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Supporting Information

Direct enhancement of intercomponent interactions in polyrotaxane and its pronounced effects on glass state properties

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Contents

1. Materials

Biscarboxyl-terminated polybutadiene was purchased from Aldrich, had $M_n = 3900$ and $M_w = 6200$, as determined by sizeexclusion chromatography (SEC) with a calibration curve using PEG standards, and had a trans/cis/vinyl unsaturation distribution of 42:37:21. γ–cyclodextrin (γ–CD) was purchased from Wacher Chemie AG. Pyridinium tribromide and *N*,*N'*-dicyclohexylcarbodiimide (DCC) were from Sigma-Aldrich, and *p*-nitrophenol was from Tokyo Chemical Industry Co., Ltd. *N*-Ethyldiisopropylamine (DIPEA) and all other chemicals and solvents were purchased from Wako Pure Chemical Industries, Ltd. and all reagents were used without further purification.

2. Measurements

^{1}H NMR spectra at 400 MHz were recorded on a JEOL JNM-AL400 spectrometer at 298 K and 343 K in deuterated chloroform ($CDCl_3$) and deuterated dimethyl sulfoxide (DMSO-d_6), respectively. Chemical shifts were calibrated using water (7.26 ppm) and DMSO (2.50 ppm) as the internal standards. Size exclusion chromatography (SEC), with DMSO/LiBr as the eluent, was performed on a Shodex OH Pack SB-G and two Shodex OHpac SB-806MHQ columns at 323 K with 0.4 mL/min, using refractive index detection and PEG standards. The LiBr concentration was 10 mM.

X-ray diffraction (XRD) measurements were performed using an x-ray diffractometer (Rigaku SmartLab) with Cu Kα radiation (λ = 1.542 Å). Heat-flux differential scanning calorimetry (DSC) was performed using a DSC7000X instrument with a liquid nitrogen cooling system (Hitachi High-Tech Science Corporation). Each sample was sealed in an aluminum pan. The scanning rate was 10 K/min. Attenuated total reflectance-Fourier transform infrared (ATR-FT-IR) spectra were recorded on a Nicolet 4700 (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection (ATR) accessory (DurasamplIR II, SensIR Technologies) in air.

Viscoelastic measurements for the thermoformed polyrotaxane films were performed by a strain-controlled oscillatory rheometer (RSAIII, TA Instruments). Frequency sweeps were conducted from 15 to 0.01 Hz, applying 0.05% of the oscillatory tensile strain amplitude. Time–temperature superposition was applied using a program in TA Orchestrator (TA Instruments) for the data at different temperatures to obtain master curves without vertical shifts. For temperature sweeps, 0.05% or 0.1% of the oscillatory tensile strain at 1 Hz was applied.

3. Synthesis of polybutadiene-based polyrotaxane (BPR)

BPR was synthesized by mostly following a previous report,[1] and the crude product was purified by SEC. Biscarboxyl-terminated polybutadiene (10.14 g) was dissolved in dry dichloromethane (22 mL). 28 mL of 1M solution of DCC in dichloromethane was added and then stirred at room temperature (20–25 °C) under dried argon overnight. Then, after filtration, the obtained solution was poured into acetone to reprecipitate the product. The obtained precipitate was dissolved in dichloromethane and then reprecipitated with acetone again. The precipitate was repeatedly washed with acetone to obtain bis(*p*-nitrophenyl ester)-terminated polybutadiene (6.79 g) as a colorless viscous liquid. The esterification was confirmed by the shit of IR absorption peak from 1713 cm^{-1} to 1772 cm^{-1}.

3.81 g of the bis(*p*-nitrophenyl ester)-terminated polybutadiene was dissolved in THF (46 mL), and then it was dropped into the supersonically agitated aqueous solution of *γ*–CD (80.16 g/460 mL) slowly over 90 min. Then, the mixture was stirred at room temperature for 4 days. The resultant white suspension was freeze-dried to obtain the crude inclusion complex, so-called pseudo-polyrotaxane.

