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Supporting Information for

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Phase Separation-Induced Glass Transition in Critical Miscible Condition

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4 Mayu Watanabe¹, Dong Shi², Ryuji Kiyama^{2,3}, Kagari Maruyama¹, Yuichiro Nishizawa⁴, Takayuki Uchihashi⁴,
5 Jian Ping Gong^{2,5}, Takayuki Nonoyama*²

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7 ¹Graduate School of Life Science, ²Faculty of Advanced Life Science, Hokkaido University, North 21 West 11,
8 Kita-ku, Sapporo 001-0021, Japan

9 ³Laboratoire de Sciences et Ingénierie de la Matière Molle, CNRS, ESPCI Paris, PSL Research University, 10 rue
10 Vauquelin, 75005 Paris, France

11 ⁴Graduate School of Science, Nagoya University, Furo-cho, Chukusa-ku, Nagoya 464-8601, Japan

12 ⁵Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, North 21 West 11,
13 Kita-ku, Sapporo 001-0021, Japan

14

15 E-mail: nonoyama@sci.hokudai.ac.jp (T. Nonoyama)

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33 1. Experiment

34 1.1 Materials

35 Isobornyl acrylate (IBXA) was provided from Osaka Organic Chemical Industry Co., Ltd., Osaka Japan.
36 Triethyl phosphate (TEP) and dibutyl adipate (DBA) were purchased from Tokyo Chemical Industry Co., Ltd.,
37 Tokyo, Japan. Dibutyl Phthalate (DBP), benzophenone (BP), acetone, acetonitrile, 1-butanol, n-butyl acetate, γ -
38 butyrolactone, carbon tetrachloride, chloroform, cyclohexane, diacetone alcohol, dibasic ester, diethyl ether,
39 diethylene glycol, *N,N'*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, ethanol, ethyl
40 acetate, methanol, methyl acetate, methyl ethyl ketone, methyl isobutyl ketone, n-methyl-2-pyrrolidone, methylene
41 dichloride, propylene carbonate, propylene glycol monoethyl ether, tetrahydrofuran, and toluene were purchased
42 from Fujifilm Wako Co., Ltd., Osaka, Japan. All chemicals were used without any purification. 0.38 mm-thick
43 polyethylene terephthalate film with silicone coating (PET-S) was purchased from Cross Point Co., Ltd.,
44 Sapporo, Japan.

45

46 1.2 Synthesis of pure PIBXA and PIBXA-plasticizer blend

47 The pure PIBXA was synthesized by the UV-irradiated radical polymerization. 0.1 mol% BP initiator
48 (referred to IBXA concentration) was added to liquid IBXA monomer (4.7 M). The solution was poured into a mold
49 constructed from 1-mm thick silicone spacer sandwiched by pair PET-S attached glass plates. UV light with 2000
50 mW/cm² (UAW365-31110-1212F, Sentech Co., Ltd., Osaka, Japan) was irradiated to the mold for 15 min. For the
51 samples of PIBXA with plasticizers (TEP, DBP, and DBA), the plasticizer was added to the above monomer-
52 initiator mixture with fractions of 10, 20, and 30 wt%. All plasticizers were well-mixed with the IBXA liquid
53 monomer. The synthesis was done in the same manner.

54

55 1.3 Calculation of Hansen solubility parameter (HSP) with variable temperatures

56 The HSP of pure PIBXA was experimentally calculated in the following solubility test. Around 2.0 g of
57 synthesized PIBXA was collected in the test glass tubes. Then, around 0.6 mL of a solvent, whose HSP was known,

58 was added in the tube. The ratio of PIBXA/solvent was fixed to 2/0.6 g/mL. The 28 kinds of solvents used in the
59 test were listed in **Table S1**. The sealed tubes were kept in the objective temperatures for 24 hours. After the
60 isothermal retention, the solubility state was scored as follows. If the PIBXA dissolved or absorbed all the added
61 solvent, it was recorded as a good solvent (Score 1). The other states like no absorption and phase separation were
62 recorded as a poor solvent (Score 0). Finally, the HSP coordinate and interaction radius (R_0) of PIBXA were
63 calculated as a center and radius of the sphere which included the positions of score 1 solvents and excluded the
64 score 0 solvents, determined by the least-squares fitting of sphere on the HSPiP[®] software (ver. 5.407). The tests
65 when solvents evaporated in high temperatures were excluded in the fitting. The HSPs of TEP, DBP, and DBA at
66 reference temperature were referred to the HSPiP[®] database. The test temperatures were kept at 25, 35, 45, and 55
67 °C in an aluminum block heater (MG-3100, Tokyo Rikakikai Co., Ltd., Tokyo, Japan).

