Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

One-pot synthesis of dual supramolecular associative copolymers by using a novel acrylate monomer bearing urethane and pendant pyridine groups

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1. Experimental section

1.1 Materials

2-isocyanatoethyl acrylate (ICNA), 4-pyridinemethanol (4PyOH), ethyl acrylate (EA), the radical initiator (*2,2'*-azobis(isobutyronitrile, AIBN), and other organic solvents were purchased from TCI. The chain transfer agent (CTA, 2-cyano-2-propyl dodecyl trithiocarbonate) and zinc(II) trifluoromethanesulfonate ($Zn(OTf)_2$) were purchased from Aldrich. The polymerization inhibitors in EA were removed by passing through an aluminum oxide column before polymerization. The other chemicals were all used as received.

1.2 Synthesis of the copolymers

The acrylate-type monomer having both urethane and pyridine pendant groups (4PyA) was synthesized by reacting ICNA and 4PyOH in anhydrate dimethylformamide (DMF); the feed ratio and concentration was set as ICNA:4PyOH = 1:1.15 and 25 wt%, and the reaction was carried out at 40 ºC for 3 h. The slight excess of 4PyA is to attain 100% reaction conversion of the NCO group of ICNA. After the 4PyA synthesis, we added EA monomers, chain transfer agent (CTA), radical initiator, and an appropriate amount of DMF to the above reaction solution of 4PyA under N_2 gas atmosphere. We also applied 5 min N_2 bubbling before starting the RAFT polymerization. The copolymerization was carried out by varying the monomer feed mole ratio as [4PyA]:[EA] = 2:8, 4:6, 5:5, 6:4, and 8:2 to estimate the radical reactivity ratio of 4PyA and EA.

1.3 Characterization of the synthesized polymers

The dispersity indices (*Đ*s) and molecular weights of the polymers were determined by size exclusion chromatography (SEC). The set up consisted of Shodex KD803+804 columns that combined with a Tosoh DP8020 pump system and an RI detector (Tosoh RI-8020). A mixture of DMF with LiBr (0.05 wt%) was used as the eluent at a flow rate of 0.5 ml/min. The elution volume was calibrated with a standard series of poly(methyl methacrylate)s. The fraction of monomer units in the copolymers was estimated from ^{1}H-NMR in *d*-DMSO with using a Bruker Analytik DPX400 spectrometer (400 MHz).

1.4 Spectroscopy

Fourier transform infrared spectroscopy (FT-IR) studies were performed at room temperature to detect the supramolecular association. The instrument was an FT/IR-6300 spectrometer (JASCO) combined with a microscopic positioning tool. The measurement samples were prepared by drop casting from a methanol solution.

1.5 Physical property analysis

Differential scanning calorimetry (DSC) measurements were carried out using a DSC7020 (HITACHI) instrument. The first heating was conducted from 50 to 130 °C, then the temperature was decreased to -90 °C. The second heating was applied from -90 to 130 °C. The temperature change rate was set to be 10 °C/min, and all the measurements were performed under N_2 gas flow. The T_g values were calculated at the midpoint of the heat capacity change between the liquid and glassy states. Viscoelastic property was investigated by temperature-sweep rheology. An MCR302 (Anton Paar) instrument with 8 mm parallel plates was used. The measurements were performed within a linear regime at a frequency of 6.28 rad/s under N_2 gas atmosphere unless specifically noted. The temperature was cooled from the liquid region to the glassy region with a temperature ramp rate of 3 °C/min.

2. ^{1}H-NMR analysis for 4PyA

Table S1. Attribution of signals and integral values for ^{1}H-NMR spectra of 4PyA synthesis in Figure 2(a) (see main text).

	σ (ppm)	integral found	expected
H_a	~5.1	2.2	2.0
H_b	~7.6	1.0	1.0
H_c	~7.3	2.4	2.0
H_d	~8.6	2.2	2.0
H_e	~4.1	2.2	2.0
H_f	~3.3	2.3	2.0

3. ^{1}H-NMR spectra and SEC data for copolymers

Figure S1 represents ^{1}H-NMR spectra for the copolymer, 4PyA-*co*-EA. The assignment of proton signals is provided as indicated in Figure S2. Table S2 summarizes the integral value ratio for the characteristic signals in the ^{1}H-NMR spectra to determine the copolymer composition.