For end-capping of the complex, a solution of DIPEA (2.0 mL) in dried acetonitrile (400 mL) was added and then stirred 4 days at room temperature under dried argon. The obtained white slurry was centrifugated to remove the supernatant, and then the precipitate was dissolved in dimethyl sulfoxide (DMSO, 300 mL). This solution was poured into dichloromethane to reprecipitate the product. The obtained precipitated was repeatedly washed with dichloromethane and then dried under vacuum. The dried solid was dissolved in DMSO and then poured into deionized water to be reprecipitataed. The precipitated was washed repeatedly with deionized water and then freeze-dried to obtain a crude BPR (3.77 g) as white powder. Because the crude BPR contains a CD-terminated polybutadiene as a minor component, which tend to form micelle,[2] it was separated by SEC with DMSO/LiBr as an eluent. The impurity has an elution time around 33 min, whereas the retention time of BPR is around 40 min. The fraction of BPR was collected and then poured into deionized water to reprecipitate BPR. The obtained precipitated was freeze-dried to yield refined BPR as a white powder.

4. Definition and calculation of polyrotaxane coverage

Coverage, ϕ, is a measure of how densely a main chain polymer is packed with CDs. A close packing corresponds to $\phi = 1$. Based on the study of a molecular model, $\phi = 1$ has been defined as the state in which two CDs include three repeating units of 1,4-polybutadiene.[3] On the other hand, because of the unsaturation distribution of polybutadiene in our case, we employ a synonymous definition in which a single CD covers a six-carbon unit in the close-packed PR.[2] Thus, from the molar ratio obtained by the ^{1}H NMR spectrum in Figure 1, ϕ is estimated to be 0.33.

5. Bromination of the threading polymer of BPR

BPR (196 mg) was dissolved in anhydrous DMSO (6 mL). Another DMSO solution of pyridinium tribromide (475 mg/ 2.0 mL) was added to the BPR solution, and then stirred at room temperature overnight in a light-resistant glass tube. Then, the reaction solution was poured into deionized water to reprecipitate the product and then the obtained suspension was neutralized by 1M NaOH aqueous solution. The precipitate was washed with deionized water repeatedly, and then freeze-dried to yield Br-BPR as a white powder (229 mg).

6. ^{1}H NMR spectrum of Br-BPR measured in DMSO-d_6/D_2O (Figure S1)

After the measurement in DMSO-d_6 (the obtained spectrum is shown in Figure 1), small amount of D_2O was added to simplify the spectrum without peaks of OH groups. Peaks around 5.5 ppm that indicate unreacted unsaturated carbon is barely observed.

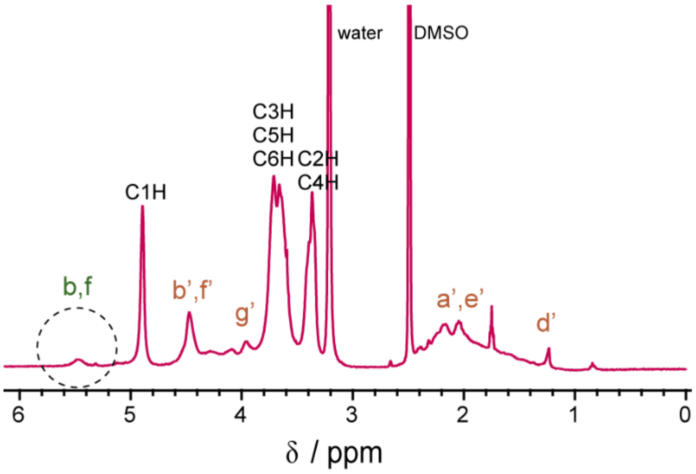

Figure S1. ^{1}H NMR spectrum of BPR (400 MHz, 343 K) in DMSO-d_6 with a small amount of D_2O.