68 The α was calculated from the change of density (ρ) in the temperature variation. The density of 28 kinds
69 of solvents and 3 plasticizers in different temperatures were measured by an oscillatory density meter (DMA5001,
70 Anton Paar, GmbH, Graz, Austria) (**Figure S1**). The measurement range of temperature was varied considering the
71 boiling point of each solvent. 4 points at least were measured to obtain α . The α had good negative correlation to
72 the boiling point (**Figure S2**). Calculation of the HSP coordinate and R_0 of PIBXA in different temperatures was
73 referred to corrected HSPs of 28-kind solvents and the score of solubility test in each temperature.

74

75 **1.4 Turbidity measurement**

76 Progress of the phase separation with changing temperature was evaluated by using a UV-visible
77 spectrophotometer (UV-1800, SHIMADZU Co., Ltd., Kyoto, Japan). The samples were set in a quartz cuvette, and
78 the transmittance was measured with 550 nm wavelength. The temperature was changed from 25 to 100 °C with
79 0.1°C/min heating ramp.

80

81

82

83 **1.5 Temperature modulated differential scanning calorimetry (MDSC)**

84 MDSC measurements were performed on a differential scanning calorimetry (Discovery X3 DSC, TA
85 instruments Inc., DE, US) to determine T_g . The sample was filled in an aluminum pan and sealed. A small hole was
86 punched in the lid to keep the constant pressure. The measurement was carried out under nitrogen gas atmosphere
87 from -20 to 140 °C at 2 °C/min global temperature ramp. The modulation amplitude and period of sine wave were
88 0.5 °C and 40 sec, respectively. The T_g was determined from a profile of reversing heat flow.

89

90 **1.6 Rheometry**

91 Rheological measurements were performed by a rheometer (MCR 702e, Anton Paar, GmbH, Graz,
92 Austria). The disc shape specimen with 15 mm diameter was mounted between the parallel plate geometries. The
93 sinewave-shear deformation was applied at 10 rad/s angular frequency and 0.1% strain. Temperature was varied
94 from 25 to 130 °C with 0.1 °C/min ramp.

95

96 **1.7 Scanning electron microscopy (SEM)**

97 Observation of morphology was performed by using SEM (JSM-6010LA, JEOL Co., Ltd., Tokyo, Japan).
98 Samples annealed at each temperature were quenched in liquid nitrogen. Then sample was fixed with double-side
99 carbon tape on brass stage. The acceleration voltage was 10 kV.

100

101 **1.8 Elastic modulus mapping by using atomic force microscopy (AFM)**

102 The morphology and elastic modulus distribution of the sample's surface were evaluated by laboratory-
103 built high-speed AFM ¹. The measurement samples were finely ground glued and fixed using glue on a glass stage
104 with $\phi = 1.5$ mm. All measurements were performed in air and the cantilever was ARROW-UHFAuD-20 (spring
105 constant: ~ 1 N/m, resonance frequency: ~ 1300 kHz in air, from NANO WORLD). The oscillation amplitude of the
106 cantilever was detected by the optical lever method using a laser with a wavelength of 680 nm. Topological images
107 were acquired at a rate of 1 s/frame. The mechanical properties of the sample surface were evaluated by force

108 mapping measurements, in which height information and force-indentation curves are alternately acquired at high
109 speed, based on inline force curve measurements (see inline force curve measurements) ². Young's modulus was
110 estimated by fitting analysis of the obtained force curve with the Derjaguin–Muller–Toporov (DMT) model.