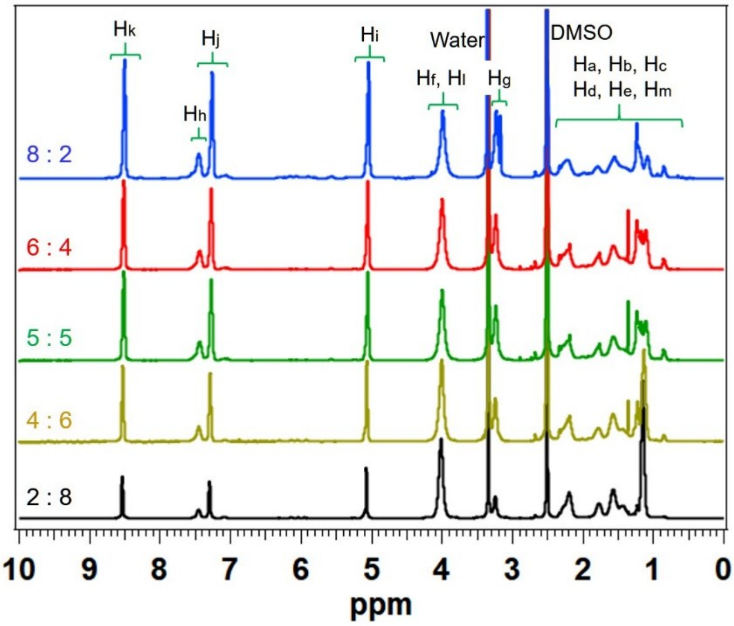

Figure S1. ^{1}H-NMR spectra for 4PyA-*co*-EA. The ratio in each spectrum corresponds to the feed mole ratio, [4PyA] : [EA]. The assignment of proton signals is provided in Figure S2.

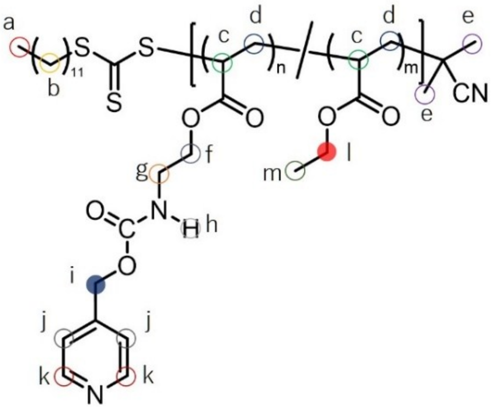

Figure S2. Assignment for proton signals for ^{1}H-NMR spectra in Figure S1. Hx with alphabet (x) in Figure S1 corresponds to the protons with the same alphabet in the chemical structure shown in Figure S2.

Table S2. Integral value ratio of the characteristic signals for 4PyA-*co*-EA

Feed ratio ([4PyA] : [EA])	Integral value for H_i	Integral value for H_l
2 : 8	2.0	8.0
4 : 6	3.9	6.1
5 : 5	5.0	5.0
6 : 4	6.0	4.0
8 : 2	7.8	2.2

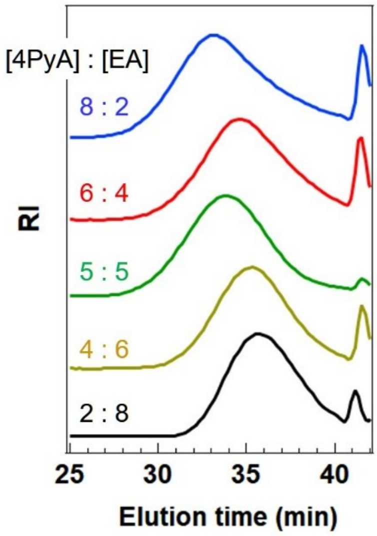

Figure S3. SEC curves for 4PyA-*co*-EA. The ratio in each spectrum corresponds to the feed mole ratio. Note that the sharp peak appeared at later than 40 min is due to the solvent.

