9,9-Diaryl-4,5-diazafluorene-Based *Cardo* Polymer; Synthesis and Characteristic Properties

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ABSTRACT: To open out new aspects of 9,9-diarylfluorene (DAF)-based polymers with high performances, 9,9-(4-hydroxyphenyl)-4,5-diazafluorene (**N-BPF**) was designed as a new *cardo* structure and the properties of poly(ether ketone)s (**N-PEKs**) containing **N-BPF** skeletons were examined in detail. **N-PEKs** were synthesized in high yields via polycondensation of **N-BPF** with difluoroarenes. **N-PEKs** showed *cardo* polymer-specific properties such as high thermal stability and high solubility in organic solvents. The addition of *p*-toluenesulfonic acid (TsOH) to **N-PEK** resulted in the formation of network polymer based on interchain hydrogen bonds. It turned out that the films of network polymer are flexible and transparent and exhibit high refractive index and low birefringence. The effects of feed ratio of TsOH to **N-PEK** were also evaluated on the mechanical properties of network polymer. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4541–4549

KEYWORDS: *cardo* structure; heteroatom-containing polymers; high-performance polymers; poly(ether ketones); refractive index; low birefringence

INTRODUCTION As 9,9-diarylfluorene (**DAF**)-based polymers exhibit unique properties such as high thermal stability, high solubility in organic solvents, amorphous nature, high filler-dispersing ability, high refractive index, and low birefringence, they have attracted considerable interests in the field of high-performance polymer materials such as optical materials,[1–6] gas permselective film,[7–9] high filler dispersible matrix polymer,[10–12] heat-resistance resin,[13–21] and so forth.[22–29] These excellent properties are attributed to the *cardo* structure of **DAF** in which aryl substituents at the quaternary carbon center of alicyclic moiety occupy different planes [Fig. 1(a)]. To explore the useful derivatives of **DAF**-based polymers, we have previously reported the synthesis of modified *cardo* structure-based polymers such as silafluorene-type *cardo* polymer,[30] sulfur-containing polymers,[3,19] 9,9′-spirobifluorene-based polymers,[31–34] and their excellent properties such as higher thermal stability, higher refractive index, and lower birefringence than those of the corresponding **DAF**-containing polymers. We have recently focused our attention on the fusion of 4,5-diazafluorene[35–38] into a new *cardo* structure. Because the *cardo* polymer consisting of 4,5-diazafluorene-based *cardo* units (**N-BPF**) has the regularly arranged nitrogens in the side chain, the applications of **N-BPF** that use the characteristics of the nitrogen functionality seem interesting from new aspects of **DAF**-based polymers. In this article, we describe the synthesis and properties of **N-BPF**-based *cardo* polymers and the network polymers obtained by interchain hydrogen bonds of **N-BPF**.

EXPERIMENTAL

Materials

4,5-Diazafluorenone (**1**),[39] 1,4-bis(4-fluorobenzoyl)benzene (**2a**),[40] 5-*tert*-butyl-1,3-bis(4-fluorobenzoyl)benzene (**2b**),[41] 2,5-bis(4-fluorophenyl)−1,3,4-oxazole (**2d**),[42] and 1,5-bis(4-fluorobenzoyl)−2,6-dimethylnaphthalene (**2e**)[43] were prepared according to the literature. 4,4′-Difluorobenzophenone (**2c**) available from TCI® was purified by recrystallization from EtOH. Other commercially available materials were used without further purification.

Measurements

^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JEOL AL-400 spectrometer using $CDCl_3$, DMSO-d_6, and CD_3OD as the solvent and tetramethylsilane as an internal standard. The viscosity of **N-PEKs** was evaluated by Ostwald viscometer in *N*-methypyrrolidone (NMP) solution (0.50 g dL^{-1}) at 30 °C. Tensile testing (stress–strain)

Additional Supporting Information may be found in the online version of this article.

