Supplementary Information (SI) for RSC Applied Polymers.

Supporting Information

High-Refractive-Index Copolymers Produced by Radical Copolymerization of Aromatic Heterocyclic Monomers in Deep Eutectic Solvents

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Experimental Section

1. Materials

2,2′-Azobis(isobutyronitrile) (AIBN, 97 %) was purchased from Kanto Chemical and purified via recrystallization from methanol. Methyl methacrylate (MMA, Tokyo Kasei Kogyo, 99%) was purified by distillation under vacuum. *N*-Vinylcarbazole (NVC, >98%) was purchased from Tokyo Kasei Kogyo, and recrystallized two times from methanol. Benzothiazoyl vinyl sulfide (BTVS) was synthesized by the reaction of 2-mercaptobenzothiazole with 1, 2-dibromoethane, and purified by vacuum distillation, as described previously.[1] 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Tokyo Kasei Kogyo, >98.0%), and all the other materials were used as received.

Three hydrophobic NADESs were prepared from naturally derived compounds (melting point = 49.0–52.0 °C for Thy: thymol, 28 °C for Men: (+/-)-menthol, 68–72 °C for Cou: coumarin, 38.0–41.0 °C for Tdc: 1-tetradecanol) by simple mixing two solids at a suitable feed ratio (Thy/Cou (1/1), Thy/Men (1/1), and Tdc/Men (1/2)) at room temperature, as reported previously.[2,3] Hydrophilic ChCl/Urea (1/2) DES was formed by stirring the two solids at a ChCl/urea ratio of 1:2 (melting point = 303 °C for ChCl: choline chloride and 134 °C for urea) at 80 °C until a homogeneous colorless liquid was obtained, as reported previously.[4] Hydrophilic $ZnCl_2$/Urea (1/3.5) DES was formed by stirring the two solids (melting point = 293 °C for $ZnCl_2$ and 134 °C for urea) at 100 °C until a homogeneous colorless liquid was obtained, as reported previously.[5]

2. Polymer Synthesis

2-1. Thermally-induced copolymerization

A typical procedure for the thermally-induced free radical copolymerization of MMA and BTVS is as follows (Run 2 in Table 1): thymol (297 mg, 1.98 mmol) and coumarin (289 mg, 1.98 mmol) were placed in a 10 mL glass vial equipped with a magnetic stirring, and the mixture was stirred under ambient conditions (approximately 25 °C in the air) until a homogeneous solution was obtained. Subsequently, MMA (200 mg, 2.00 mmol), BTVS (387 mg, 2.00 mmol), AIBN (3.3 mg (0.02 mmol) were added to the hydrophobic NADES (Thy/Cou (1/1)), and the mixture was transferred into a glass polymerization ampule equipped with a magnetic stir bar. After the solution was degassed by three freeze-evacuate-thaw cycles, the ampule was flame-sealed under vacuum, and then it was stirred at 60 °C for 24 h. The reaction was stopped by rapid cooling with liquid nitrogen. After the reaction mixture was diluted by adding a small amount of $CHCl_3$, the mixture was poured into a large excess of hexane to precipitate the product. The resultant copolymer was filtrated and then dried under vacuum to afford P(MMA-*co*-BTVS) as a pale yellow solid (0.188 g, yield = 32 %).

The same thermally-induced copolymerization procedure was employed for the synthesis of P(MMA-*co*-BTVS)s in different hydrophobic NADESs and hydrophilic DESs. When the hydrophilic DESs were employed, the polymerization mixture was poured into a large excess of methanol to precipitate the product.

The MMA/BTVS copolymer composition was calculated by the sulfur content determined by elemental analysis (equation 1).

$$\text{Sulfur content (obsd)} = \frac{(\text{Sulfur content (calcd) in BTVS/MW of BTVS})\times \text{x}}{(1\text{-x})\times \text{MW of MMA} + \text{x}\times \text{MW of BTVS}} \quad (1)$$

where sulfur content (obsd) represents sulfur content of the P(MMA-*co*-BTVS) determined by elemental analysis, and x represents the fraction of the BTVS and 1-x represents the fraction of MMA, respectively.

P(MMA-*co*-NVC)s were synthesized using the same thermally-induced copolymerization procedure in different hydrophobic NADESs and hydrophilic DESs. The MMA/NVC copolymer composition was calculated by the nitrogen content determined by elemental analysis (equation 2).

$$\text{Nitrogen content (obsd)} = \frac{(\text{Nitrogen content (calcd) in NVC/MW of NVC})\times \text{x}}{(1\text{-x})\times \text{MW of MMA} + \text{x}\times \text{MW of NVC}} \quad (2)$$

where nitrogen content (obsd) represents nitrogen content of the P(MMA-*co*-NVC)s determined by elemental analysis, and x represents the fraction of the NVC and 1-x represents the fraction of MMA, respectively.

P(BTVS-*co*-NVC)s were synthesized using the same thermally-induced copolymerization procedure in different hydrophobic NADESs and hydrophilic DESs. The BTVS/NVC copolymer composition was calculated by the sulfur content determined by elemental analysis (equation 3).

$$\text{Sulfur content (obsd)} = \frac{\text{(Sulfur content (calcd) in BTVS/MW of BTVS)}\times\text{x}}{\text{(1-x)}\times\text{MW of NVC} + \text{x}\times\text{MW of BTVS}} \quad (3)$$

where sulfur content (obsd) represents sulfur content of the P(BTVS-*co*-NVC) determined by elemental analysis, and x represents the fraction of the BTVS and 1-x represents the fraction of NVC, respectively.

2-2. Photo-induced copolymerization

A typical procedure for the photo-induced free radical copolymerization of MMA and BTVS is as follows (Run 4-2 in Table S8): Thymol (297 mg, 1.98 mmol) and menthol (298 mg, 1.91 mmol) were placed in a 10 mL glass vial equipped with a magnetic stirring, and the mixture was stirred under ambient conditions (approximately 25 °C in the air) until a homogeneous solution was obtained. Subsequently, MMA (200 mg, 2.00 mmol), BTVS (387 mg, 2.00 mmol), and DMPA (5.1 mg, 0.02 mmol) were added to the hydrophobic NADES (Thy/Men (1/1)). The mixture was irradiated with a 365 nm wavelength LED–UV light (HLV-24UV365-4WNRBT, CCS Inc., 10 cm away, 120–130 mW/cm^2) for 15 min under ambient atmosphere. After the reaction mixture was diluted by adding a small amount of $CHCl_3$, the mixture was poured into a large excess of hexane to precipitate the product. The resultant copolymer was filtrated and then dried under vacuum to afford P(MMA-*co*-BTVS) as a pale yellow solid (0.188 g, yield = 32%).