4. Copolymerization of 4VP and EA

The synthesis of copolymer, poly(4-vinylpyridine-*co*-ethyl acrylate) (coded as 4VP-*co*-EA), is described below. 4VP, EA, CTA, and AIBN were dissolved and homogenized by anhydrated DMF in a 25 mL flask under a N_2 gas atmosphere. The weight fraction of total monomer in the DMF solution was kept to be 25% while the feed ratios of 4VP and EA were varied according to [4VP] : [EA] = 2 : 8, 4 : 6, 5 : 5, 6 : 4, and 8 : 2 to estimate the radical reactivity ratios. The mole ratio of total monomer, CTA, and AIBN was kept to be $[M_{total}]$ (= $[M_{EA}+M_{4VP}]$): [CTA] : [AIBN] = 500 : 1 : 0.2. After N_2 bubbling for 5 min, the polymerization was launched at 90 °C. The monomer conversion was limited to be less than 20% for accurate investigation of radical reactivity ratios.

The green plots in Figure S4a show the relationship between the mole fraction of 4VP in the feed (f_{feed} = [4VP] / ([4VP] + [EA])) and the mole fraction of the 4VP units in the copolymer chains (f_{chain}) determined by ^{1}H-NMR. The plots for 4VP-*co*-EA significantly deviated from the proportional line, unlike the case of 4PyA-*co*-EA. This already means the radical reactivity ratios were very different between the two monomers. Figure S4b represents the K-T plot for 4VP-*co*-EA. From the slope of the linear relationship, the radical reactivity ratios were calculated to be 2.78 for 4VP and 0.33 for EA.

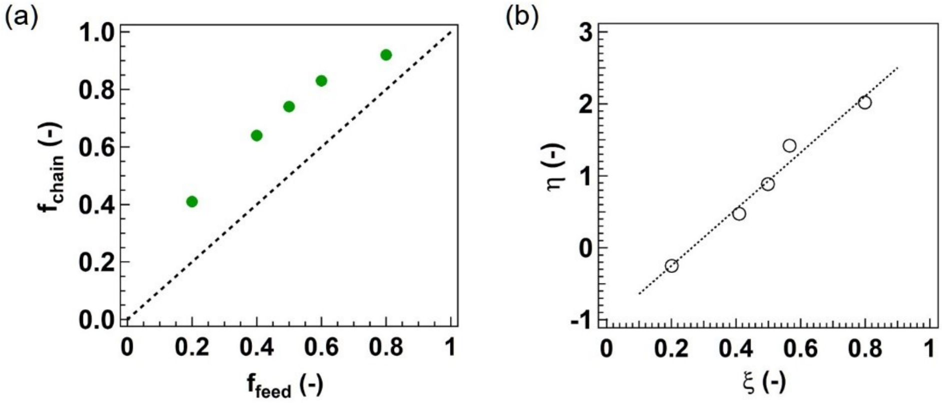

Figure S4. (a) Relationship between monomer feed ratio and composition in the copolymer. The broken line represents the proportional line. (b) Plot based on the Kelen-Tüdos (K-T) method. The broken line indicates the approximation straight line between points (please see the explanation of η and ξ in the text).

5. Summary of molecular characteristics for 4PyA-*co*-EA copolymers

Tables S3 summarizes the molecular characteristics for the copolymers, including number average molecular weight (M_n), $Đ$, monomer unit composition in the copolymers (f_{chain}). The polymerization time is also provided in each Table. Please also see the ^{1}H-NMR and SEC data in Figure S1 and S3.

Table S3. Molecular characteristics for 4PyA-*co*-EA

Feed ratio ([4PyA] : [EA])	Time^a (h)	M_n^{b} (kDa)	$Đ$^{b}	f_{chain} ^{c}
2 : 8	1	7.5	1.36	0.20
4 : 6	18	9.7	1.24	0.39
5 : 5	18	10.0	1.27	0.50
6 : 4	18	10.2	1.31	0.60
8 : 2	18	11.8	1.45	0.78

$^{a)}$ Polymerization time. $^{b)}$ Number average molecular weights (M_n) and dispersity indices ($Đ$), which were determined by SEC in DMF with LiBr. PMMA standards were used for the estimation. $^{c)}$ Mole fraction of 4PyA units in the copolymers (f_{chain}) determined by ^{1}H-NMR, and the values were used for the plots in Figure 3a.