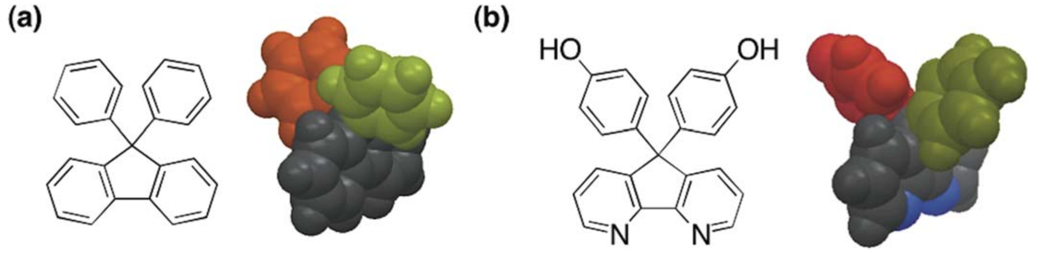


FIGURE 1 Structures and the space-filling models of DFT-optimized geometries (B3LPY, 6–31G**) of (a) 9,9-Diarylfluorene **DAF** and (b) 9,9-bis(4-hydroxyphenyl)−4,5-diazafluorene **N-BPF**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was conducted in a Shimadzu AG-IS test machine by using (5.0 mm × 20.0 mm) specimens at a strain rate of 10 mm min^{-1}. The glass transition temperatures (T_g) were measured with a Shimadzu DSC-60 instrument at a heating rate of 10 °C min^{-1} under a nitrogen (flow rate 50 mL min^{-1}). Thermo gravimetric analysis (TGA) was performed with a Shimadzu TGA-50 instrument at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere and on air atmosphere (flow rate 50 mL min^{-1}). The solubility of polymers was evaluated by using 3 mg of polymer to 1 mL of solvent. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Melting points were measured with a Stuart Scientific SMP3. Ultraviolet-visible (UV-vis) spectra were recorded on a JASCO V-550 UV-vis spectrometer. The refractive indices of the polymers were measured with an Abbe refractometer (DR-M2/1550, ATAGO Co.). The birefringence values of the films were evaluated by taking the pictures of films placed between two cross-axis polarizing films. Retardations were measured using a polarized optical microscope (OPTIPHOTO-POL, Nikon Co.) under the cross-Nicols (588 nm). Transmittance of the films was evaluated with a UV-vis spectrophotometer (JASCO V-550) across a scanning range of 300 to 700 nm.

Film Preparation

Polymer films of the **N-PEKs** were prepared for the evaluation of refractive index and birefringence with a casting method using the NMP solutions of the corresponding polymers at 150 °C. The films used for the evaluation of transparency were prepared by a casting method using the NMP solutions of the corresponding polymers and annealed gently at 100 °C for long time enough to remove the solvent.

Synthesis of N-BPF

A solution of 4,5-diazafluorenone **1**[39] (4.00 g, 22.0 mmol), phenol (9.28 g, 98.6 mmol), 3-mercaptopropionic acid (200 μL, 2.4 mmol), and methanesulfonic acid (5.6 mL, 86 mmol) in chlorobenzene (40 mL) was heated at 90 °C for 7 h under argon atmosphere. The mixture was cooled to room temperature and concentrated *in vacuo* to remove chlorobenzene. The residue was poured into sat. aq. $NaHCO_3$. The resulting precipitates were filtered off and washed with MeOH and $CHCl_3$. The crude was purified by recrystalization from DMF–MeOH or DMF–H_2O to give a white cotton solid (6.31 g, 82%).

m.p. > 314 °C (decomp.); ^{1}H NMR (400 MHz, CD_3OD, δ): 8.56 (dd, $J = 4.9$, 1.5 Hz, 2H), 7.85 (dd, $J = 7.8$, 1.5 Hz, 2H), 7.35 (dd, $J = 4.9$, 1.5 Hz, 2H), 6.78 (d, $J = 8.6$ Hz, 4H), 6.47 (d, $J = 8.6$ Hz, 2H) ppm; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 9.41 (s, 2H), 8.66 (d, $J = 4.6$ Hz, 2H), 7.90 (d, $J = 8.1$ Hz, 2H), 7.40 (dd, $J = 8.1$, 4.6 Hz, 2H), 6.90 (d, $J = 8.5$ Hz, 4H), 6.64 (d, $J = 8.5$ Hz, 4H) ppm; ^{13}C NMR (100 MHz, CD_3OD, δ): ~162.2, 157.9, 150.1, 149.9, 135.9, 133.0 129.8, 125.0 117.9, 39.5 ppm; IR (KBr): $\nu = 3222$ (br), 1612, 1511, 1208, 1043, 735 cm^{-1}.