3. Instrumentation

The NMR spectra were recorded on a JEOL JNM-ECX400 (400 MHz). Elemental carbon, hydrogen, nitrogen, and sulfur were analyzed using a Perkin-Elmer 2400 II CHNS/O analyzer. The M_n and M_w/M_n were estimated by size exclusion chromatography (SEC) relative to polystyrene standards using a Tosoh HPLC HLC-8220 system equipped with refractive index and ultraviolet detectors, four consecutive hydrophilic vinyl polymer-based gel columns (TSK-GELs α-M, α-4000, α-3000, α-2500, with TSK-guard column α), with DMF containing 10 mM LiBr as the eluent at a flow rate of 1.0 mL/min.[1,6] Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min under a nitrogen atmosphere on a SEIKO TG/DTA6200 instrument. Differential scanning calorimetry (DSC) analysis was performed using a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C /min under nitrogen. The transparency was evaluated measured by UV-vis measurement using a JASCO V-630BIO UV−vis spectrophotometer. The samples were prepared by drop-casting as follows: 5 mg of the polymer $CHCl_3$ solution (1.0 wt %) was placed on the glass substrate, and it was allowed to evaporate overnight in an ambient atmosphere. Wavelength-dependent refractive indices $n(\lambda)$ of spin-coated polymer thin films were evaluated by a spectroscopic ellipsometer (J.A. Woollam M-2000U), as described previously.[6,7] Briefly, Cauchy function for the refractive index $n(\lambda) = A + B/\lambda^2 + C/\lambda^4$ was employed for evaluation of the wavelength-dependence of refractive index. The accuracy of the refractive index was confirmed by Coefficients of Cauchy's relation determined by least squares fit for more than four different refractive indexes. The homogenous polymer thin films were prepared by spin-coating from $CHCl_3$ solutions (conc. = 1.0 wt %, 1500 rpm for 90 s) on a silicon wafer. The Abbe number (ν_D) was calculated for the polymers as $\nu_D = (n_D - 1)/(n_F - n_C)$, where n_D, n_F, and n_C are the refractive indices of materials at wavelength of 589.3, 486.1, and 656.3 nm, that correspond to sodium D, hydrogen F, and hydrogen C line, respectively.

Table S1. Solubility and miscibility of the monomers and corresponding homopolymers in hydrophobic NADESs and hydrophilic DESs

	Thy/Cou	Thy/Men	Tdc/Men	ChCl/urea	$ZnCl_2$/urea
MMA monomer	++	++	++	++	++
BTVS monomer	++	++	-	-	-
NVC monomer	+	+	-	-	-
PMMA	+	+	-	-	-
PBTVS	+	+	-	-	-
PNVC	+	+	-	-	-

++ : miscible, + : soluble at room temperature (approximately 1.0 mg/mL), - : insoluble/immiscible at room temperature.

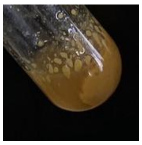
Table S2. Solubility and miscibility of the monomers, corresponding homopolymers, and DESs in conventional solvents

	H_2O	DMF	Methanol	THF	Chloroform	1-Hexane
MMA monomer	+-	++	++	++	++	++
BTVS monomer	-	++	++	++	++	++
NVC monomer	-	+	+	+	+	+
PMMA	-	+	-	+	+	-
PBTVS	-	+	-	+	+	-
PNVC	-	+	-	+	+	-
Thy/Cou	-	++	++	++	++	++
Thy/Men	-	++	++	++	++	++
Tdc/Men	-	++	++	++	++	++
ChCl/urea	++	++	++	++	++	++
$ZnCl_2$/urea	++	++	++	++	++	++

++ : miscible, + : soluble at room temperature (approximately 1.0 mg/mL), - : insoluble/immiscible,

+- : miscible/soluble in a diluted condition.

Table S3. Thermally-induced radical polymerization of BTVS in hydrophobic NADESs [a)]

Run	DES	Yield [b)]	M_n [c)]	M_w/M_n [c)]	Appearance
1	Thy/Cou	16	2600	1.68	
2	Thy/Men	19	3000	1.75	
3	Tdc/Men	20	5400	1.99	

[a)] Polymerization with AIBN at 60 °C for 24 h. $[I]_0/[M]_0 = 1/100$. [b)] Hexane insoluble part. [c)] Measured by SEC using PSt in DMF.

Table S4. Photo-induced radical polymerization of BTVS in hydrophobic NADESs [a)]

Run	DES	Yield [b)]	M_n [c)]	M_w/M_n [c)]
1	Thy/Cou	14	3100	1.76
2	Thy/Men	34	4400	1.77
3	Tdc/Men	21	5100	2.22

[a)] Polymerization with DMPA at room temperature for 15 min. $[I]_0/[M]_0 = 1/100$. [b)] Hexane insoluble part. [c)] Measured by SEC using PSt in DMF.

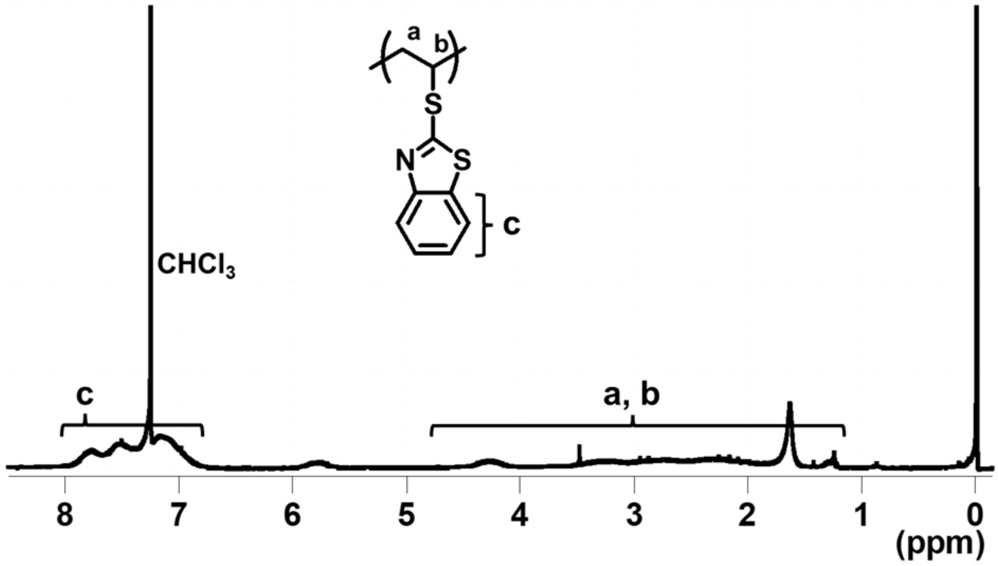


Figure S1. ^{1}H NMR spectrum (CDCl$_3$) of PBTVS (Run 1 in Table S3).

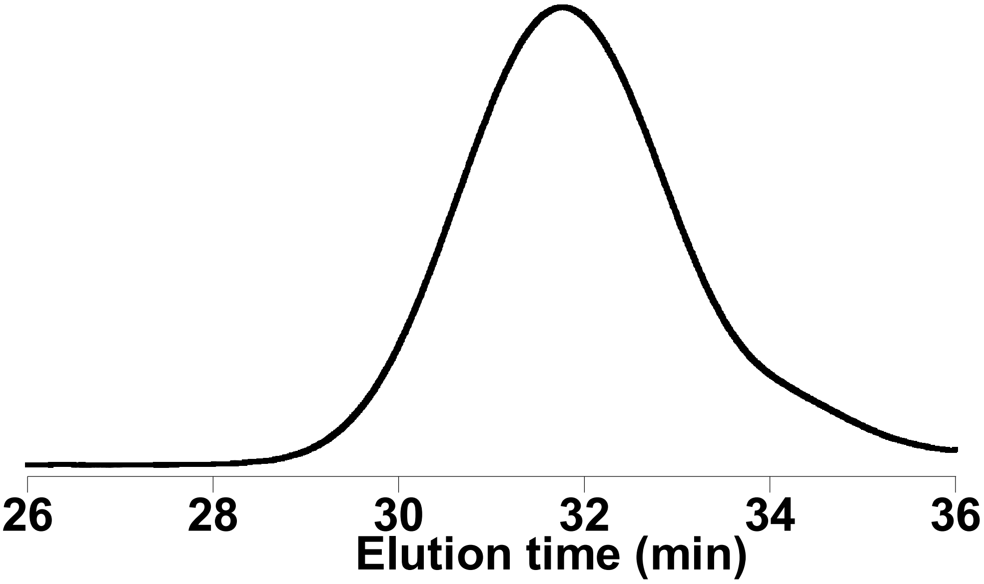
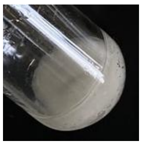


Figure S2. SEC curve of PBTVS (Run 3 in Table S1).

