



Figure S12: Comparison of the distribution function  $P(n_s)$  of a number of ions per chain,  $n_s$ , calculated from Poisson distribution function of the chain ends for TPiBA through a combination of Eqs S9 and S10, and that calculated for random ionomer at  $p_c$  by Eq S11.

#### References

(1) Liu, Y. Synthesis and Characterization of Well-defined, Amphiphilic, Ionic Copolymers. University of Akron, 2011.

(2) Wu, S.; Liu, S.; Zhang, Z.; Chen, Q. Dynamics of Telechelic Ionomers with Distribution of Number of Ionic

Stickers at Chain Ends. Macromolecules 2019, 52, 2265-2276.

(3) Schwab, M.; Stühn, B. Thermotropic Transition from a State of Liquid Order to a Macrolattice in Asymmetric Diblock Copolymers. *Physical review letters* **1996**, 76, 924.

(4) Kinning, D. J.; Thomas, E. L. Hard-sphere Interactions between Spherical Domains in Diblock Copolymers. *Macromolecules* **1984**, 17, 1712-1718.

(5) Yan, T.; Schröter, K.; Herbst, F.; Binder, W. H.; Thurn-Albrecht, T. What Controls the Structure and the Linear and Nonlinear Rheological Properties of Dense, Dynamic Supramolecular Polymer Networks? *Macromolecules* **2017**, *50*, 2973-2985.

(6) Guth, E. On the Hydrodynamical Theory of the Viscosity of Suspensions. *Phys. Rev* 1938, 53, 322-325.