lit.[38] ^{1}H NMR (DMSO-d_6, δ): 9.44 (s, 2H), 8.67 (d, 2H), 7.93 (d, 2H), 7.42 (dd, 2H), 6.92 (d, 4H), 6.66 (d, 4H) ppm; ^{13}C NMR (DMSO-d_6, δ): 164.1, 163.2, 160.8, 131.6, 129.2, 128.6, 126.4, 123.5, 116.1, 114.0 ppm.

Typical Procedure of Synthesis of N-PEK: Synthesis of N-PEK1

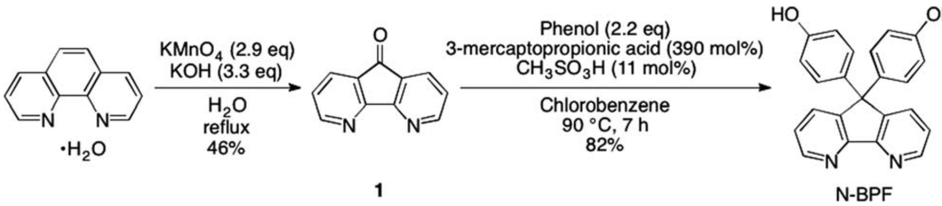
Bis(4-hydroxyphenyl)-4,5-diazafluorene (150 mg, 425 μmol), K_2CO_3 (118 mg, 850 μmol), and diphenylsulfone (1.7 g) was placed in a 50 mL round-bottom flask under argon atmosphere. The mixture was heated at 170 °C for 2 h and cooled to room temperature. 1,4-Bis(4-fluorophenylbenzoyl)benzene **2a**[40] (137 mg, 425 μmol) was added to the mixture, and then, the mixture was heated at 220 °C for 2 h. The mixture was cooled to room temperature, poured into MeOH, and the resulting precipitates were collected by filtration and washed with MeOH. The crude polymer was dissolved with $CHCl_3$, and the solution was filtered through a Celite® pad. The filtrate was reprecipitated into MeOH to give solids, which were collected by filtration and dried *in vacuo* overnight to give the corresponding polymer **N-PEK1** (245 mg, 91%) as a white solid.

N-PEK1

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.76 (br, 2H), 7.82–7.79 (m, 10H), 7.34–7.31 (m, 2H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.03 (d, $J = 8.5$ Hz, 4H), 6.98 (d, $J = 8.4$ Hz, 4H) ppm; IR (KBr): $\nu = 3056$, 1656, 1591, 1495, 1401, 1242, 994 cm^{-1}.

N-PEK2

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75 (d, $J = 3.4$ Hz, 2H), 7.98 (br, 2H), 7.86 (br, 1H), 7.80–7.79 (m, 6H), 7.32–7.29 (m, 2H), 7.20 (d, $J = 8.8$ Hz, 4H), 7.00 (d, $J = 8.8$ Hz, 4H), 6.97 (d,



SCHEME 1 Synthesis of **N-BPF.**

TABLE 1 Synthesis of **N-PEKs**

Entry	Spacer	Products	Solvent	Temperature (Time)	Yield (%)	η_{inh}[a] (dL g^{-1})
1	2a	N-PEK1	DMAc	140 °C, 2 h → 170 °C, 3 h	–[b]	–[b]
2	2a	N-PEK1	NMP	140 °C, 2 h → 170 °C, 4 h	75	0.25
3	2a	N-PEK1	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	91	0.24
4	2b	N-PEK2	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	89	0.25
5	2c	N-PEK3	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	80	0.27
6	2d	N-PEK4	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	88	0.32
7	2e	N-PEK5	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	99	0.35
8[c]	2e	co-N-PEK5[d]	Diphenylsulfone	170 °C, 2 h → 220 °C, 2 h	99	0.29