Table S5. Thermally-induced radical polymerization of MMA in hydrophobic NADESs [a)]

Run	DES	Yield [b)]	M_n [c)]	M_w/M_n [c)]	Appearance
1	Thy/Cou	85	48000	1.71	-
2	Thy/Men	7.8	39000	2.21	
3	Tdc/Men	64	120000	2.74	

[a)] Polymerization with AIBN at 60 °C for 24 h. $[I]_0/[M]_0 = 1/100$. [b)] Hexane insoluble part. [c)] Measured by SEC using PSt in THF.

Table S6. Photo-induced radical polymerization of MMA in hydrophobic NADESs [a)]

Run	DES	Yield [b)]	M_n [c)]	M_w/M_n [c)]	Appearance
1	Thy/Cou	16	2200	2.46	
2	Thy/Men	9.3	1600	2.14	
3	Tdc/Men	6.4	1200	2.01	

[a)] Polymerization with DMPA at room temperature for 15 min. $[I]_0/[M]_0 = 1/100$. [b)] Hexane insoluble part. [c)] Measured by SEC using PSt in DMF.

Table S7. Thermally-induced radical copolymerization of aromatic heterocyclic monomers at 80 ℃ in DESs a)

Entry	Monomer (M_1/M_2)	$[I]_0/[M_1]_0/[M_2]_0$	DES	Yield b) (%)	M_n c) (SEC)	M_w/M_n c) (SEC)	n/m d)
CP1-7	MMA/BTVS	1/100/100	Tdc/Men	59	15000	2.49	n.d.
CP1-8			ChCl/urea	52 e)	29000	3.13	53/47
CP1-9			$ZnCl_2$/urea	81 e)	40000	2.74	58/42
CP2-7	MMA/NVC	1/100/100	Tdc/Men	92	60000	3.49	48:52 f)
CP2-8			ChCl/urea	57 e)	38000	4.61	49:51 f)
CP2-9			$ZnCl_2$/urea	70 e)	130000	2.45	46:54 f)
CP3-9	BTVS/NVC	1/100/100	bulk	35	12000	1.84	71:29
CP3-10			Thy/Men	6.4	2400	1.59	69:31
CP3-11			Tdc/Men	21	4500	1.86	71:29
CP3-12			ChCl/urea	49 e)	9700	2.07	67:33
CP3-13			$ZnCl_2$/urea	43 e)	4300	2.87	54:46

a) Copolymerization with AIBN in DES at 80 ℃ for 24 h.
b) Hexane insoluble part.
c) Measured by SEC using PSt standard in DMF.
d) Evaluated from sulfur content determined by elemental analysis.
e) Methanol insoluble part.
f) Evaluated from nitrogen content determined by elemental analysis.

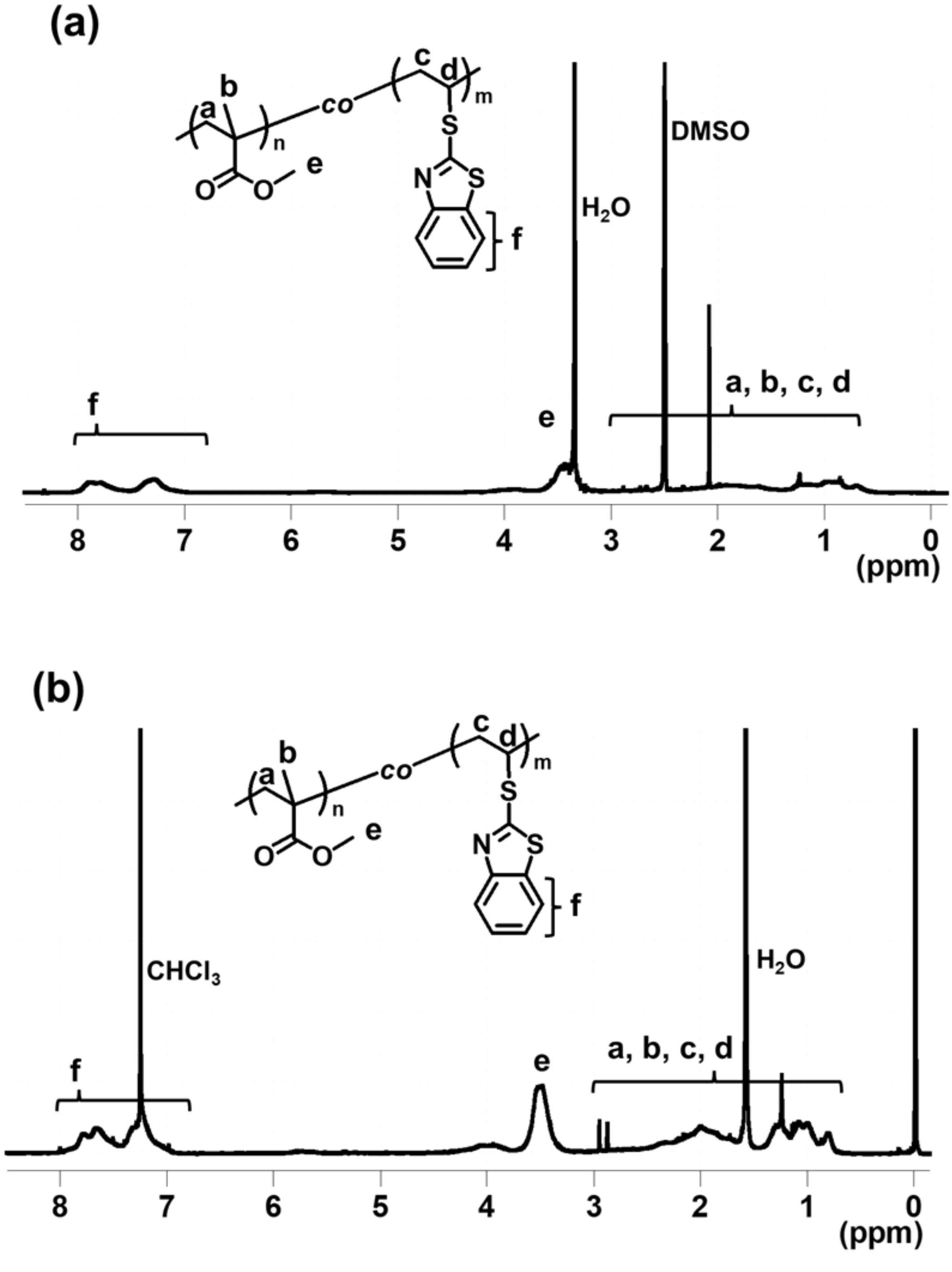


Figure S3. ^{1}H NMR spectra of P(MMA-*co*-BTVS)s (Table 1): (a) CP1-4 in DMSO-d_6 and (b) CP1-5 in $CDCl_3$.