111

112 **1.9 Gel permeation chromatography (GPC)**

113 Molecular weight of PIBXA in PIBXA-TEP blend was measured by a GPC system constructing from
114 Chromaster[®] Organizer, Column Oven, Pump 5110 (Hitachi High-Tech Corp., Tokyo, Japan), refractive index
115 detector (Optilab rEX, Shoko Science Co., Ltd., Yokohama, Japan), multi angle light scattering (DAWN HELEOS-
116 A, Wyatt Technology Corp., CA, US), and autosampler 5210 (Hitachi High-Tech Corp.). The Guard column and
117 main column for THF were KF-G 4A and KF-806M of Shoko Science Co., Ltd., respectively. The PIBXA-TEP
118 blend was dissolved in toluene. The solution was dropped in 5-fold volume ethanol to obtain the PIBXA precipitate.
119 After washing and drying, the PIBXA was dissolved in THF (high performance liquid chromatography grade with
120 stabilizer added) with 5 mg/mL concentration. The flow rate, elution time, dn/dc , second virial coefficient were
121 1.0 mL/min, 40 min, 0.089, and 0.000, respectively. Debye model was applied for the calculation.

122

123 **Reference in Supporting information**

- 124 1. T. Ando, T. Uchihashi, T. Fukuma, *Prog. Surf. Sci.* **2008**, *83*, 337-437.
- 125 2. C. Ganser and T. Uchihashi, *Nanoscale*, **2019**, *11*, 125-135.

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Chemical	CAS Number	Boiling point (°C)	HSP at 25 °C *			Solubility Scores				$\alpha \times 10^3$ (K ⁻¹)
			δd (MPa ^{1/2})	δp (MPa ^{1/2})	δh (MPa ^{1/2})	25 (°C)	35 (°C)	45 (°C)	55 (°C)	
Plasticizers										
Triethyl Phospahte (TEP)	78-40-0	215	16.7	11.4	9.2	-	-	-	-	0.970
Dibutyl Phthalate (DBP)	84-74-2	340	17.8	8.6	4.1	-	-	-	-	0.800
Dibutyl Adipate (DBA)	105-99-7	305	16.3	3.7	4.9	-	-	-	-	0.909
Solvents for solubility test										
Acetone	67-64-1	56	15.5	10.4	7.0	0	0	evap.**	evap.	1.505
Acetonitrile	75-05-8	82	15.3	18.0	6.1	0	0	0	0	1.481
1-Butanol	71-36-3	118	16.0	5.7	15.8	0	0	0	1	1.007
n-Butyl Acetate	123-86-4	126	15.8	3.7	6.3	1	1	1	1	1.235
γ -Butyrolactone	96-48-0	204	18.0	16.6	7.4	0	0	0	0	0.897
Carbon Tetrachloride	56-23-5	77	17.8	0.0	0.6	1	1	1	evap.	1.291
Chloroform	67-66-3	61	17.8	3.1	5.7	1	1	1	evap.	1.342
Cyclohexane	110-82-7	81	16.8	0.0	0.2	1	1	1	1	1.289
Diacetone Alcohol	123-42-2	166	15.8	8.2	10.8	0	0	0	0	1.004
Dibasic Ester (DBE)	95481-62-2	~200	16.2	6.5	8.4	0	0	0	0	0.981
Diethyl Ether	60-29-7	35	14.5	2.9	4.6	1	1	evap.	evap.	1.638
Diethylene Glycol	111-46-6	244	16.6	12.0	19.0	0	0	0	0	0.662
N,N'-Dimethyl Formamide (DMF)	68-12-2	153	17.4	13.7	11.3	0	0	0	0	1.048
Dimethyl Sulfoxide (DMSO)	67-68-5	189	18.4	16.4	10.2	0	0	0	0	0.940
1,4-Dioxane	123-91-1	101	17.5	1.8	9.0	1	1	1	1	1.144
Dipropylene Glycol	2396-61-4	231	16.5	10.6	17.7	0	0	0	0	0.771
Ethanol (EtOH)	64-17-5	78	15.8	8.8	19.4	0	0	0	0	1.163
Ethyl Acetate (EA)	141-78-6	77	15.8	5.3	7.2	1	1	1	1	1.460
Methanol (MeOH)	67-56-1	65	14.7	12.3	22.3	0	0	0	0	1.266
Methyl Acetate (MA)	79-20-9	57	15.5	7.2	7.6	1	1	1	evap.	1.476
Methyl Ethyl Ketone (MEK)	78-93-3	80	16.0	9.0	5.1	1	1	1	1	1.393
Methyl Isobutyl Ketone (MIBK)	108-10-1	116	15.3	6.1	4.1	1	1	1	1	1.211
n-Methyl-2-Pyrrolidone (NMP)	872-50-4	202	18.0	12.3	7.2	0	0	0	0	0.891
Methylene Dichloride (DCM)	75-09-2	40	17.0	7.3	7.1	1	1	evap.	evap.	1.391
Propylene Carbonate	108-32-7	240	20.0	18.0	4.1	0	0	0	0	0.909
Propylene Glycol Monoethyl Ether	1569-02-4	120	15.7	6.5	10.5	0	0	1	1	1.109
Tetrahydrofuran (THF)	109-99-9	66	16.8	5.7	8.0	1	1	1	evap.	1.285
Toluene	108-88-3	110	18.0	1.4	2.0	1	1	1	1	1.130