[a] The viscosity was measured by using a polymer solutions (0.50 g dL^{-1}) in NMP at 30 °C.
[b] Polymer was not obtained.
[c] Polymerization was performed with **5e** (1.0 equiv), **BPF** (0.9 equiv), and **N-BPF** (0.1 equiv) in the presence of K_2CO_3 (1.0 eq).
[d] Composition of **BPF** and **N-BPF** was estimated to 12:88.

$J = 8.8$ Hz, 4H), 1.85 (s, 9H) ppm; IR (KBr): $\nu = 2969$, 1653, 1591, 1498, 1244, 1163, 953 cm^{-1}.

N-PEK3

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75 (br, 2H), 7.79 (d, $J = 8.2$ Hz, 2H), 7.79–7.41 (m, 4H), 7.31–7.29 (m, 2H), 7.19 (d, $J = 8.4$ Hz, 4H), 7.00 (d, $J = 8.2$ Hz, 4H), 6.97 (d, $J = 8.4$ Hz, 4H) ppm; IR (KBr): $\nu = 1653$, 1593, 1497, 1399, 1240, 1161, 1014, 928 cm^{-1}.

N-PEK4

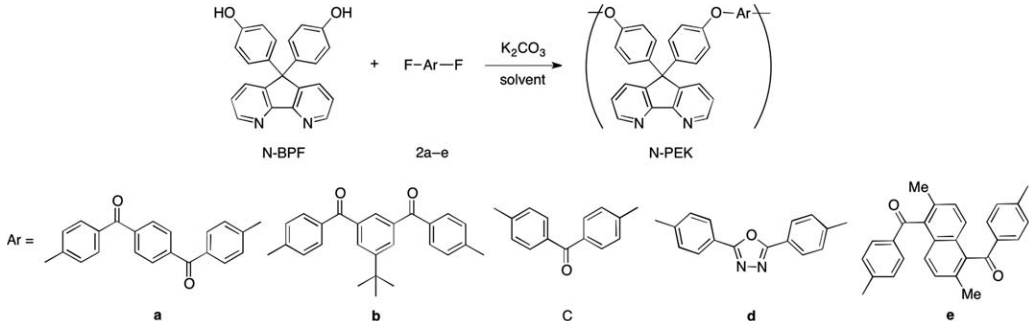
^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.78 (br, 2H), 8.05 (d, $J = 8.5$ Hz, 4H), 7.80 (d, $J = 8.3$ Hz, 2H), 7.34–7.30 (m, 2H), 7.20 (d, $J = 8.5$ Hz, 4H), 7.08 (d, $J = 8.5$ Hz, 4H), 6.96 (d, $J = 8.5$ Hz, 4H) ppm; IR (KBr): $\nu = 3058$, 1598, 1488, 1400, 1242, 1168, 1013, 749 cm^{-1}.

N-PEK5

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.75 (d, $J = 4.6$ Hz, 4H), 7.77–7.75 (m, 6H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.31–7.29 (m, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.18 (d, $J = 8.5$ Hz, 4H), 6.95 (d, $J = 9.0$ Hz, 4H), 6.93 (d, $J = 8.5$ Hz, 4H), 2.25 (s, 6H) ppm; IR (KBr): $\nu = 3056$, 2963, 1663, 1590, 1496, 1243, 1154 cm^{-1}.

Preparation of Network-Polymer Film

N-PEK (10 mg) was dissolved in NMP (300 μL) in 5 mL flask. A solution of *p*-toluenesulfonic acid monohydrate $TsOH\cdot H_2O$ in NMP (100 μL) was added to the polymer solution, and the mixture was stirred for 5 min. The resulting solution was casted to a glass plate, heated at 100 °C for 24 h, dried *in vacuo* at 80 °C under vacuum for 12 h to give the corresponding network film.