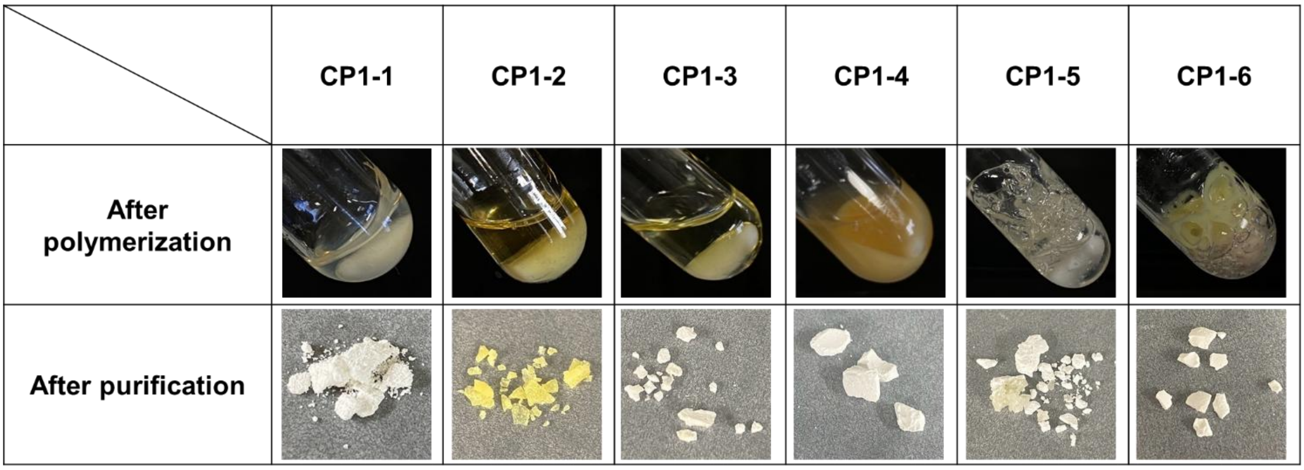


Figure S4. Photographs of representative P(MMA-*co*-BTVS) samples (Table 1); polymerization mixtures just after the copolymerization (above) and isolated samples after the purification via reprecipitation (below).

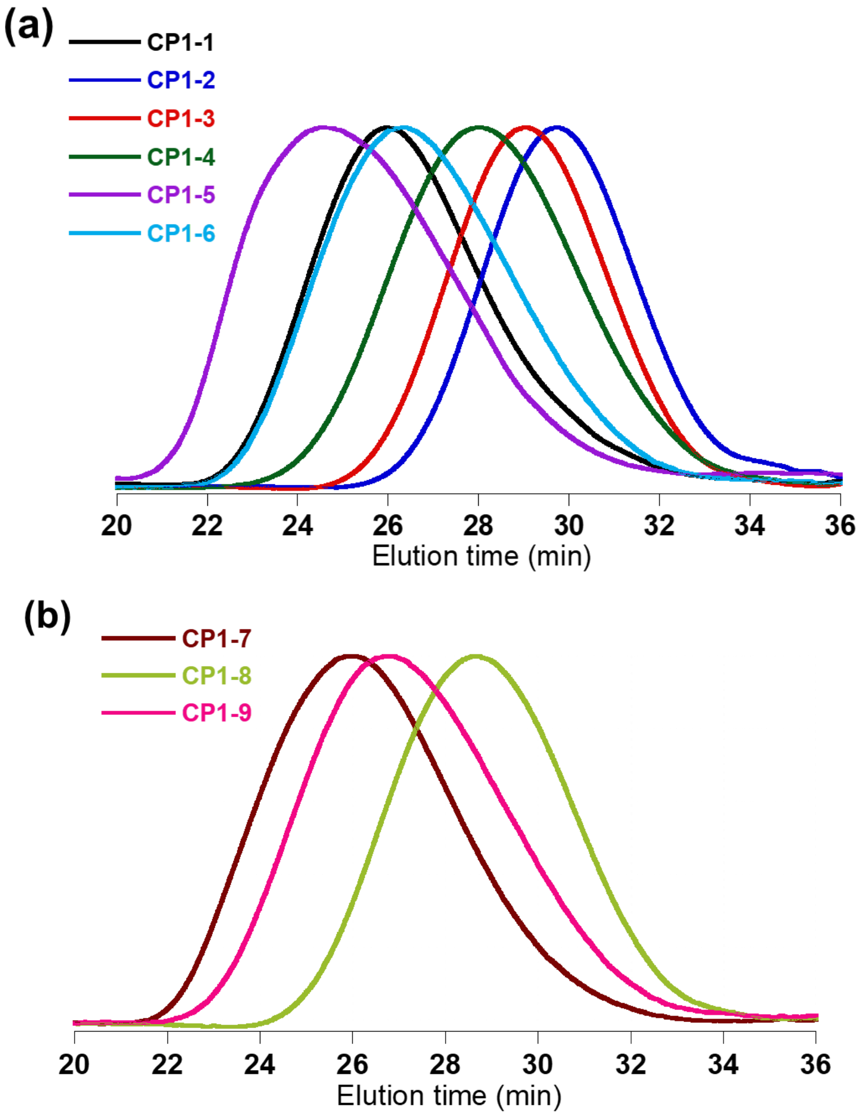


Figure S5. SEC curves of P(MMA-*co*-BTVS)s prepared by thermally-induced copolymerization at (a) 60 °C and (b) 80 °C (Table 1 and Table S7).

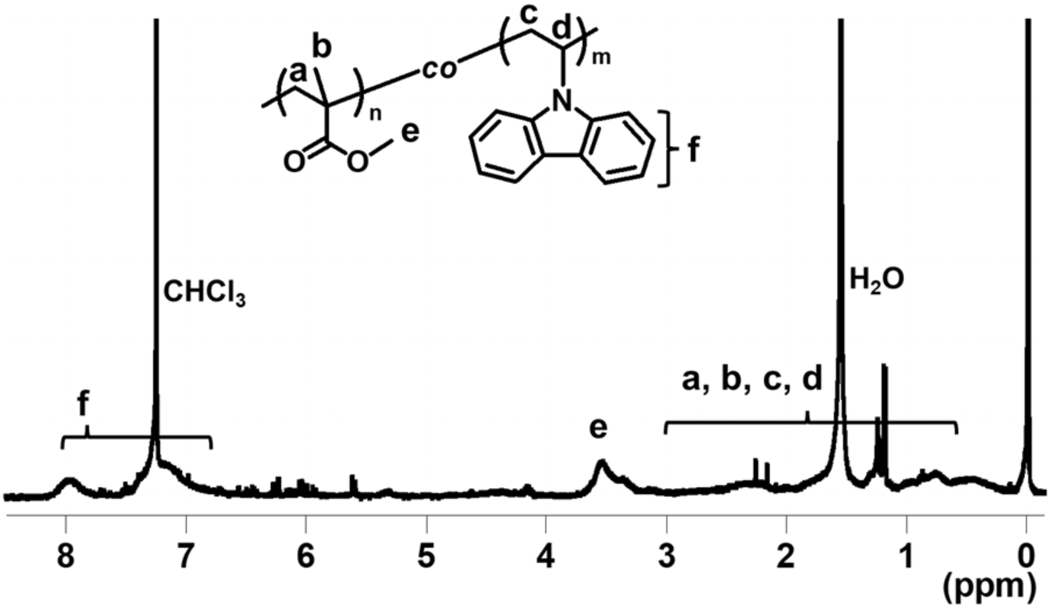


Figure S6. ^{1}H NMR spectrum (CDCl$_3$) of P(MMA-*co*-NVC) (CP2-2 in Table 1).