7. FT-IR spectra of BPR and brominated derivatives (Figure S2)

In addition to BPR and Br-BPR, partially brominated BPRs were prepared in small amounts by changing the added amount of pyridinium tribromide. Measurements were performed Nicolet 4700 (Thermo Electron Co., Ltd.) equipped with a diamond attenuated total reflection (ATR) accessory (DurasamplIR II, SensIR Technologies Technologies) in air.

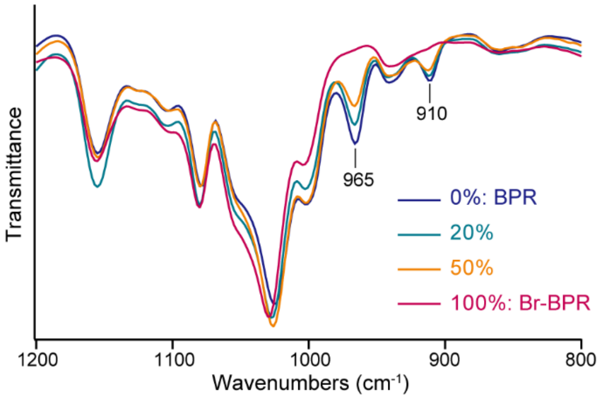

Figure S2. Partial ATR-FTIR spectra of BPR and its brominated derivatives with different degrees of the modification. Peaks at 965 and 910 cm^{-1}.

8. Synthesis of propionylated BPR (PrBPR) and its brominated derivative (Br-PrBPR)

PrBPR was synthesized from a newly prepared BPR. Elimination of the above-mentioned impurity (CD-terminated polybutadiene) was not done and used for further modification. 1.21 g of the BPR and lithium chloride (1.0 g) was dissolved in dried *N*,*N*-diemthylformamide (50 mL). Dried pyridine (7.2 mL) and 4-dimethylaminopyridine (0.96 g) were added, and then propionic anhydride (11.5 mL) was added dropwise. The reaction solution was stirred at room temperature overnight. Then, the solution was poured into methanol to reprecipitate the product. The obtained precipitated was repeatedly washed with deionized water, and then freeze-dried to yield PrBPR (1.13 g) as a white solid.

Bromination of PrBPR was performed by a similar way to that in the case of BPR. 759 mg of PrBPR was dissolved in dried DMSO (18 mL) and then another solution of pyridinium tribromide in DMSO (1.76 g/ 4 mL) was added. The reaction solution was stirred at room temperature overnight in a light-resistant glass tube. Then, the reaction solution was poured into deionized water to reprecipitate the product and then the obtained suspension was neutralized by 1M NaOH aqueous solution. The precipitate was washed with deionized water repeatedly, and then freeze-dried to yield Br-PrBPR as a white powder (990 mg). The almost complete bromination was confirmed by ^{1}H NMR and FT-IR spectra shown in Figure S3.