SCHEME 2 Synthesis of **N-PEKs.**

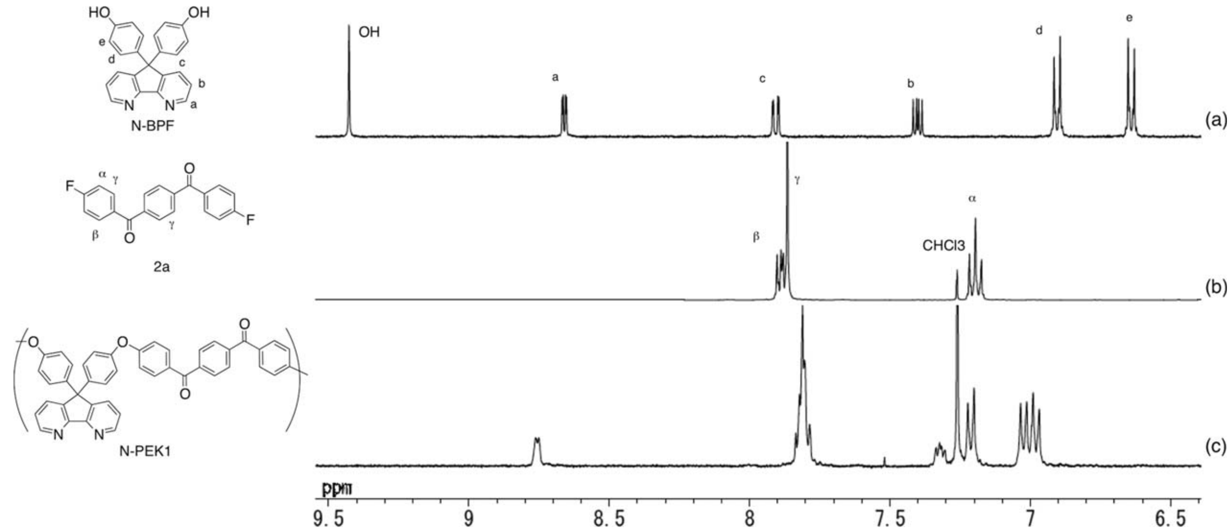


FIGURE 2 ^{1}H NMR spectra (400 MHz, 298 K) of (a) **N-BPF** in DMSO-d_6 (b) **2a** in $CDCl_3$, and (c) **N-PEK1** in $CDCl_3$.

TABLE 2 Solubility of **N-PEKs**

Entry	CH_2Cl_2	$CHCl_3$	THF	DMF	DMAc	NMP	NMP	DMSO	Toluene	Conc. HCl aq
N-PEK1	++	++	±	±	++	++	±	−	±	++
N-PEK2	++	++	++	±	++	++	+−	±	±	++
N-PEK3	++	++	±	±	++	++	±	−	±	++
N-PEK4	++	++	±	±	++	++	±	−	±	++
N-PEK5	++	++	±	±	++	++	±	−	±	++
PEK1	++	++	±	±	++	++	±	−	−	++

Solubility was evaluated by dissolving 3 mg polymer in 1 mL solvent. Key: ++, soluble; +−, soluble on heating; ±, partially soluble on heating; −, insoluble.

Synthesis of 9,9-Bis(4-methoxyphenyl)−4,5-diazafluorene 3

4,5-Diazafluorenone (1.00 g, 5.49 mmol), anisole (3.55 g, 54.9 mmol), 3-mercaptopropionic acid (2.9 μL, 33 μmol), and conc. sulfuric acid (2.9 g, 1.6 mol) were placed in a 100 mL round-bottom-flask. The mixture was stirred at room temperature for 30 min, followed by heating at 65 °C for 5 h. The resulting mixture was poured into 10% aq. NaOH to