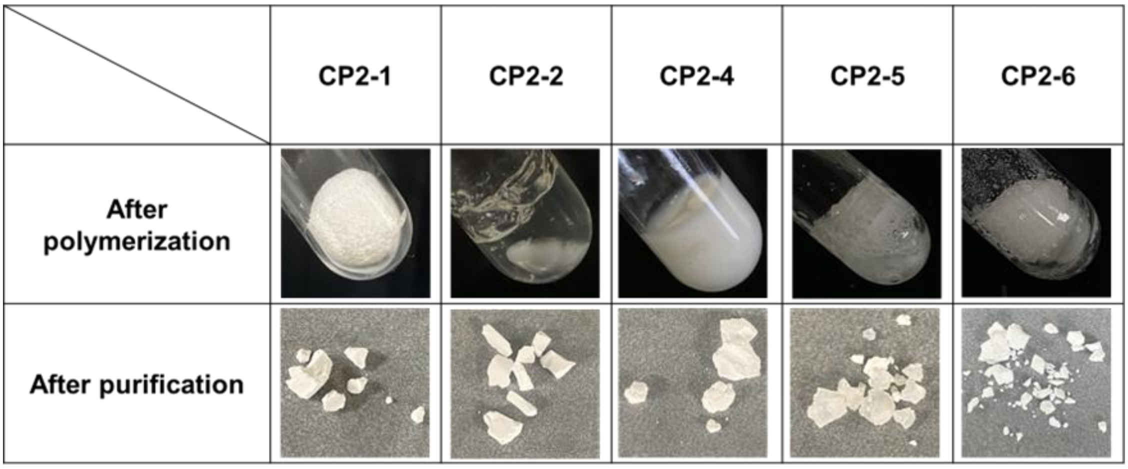


Figure S7. Photographs of representative P(MMA-*co*-NVC) samples (Table 1); polymerization mixtures just after the copolymerization (above) and isolated samples after the purification via reprecipitation (below).

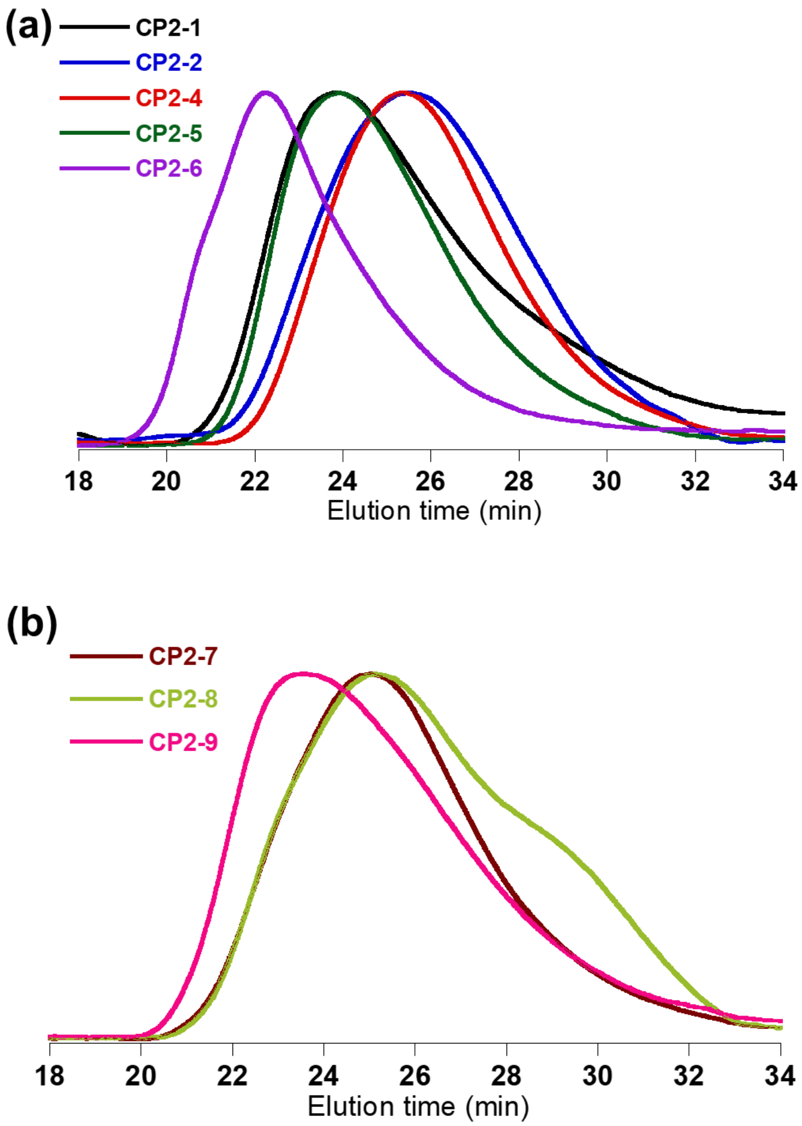


Figure S8. SEC curve of P(MMA-*co*-NVC)s prepared by thermally-induced copolymerization at (a) 60 °C and (b) 80 °C (Table 1, Table S7).

Table S8. Photo-induced radical copolymerization of the aromatic heterocyclic monomers in DESs [a)]

Entry	Monomer (M_1/M_2)	$[I]_0/[M_1]_0/[M_2]_0$	DES	Yield[b)] (%)	M_n[c)] (SEC)	M_w/M_n[c)] (SEC)
CP4-1	MMA/BTVS	1/100/100	Thy/Cou	36	8400	2.55
CP4-2			Thy/Men	32	8200	2.21
CP4-3			Tdc/Men	30	8200	4.62
CP5-1	MMA/NVC		Thy/Cou	< 5	-	-
CP5-2			Thy/Men	61	11100	2.59
CP5-3			Tdc/Men	29	7500	10.5

[a)] Polymerization with DMPA at room temperature for 15 min under UV light (LED lamp at 365 nm). [b)] Hexane insoluble part. [d)] Measured by SEC using PSt standard in DMF.