6. The values to determine *r* by the K-T method

Tables S4 summarizes the quantities used to determine *r* values based on the K-T method. Please refer to the main text for the meaning of x, y, F, G, η, and ξ.

Table S4. The values to determine *r* via the K-T method for 4PyA-*co*-EA

Feed ratio ([4PyA] : [EA])	x	y	F	G	F^{-1}	G/F	η	ξ
2 : 8	0.250	0.248	0.253	-0.760	3.960	-3.010	-0.574	0.191
4 : 6	0.667	0.633	0.702	-0.387	1.424	-0.551	-0.218	0.396
5 : 5	1.000	0.995	1.005	-0.005	0.995	-0.005	-0.002	0.484
6 : 4	1.500	1.470	1.530	0.480	0.653	0.314	0.184	0.588
8 : 2	4.000	3.525	4.539	2.865	0.220	0.631	0.510	0.809

7. Copolymerization of 4PyA and EA in the absence of unreacted 4PyOH

To check the effect of unreacted 4PyOH on the copolymerization of 4PyA and EA, we conducted the copolymerization in the absence of unreacted 4PyOH. We first attempted the synthesis of 4PyA at ICNA : 4PyOH = 1 : 1 under the same condition as described for the synthesis of 4PyA at ICNA : 4PyOH = 1 : 1.15 (i.e., 40 °C, 3h). However, the reaction conversion of isocyanate group did not reach 100%, and thus the longer reaction time, 24 h, was necessary to achieve the full conversion. The ^{1}H-NMR spectrum for 4PyA obtained by the reaction at ICNA : 4PyOH = 1 : 1 is shown in Figure S5, where there was negligible amount of unreacted 4PyOH. This pure 4PyA was used for the copolymerization with EA. The feed mole ratio was fixed to be $[M_{EA}+M_{4PyA}] : [CTA] : [AIBN] = 500 : 1 : 0.2$ in which $[M_{EA}] : [M_{4PyA}] = 4 : 1$, and the total monomer concentration in DMF solution was set to be 25 wt%. The copolymerization via RAFT was carried out at 90 °C for 20 min, and the obtained copolymer has M_n ~ 16 kDa and $Đ$ ~ 1.15. Compared with the copolymerization results in the presence of unreacted 4PyOH (please see Table S3), the $Đ$ value was smaller. In addition, the copolymerization was found to progress faster in the absence of 4PyOH. Based on the above results, we concluded that the small presence of unreacted 4PyOH (less than 0.01% in the copolymerization solution) could have some effects on the copolymerization progress.