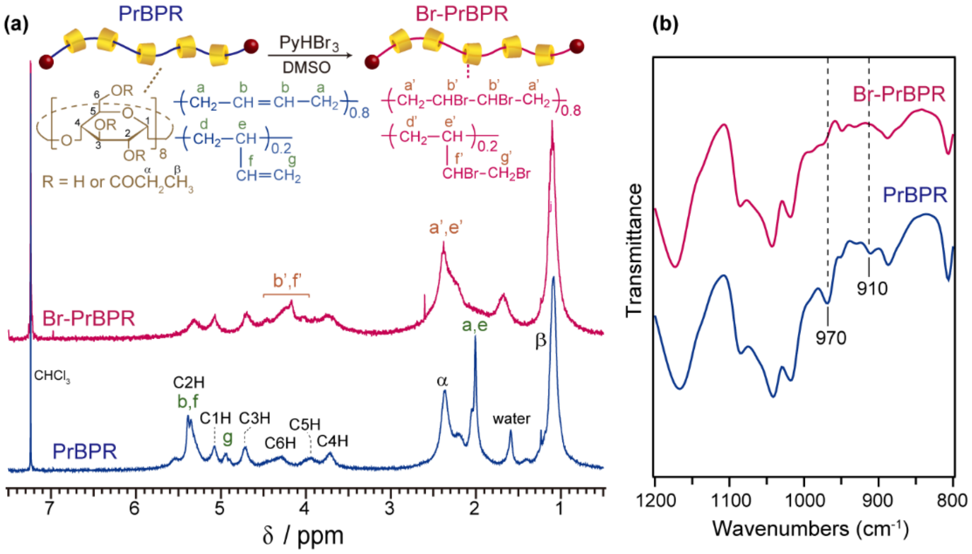

Figure S3. Partial ATR-FTIR spectra of BPR and its brominated derivatives with different degrees of the modification. Peaks at 965 and 910 cm^{-1}.

9. Film preparation by thermo-press molding

Film samples of PrBPR and Br-PrBPR were prepared by thermo-press molding under vacuum. The applied temperatures were 150 and 110 °C for PrBPR and Br-PrBPR, respectively. As a result, after rapid cooling to room temperature, about 0.2 mm thick samples were obtained.

10. Creation of master curves and analysis of the dynamics

Frequency dependences of the complex Young's modulus were measured at different temperature, and the data were horizontally shifted based on the time–temperature superposition principle to obtain a master curve at a reference temperature, T_0. The shift factor, a_T, is defined as

$$a_T = \frac{\tau_T}{\tau_{T_0}}$$

where τ_T and τ_{T_0} are the relaxation times at the measurement temperature and T_0, respectively. Figure S4 shows the master curves by using only low temperature data of PrBPR and Br-PrBPR. The successful superpositions permit us to discuss the relaxation dynamics based on the Arrhenius plots of a_T shown in Figure 4b.

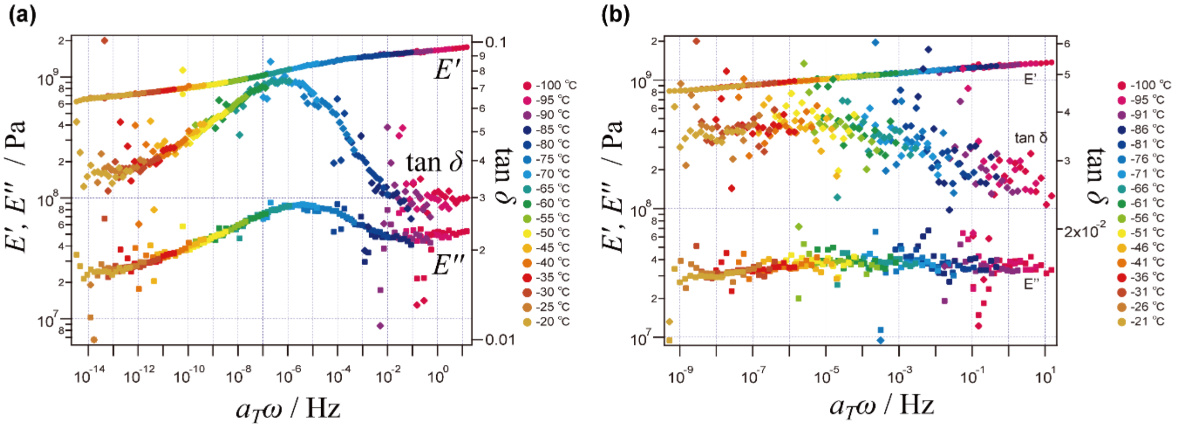

Figure S4. Master curves of PrBPR and Br-PrBPR at $T_0 = -100$ °C.

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[2] K. Kato and K. Ito, "Dynamic transition between rubber and sliding states attributed to slidable cross-links", *Soft Matter*, **2011**, *7*, 8737–8740.

[3] Harada, A.; Li, J.; Kamachi, M. *Macromolecules* **1993**, *26*, 5698-5703.