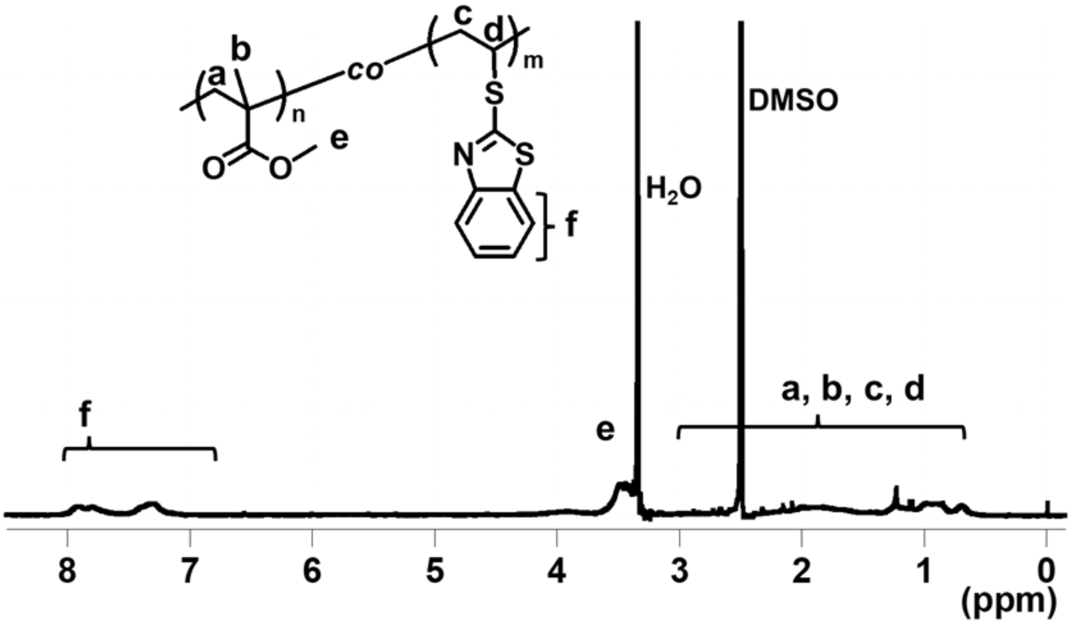


Figure S9. ^{1}H NMR spectrum (DMSO-*d*$_6$) of P(MMA-*co*-BTVS) prepared by photo-induced radical copolymerization (CP4-2 in Table S8).

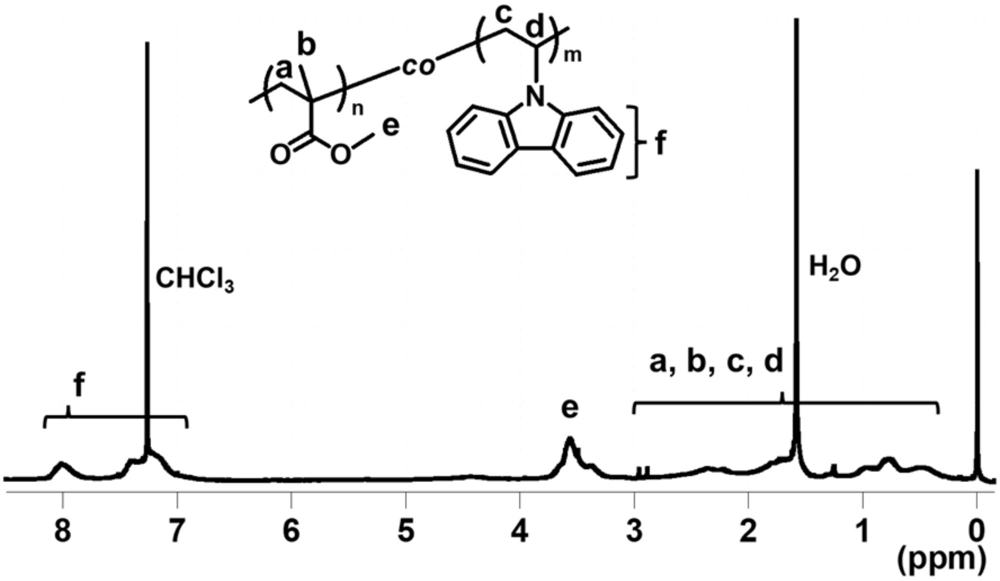


Figure S10. ^{1}H NMR spectrum (CDCl$_3$) of P(MMA-*co*-NVC) prepared by photo-induced radical copolymerization (CP5-3 in Table S8).

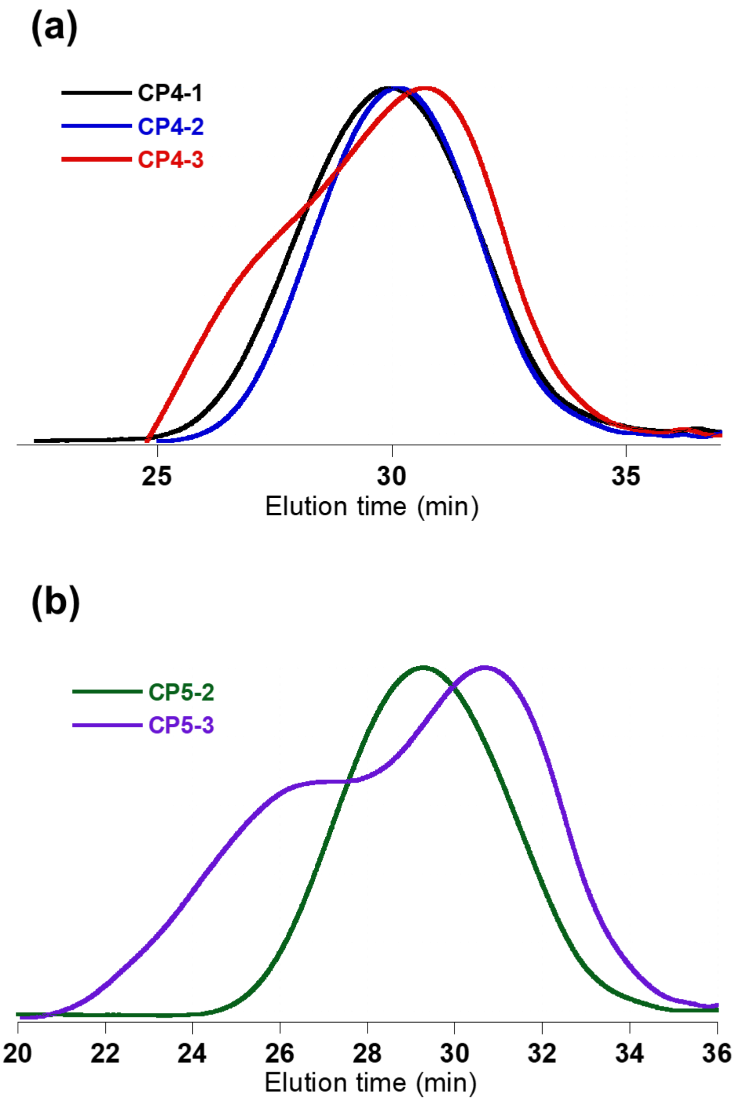


Figure S11. SEC curves of (a) P(MMA-*co*-BTVS)s and (b) P(MMA-*co*-NVC)s prepared by photo-induced radical copolymerization (Table S8).