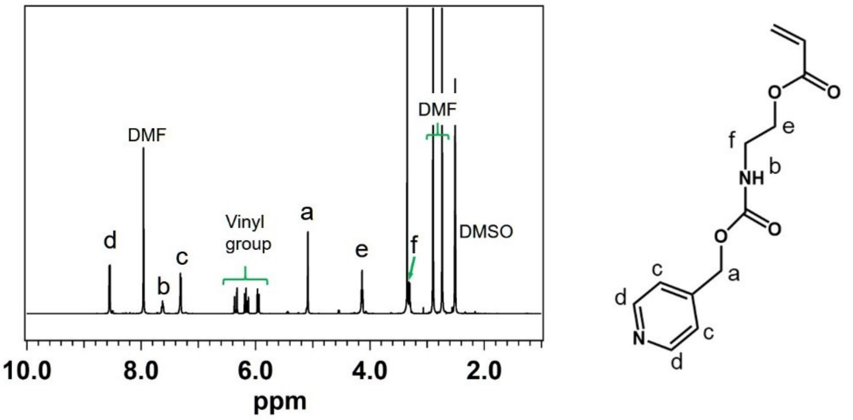

Figure S5. ^{1}H-NMR spectrum for pure 4PyA synthesized at ICNA : 4PyOH = 1 : 1

8. Molecular characterization of Neat-U and Neat-noU

The monomer (coded as 4PyA-noU) for the control sample, Neat-noU (see the chemical structure in Figure 4a), was synthesized as follows. 4-pyridinemethanol was dissolved in dried dichloromethane, and then triethylamine was added in the solution. After cooling the solution to 0 °C, a solution of acryloyl chloride in dried dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 20 h and checked by TLC for disappearance of starting material. The precipitate was filtered off, and the filtrate was concentrated in vacuum. Then the concentrated solution was re-dissolved in ethyl acetate and the precipitate was filtered off, and the filtrate was washed with aqueous solution of $NaHCO_3$ and NaCl. The organic layers were collected and dried by $MgSO_4$, and the solvent was evaporated. The crude product was purified by silica gel column chromatography with the eluent, a mixture of ethyl acetate and petroleum ether (v/v= 7:3). The compound 4PyA-noU was obtained as yellow viscous oil. The reaction was confirmed by ^{1}H-NMR.

The obtained monomer 4PyA-noU was copolymerized with EA. 4PyA-noU, EA, CTA, and AIBN were dissolved and homogenized by anhydrated DMF in a 25 mL flask under a N_2 gas atmosphere. The weight fraction of total monomer in the DMF solution was kept to be 25% while the feed ratios of 4PyA-noU and EA were [4PyA-noU] : [EA] = 2 : 8. The mole ratio of total monomer, CTA, and AIBN was kept to be $[M_{total}]$ (= $[M_{EA}+M_{4PyA\text{-}noU}]$): [CTA] : [AIBN] = 500 : 1 : 0.2. After N_2 bubbling for 5 min, the polymerization was launched at 90 °C. Characteristics of the copolymer obtained was made by ^{1}H-NMR and SEC, and the data are summarized in Table S5, where the characteristics of Neat-U was also indicated.

Table S5. Molecular characteristics of Neat-U and Neat-noU

codes	M_n ^{a} (kDa)	$Đ$ ^{a}	n_{4PyA} or $n_{4PyA\text{-}noU}$ ^{b}	n_{EA} ^{c}
Neat-U	11.7	1.28	18	72
Neat-noU	11.4	1.07	19	81

[a)] Number average molecular weights (M_n) and dispersity indices ($Đ$), which were determined by SEC in DMF with LiBr. PMMA standards were used for the estimation. [b)] average degree of polymerization of 4PyA or 4PyA-noU in the copolymer (4PyA-noU was the monomer used for preparation of Neat-noU). [c)] average degree of polymerization of EA in the copolymer.

9. SAXS data for the blend

To check the homogeneous distribution of metal salts in the system, scattering measurements were conducted. Small-angle X-ray scattering (SAXS) measurements were performed at the BL8S3 of Aichi Synchrotron Radiation Center, Aichi Science & Technology Foundation, Aichi, Japan (Proposal No. 201903070). The sample-to-detector distance was 2000 m and the X-ray wavelength was 0.15 nm. The measurements were carried out at room temperature. Figure S6 represents the SAXS profiles for Neat-U and Blend-U. In the SAXS profiles, *q* represents the scattering vector (= $4\pi \sin\theta \lambda^{-1}$), where λ and 2θ are the wavelength of X-rays and the scattering angle, respectively. There was no distinctive scattering in Blend-U data, meaning the added metal salts were well dispersed without forming aggregations.

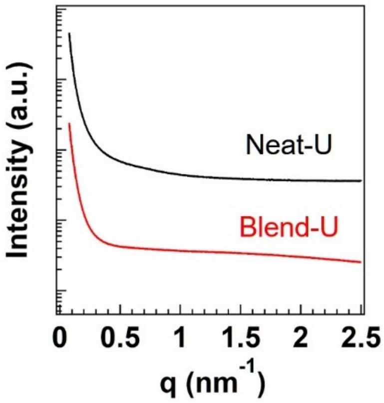

Figure S6. SAXS profiles for Neat-U and Blend-U.

10. FT-IR spectrum for Blend-noU

Figure S7 shows the FT-IR spectra for Blend-noU.