* The HSPs at reference temperature 25 °C were provided from the HSPiP® database.

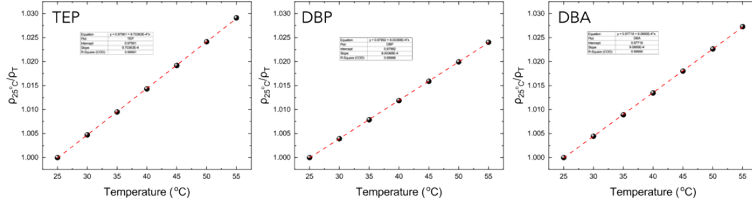
** "evap.", meaning solvent evaporation during test, was excluded from the analysis.

128

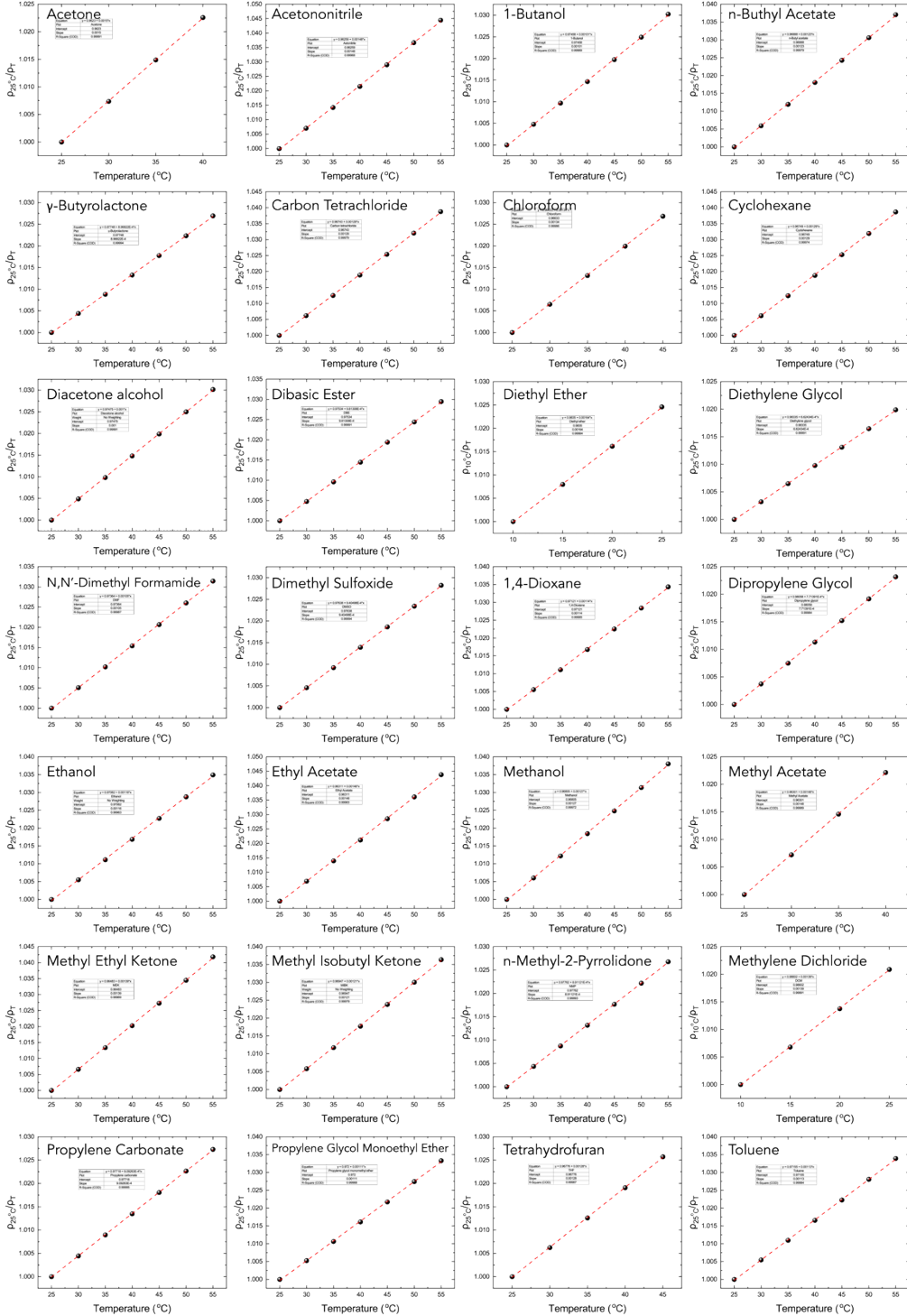
129 **Table S1** Summary of HSP and solubility test.