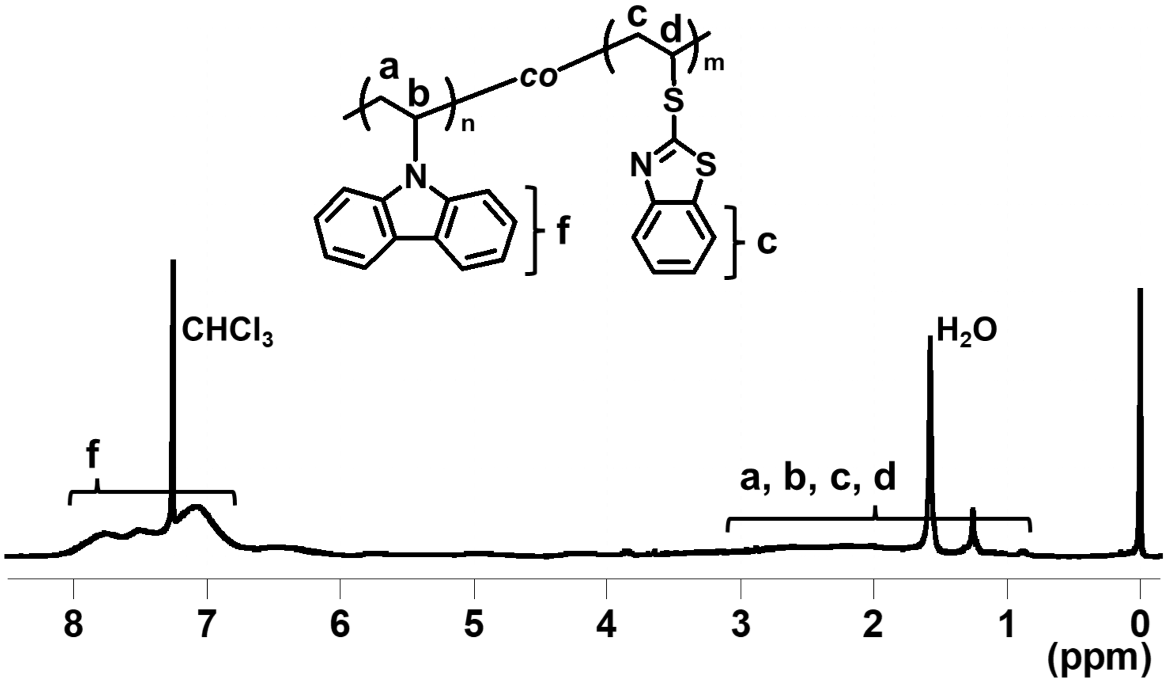


Figure S12. ^{1}H NMR spectrum ($CDCl_3$) of P(BTVS-*co*-NVC) (CP3-5 in Table 1).

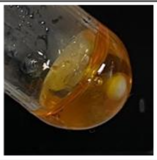
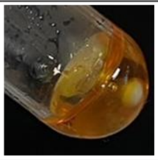
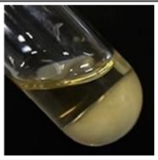
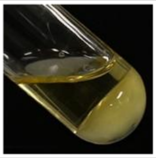
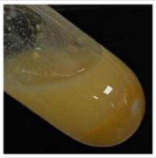
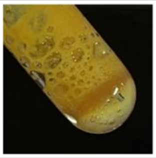
	CP3-1	CP3-2	CP3-3	CP3-4	CP3-5	CP3-6
After polymerization						
After purification						

Figure S13. Photographs of representative P(BTVS-*co*-NVC) samples (Table 1); polymerization mixtures just after the copolymerization (above) and isolated samples after the purification via reprecipitation (below).

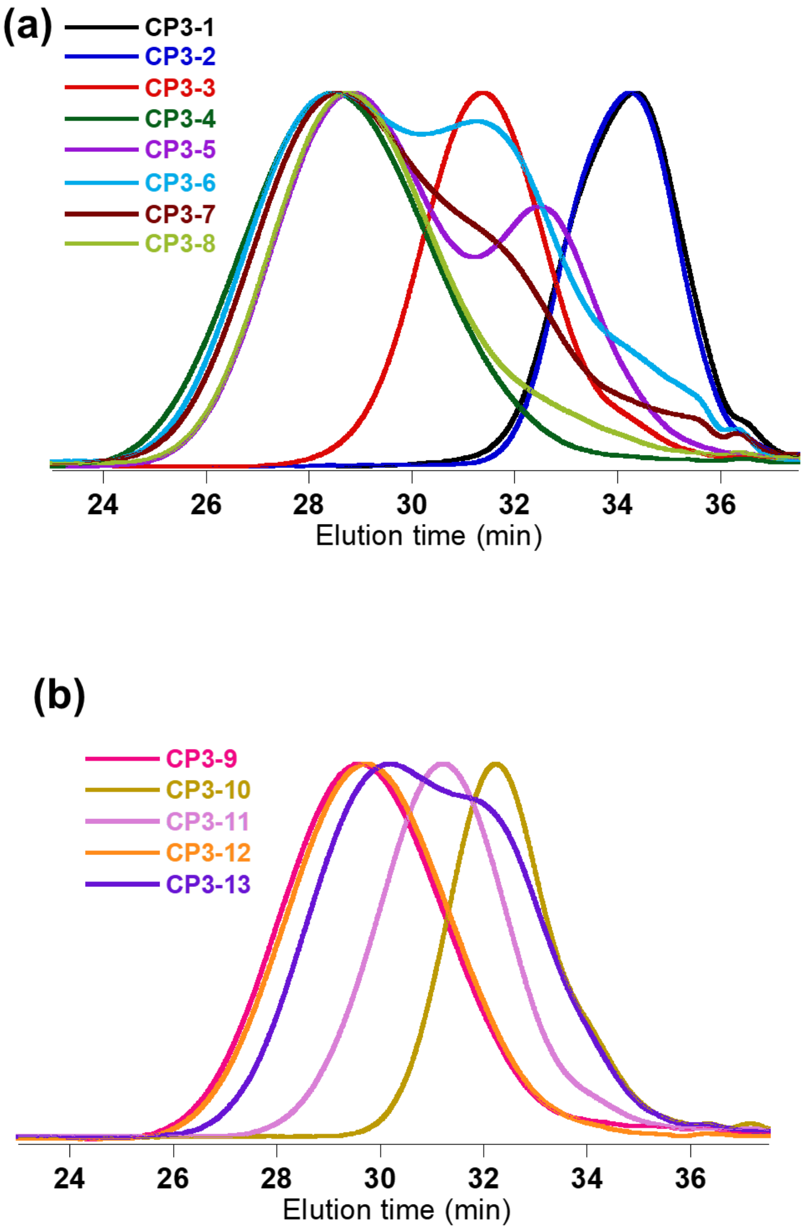


Figure S14. SEC curves of P(BTVS-*co*-NVC)s prepared by thermally induced copolymerization at (a) 60 °C and (b) 80 °C (Table 1, Table S7).

Table S9. Results of elemental analysis

Entry [a)]	C (%)	H (%)	N (%)	S (%)
CP1-1	57.35	4.87	7.76	21.67
CP1-2	56.90	5.86	5.17	15.74
CP1-3	57.96	5.42	4.04	18.63
CP1-4	57.62	5.41	4.30	19.87
CP1-5	57.23	5.17	4.68	20.60
CP1-6	56.88	4.82	5.07	23.45
CP2-1	76.35	6.76	5.03	-
CP2-2	71.77	6.84	3.39	-
CP2-3	-	-	-	-
CP2-4	76.33	6.85	4.50	-
CP2-5	74.04	7.02	5.68	-
CP2-6	74.30	6.85	4.22	-
CP3-1	82.67	5.57	7.20	3.04
CP3-2	85.4	5.90	6.72	0.37
CP3-3	57.36	3.61	6.87	27.35
CP3-4	64.01	4.33	7.51	22.83
CP3-5	67.47	4.40	7.20	19.36
CP3-6	73.13	5.29	7.96	11.32
CP3-7	69.69	4.40	7.47	16.99
CP3-8	58.82	3.91	7.29	29.40
CP3-9	64.34	4.14	7.24	23.54
CP3-10	63.79	3.96	7.20	23.01
CP3-11	63.32	4.09	7.19	23.42
CP3-12	63.39	4.42	7.91	22.28
CP3-13	68.25	5.69	7.91	17.77

[a)] For detailed sample information, see Tables 1 and S7.