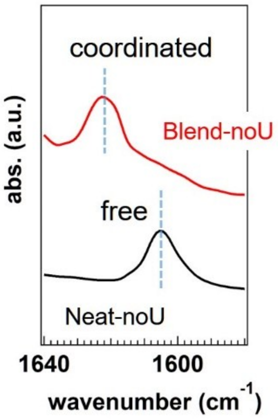

Figure S7. FT-IR spectra for Blend-noU and Neat-noU. The absorbance peak at 1605 cm^{-1} and 1625 cm^{-1} originate from free and coordinated C=N of pyridine group, respectively.

11. T_g values for the samples with different fraction of 4PyA units

To check the effect of 4PyA fraction on the T_g, we synthesized the copolymer at the feed ratio of EA : 4PyA = 5 : 5. The copolymer has $M_n \sim$ 10k and $Đ \sim$ 1.27 (see Table S3). The blend was prepared in the same way as described for Blend-U. Figure S8 shows the DSC curves for neat copolymer synthesized at 4PyA : EA = 5 : 5 (Neat-5-5) and the blend (Blend-5-5). The T_g for Neat-5-5 and for Blend-5-5 was 19.0 °C and 87.2 °C. In comparison with the result for the copolymer synthesized at EA : 4PyA = 4 : 1 (see main text), these values were much higher. This result indicates that the incorporation of higher fraction of 4PyA units can induce larger impact on the T_g.

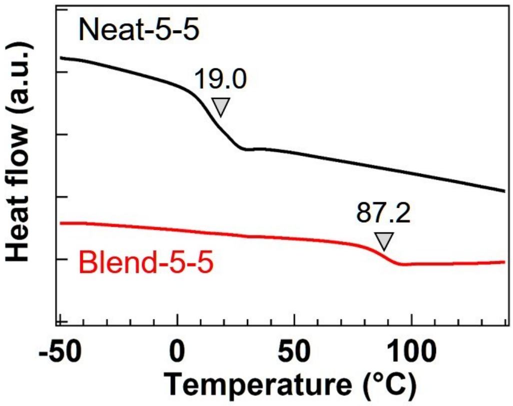

Figure S8. DSC heating thermograms (second heating) for Neat-5-5 and Blend-5-5, where the values indicate T_gs.

12. Estimation of E_a

To estimate E_a, the temperature-sweep rheology was performed with three frequencies, 1 Hz, 4 Hz, and 10 Hz. The tanδ curves with different frequencies are provided in Figure S9a and S9b. The α relaxation temperature (T_α), that was taken as the peak top of loss modulus *G”*, was shifted to higher temperatures with increasing frequencies. By assuming an Arrhenius-type relationship of T_α, the relationship between T_α and measurement frequency *f* can be written as,[S1,S2]

$$\ln f = \ln f_0 - \frac{E_a}{RT_\alpha} \qquad \text{(S1)}$$

where R represents the gas constant (f_0 is the pre-exponential factor). Figure S9c represents Arrhenius-plots of $1/T_\alpha$ and ln*f*, showing the applicability of the Arrhenius-type relationship. E_a was then estimated from the slope of the straight line to be 320 kJ/mol for Neat-U and 396 kJ/mol for Blend-U.