130

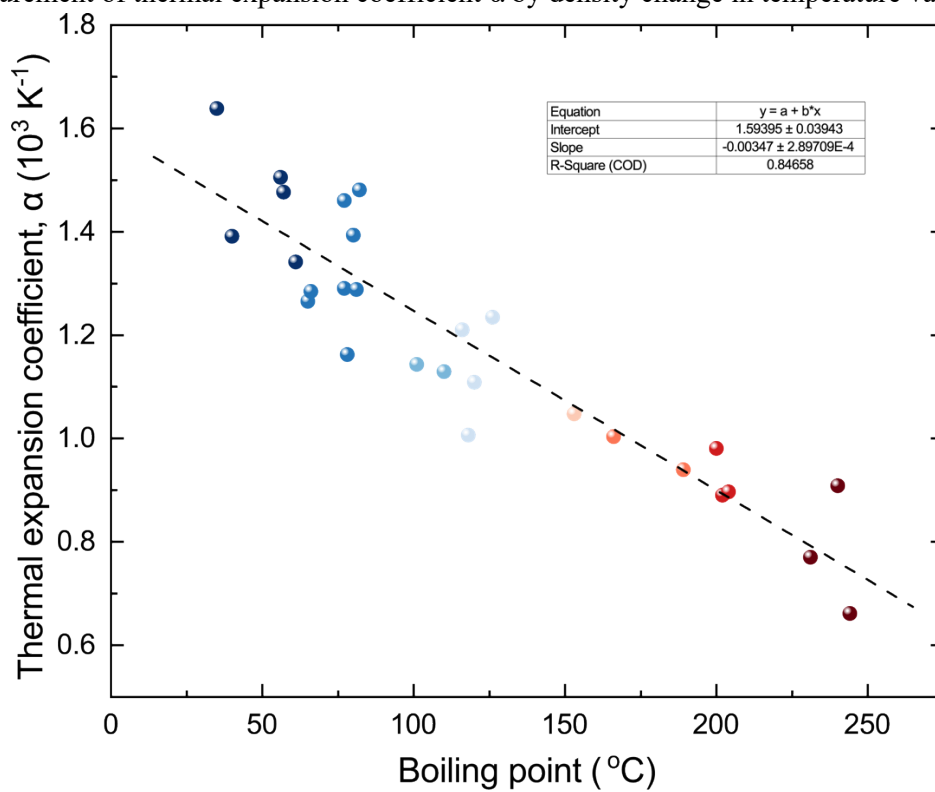
Plasticizers



Fitting Solvents



132 **Figure S1** Measurement of thermal expansion coefficient α by density change in temperature variations.



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134 **Figure S2** Relationship between thermal expansion coefficient α and boiling point for 28 solvents.
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