Table S10. Solubility of the aromatic heterocycle-containing copolymers prepared by copolymerization in DESs

	H_2O	DMSO	DMF	MeOH	EtOH	Acetone	CH_2Cl_2	THF	Ethyl acetate	Chloroform	Diethyl ether	n-Hexane
P(MMA-*co*-BTVS)	-	+-	+	-	-	-	+	+	-	+	-	-
P(MMA-*co*-NVC)	-	+	+	-	-	-	+	+	+	+	-	-
P(BTVS-*co*-NVC)	-	-	+	-	-	-	+	+	-	+	-	-

+ : soluble at room temperature (approximately 1.0 mg/mL), - : insoluble, +- : soluble in a diluted condition.

Table S11. Comparison of the refractive index and Abbe number between aromatic heterocycle-containing copolymers developed in this work and previously reported polymers [a)]

Symbol	Sample	Solvent	Refractive index (589 nm)	Abbe Number	ref [b)]
●	P(MMA-*co*-BTVS)	NADES			This work
■	P(MMA-*co*-NVC)	NADES			This work
▲	P(BTVS-*co*-NVC)	NADES			This work
○	P(BTVS)	bulk	1.7432	17.022	57
□	P(BTVS)-*b*-P(VNA)	DMF	1.7178	19.161	57
△	P(BTVS-*co*-VNA)	DMF	1.6911	17.935	57
▽	P(2TVS)	DMF	1.6925	26.712	57
○	P(2TVS-*co*-NVPI)	DMF	1.6881	23.9	58
□	P(2TVS-*co*-NPMI)	DMF	1.6288	34.6	58
△	P(1,3,4-TVS-*co*-NVPI)	DMF	1.6752	29.2	58
▽	P(3IMVS-*co*-NVPI)	DMF	1.6225	26.3	58
◇	P(MeSTVS-*co*-NVPI)	DMF	1.6901	23.5	58
○	P(carbazolylethyl methacrylate)	camphor quinone/ethyl-4-dimethylaminobenzoate	1.708	21.5	6
□	P(4-tienylstyrene)	toluene and THF/toluene	1.6669 at 633 nm	20	54
△	P(tienylmethyl methacrylate)	bulk	1.582	37.5	55
▽	P(dibromotienylmethyl methacrylate)	bulk	1.630	33.0	55
◇	P(tribromotienylmethyl methacrylate)	bulk	1.645	31.0	55
○	P(s-alkylcarbamate)		1.6610	32.0	1
□	P(TBD)		1.6780	34.8	1
△	P(thioether sulfone)		1.6859	48.6	1
○	P(phenylene thioether ether) with pyrimidine unit	NMP	1.7204 at 637 nm	21.36	52
□	Carbazole-based network polymer	bulk	1.702	20.6	16
△	Hyperbranched polyvinylsulfide	toluene	1.7839	13.1	17

○	ICl doped P(4-vinylpyridine)	iCVD/solvent treatment	1.77 at 587.6 nm	19.8	28
□	IBr doped P(4-vinylpyridine)	iCVD/solvent treatment	1.85 at 587.6 nm	14.5	28
△	Dihydroxy-substituted P(phenylene sulfide)	1,2-dichloroethane /CH_2Cl_2	1.85	17	29

a) The relationship between the refractive index and Abbe number is shown in Figure 3e.

b) The reference corresponds to that in the main text.

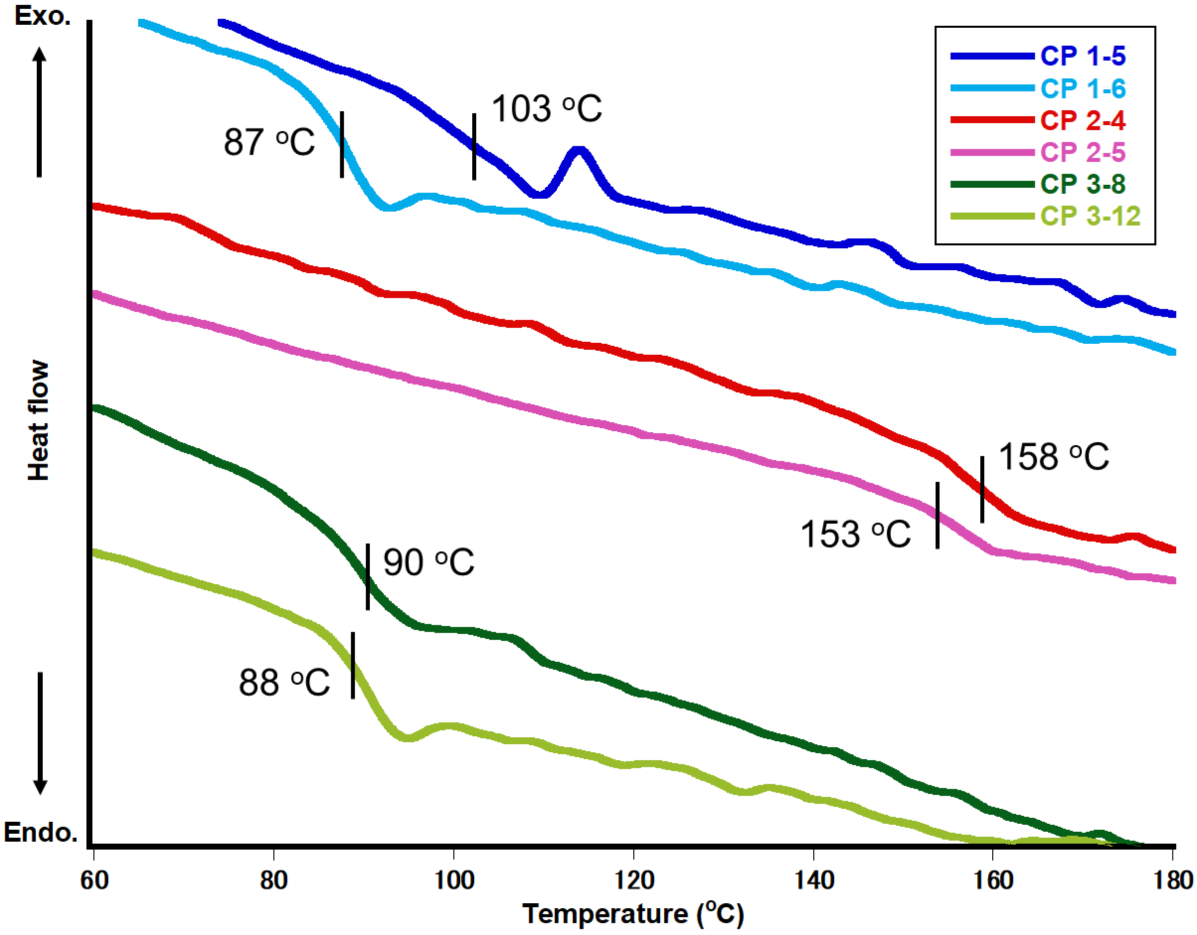


Figure S15. DSC curves of the representative copolymers, P(MMA-*co*-BTVS), P(MMA-*co*-NVC), and P(BTVS-*co*-NVC). For detailed sample information, see Tables 1 and S7.

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