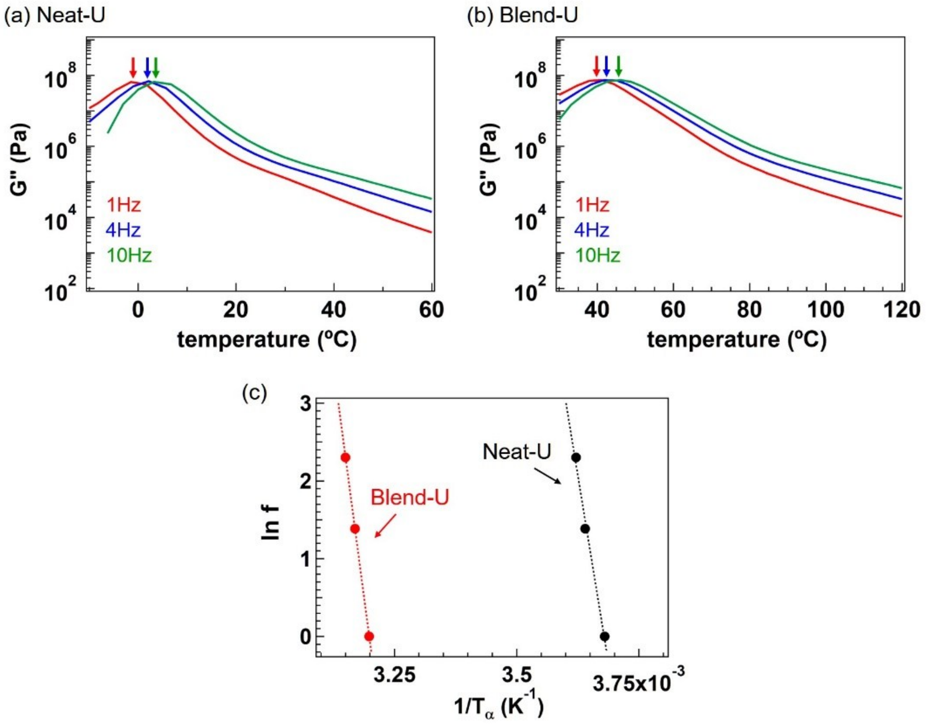

Figure S9. *G”* spectra measured at different frequencies for (a) Neat-U and (b) Blend-U. The arrows represent α relaxation temperatures. (c) Arrhenius plots of ln*f* and $1/T_\alpha$ for Neat-U and Blend-U. The broken lines represent aproximation straight lines between points.

13. Master curves for Neat-U and Blend-U

Figure S10 represents master curves for Neat-U and Blend-U, which was created based on the time-temperature superposition for the dynamic frequency sweep data with the same reference temperature of 50 °C. The retardation of the flow by the dual supramolecular association was obvious by comparing the master curves for Neat-U and Blend-U, where the frequency dependence of G' and G'' was slightly deviated from Maxwell-type scaling of $G' \sim \omega^2$ and $G'' \sim \omega^1$

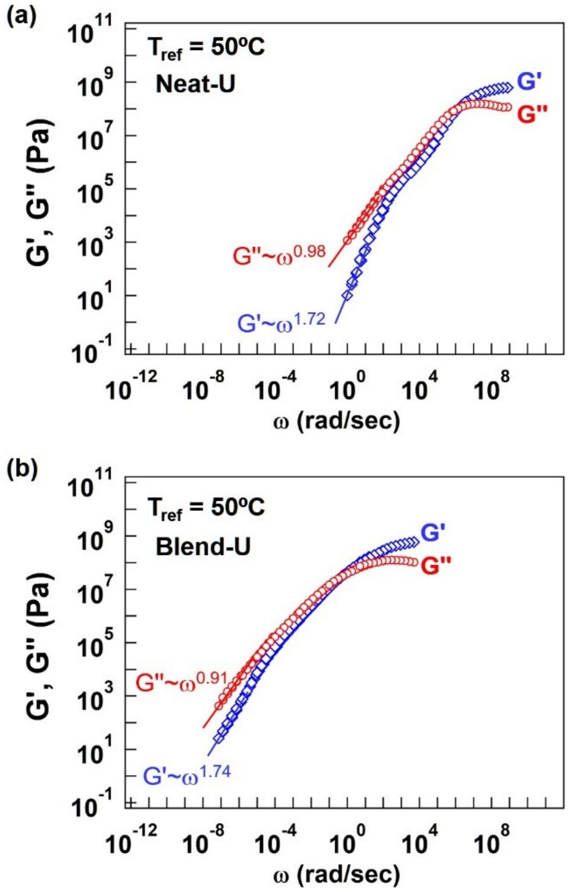

Figure S10. Master curves for Neat-U and Blend-U created with a reference temperature (T_{ref}) of 50 °C. The lines at the low frequency region are used for estimation of the frequency dependence of G' and G''.

<references>

S1) H. M. Huang, S. J. Yang, *Polymer*, 2005, 46, 8068-8078.

S2) E. Szefer, K. Stafin, A. Leszczynska, P. Zajac, E. Hebda, K. N. Raftopoulos, K. Pielichowski, *J. Polym. Sci. Pt. B-Polym. Phys.*, 2019, 57, 1133-1142.