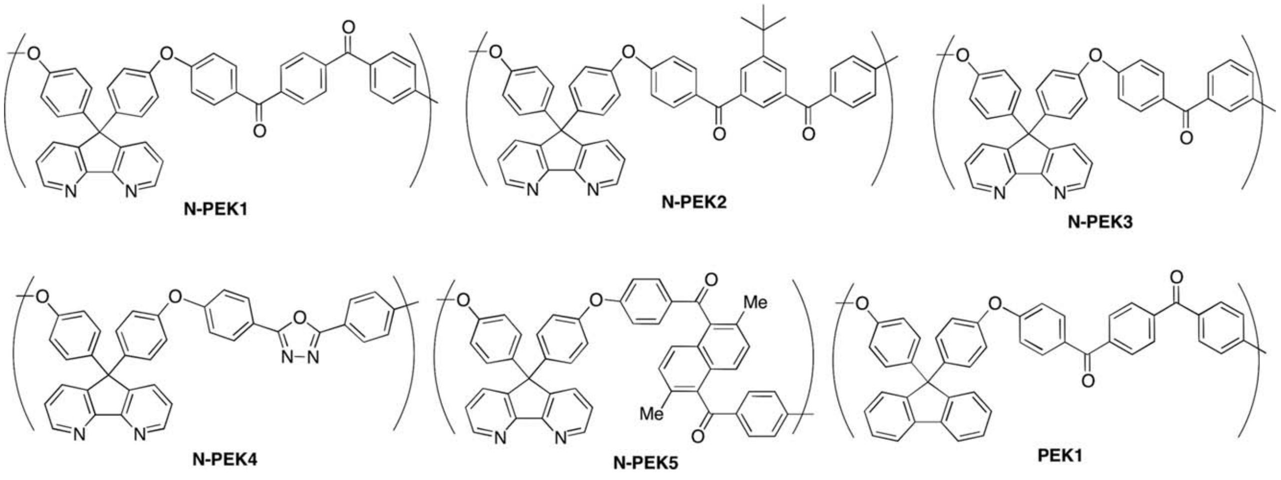


FIGURE 3 Chemical Structures of **N-PEKs** and **PEK1**.

TABLE 3 Thermal Properties of **N-PEKs**

		T_{d5}[b] (°C)		T_{d10}[b] (°C)	
Polymer	T_g[a] (°C)	N_2	Air	N_2	Air
N-PEK1	234	539	528	560	549
N-PEK2	220	494	494	521	519
N-PEK3	261	535	510	555	544
N-PEK4	290	497	493	516	517
N-PEK5	–[c]	454	448	467	575

[a] Glass transition temperatures were evaluated at a heating rate of 10 °C min^{-1} under nitrogen (50 mL min^{-1}).

[b] 5% Decomposition temperatures were measured at a heating rate of 10 °C min^{-1} under nitrogen or in air.

[c] Not determined.

precipitate a white solid, which was collected by filtration, washed with Et_2O, and dried *in vacuo* to give **3** (1.72 g, 82%).

m.p. 262.0–263.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.72 (dd, $J = 4.6$, 1.2 Hz, 2H), 7.44 (dd, $J = 7.8$, 1.2 Hz, 2H), 7.27 (dd, $J = 7.8$, 4.6 Hz, 2H), 7.08 (d, $J = 8.9$ Hz, 4H), 6.77 (d, $J = 8.9$ Hz, 4H), 3.76 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.7, 157.3, 150.0, 146.2, 135.6, 133.5, 128.8, 123.4, 113.8, 60.2, 55.2 ppm; IR (KBr): $\nu = 2949$, 2829, 1606, 1562, 1508, 1401, 1249, 1178, 1039, 813, 746 cm^{-1}.

lit,[38] m.p. 275–276 °C; ^{1}H NMR ($CDCl_3$, δ): ~8.75 (m, 2H), 8.13 (m, 4H), 8.07 (d, 4H), 7.80 (d, 2H), 7.54 (m, 2H), 7.52 (m, 2H), 7.32 (dd, 2H), 7.08 (m, 4H), 7.06 (d, 4H), 6.79 (d, 4H), 3.62 (s, 6H) ppm.

RESULTS AND DISCUSSION

Synthesis of 9,9-(4-Hydroxyphenyl)-4,5-diazafluorene (N-BPF)

According to the literature,[38] the synthesis of **N-BPF** was performed by bubbling HCl gas to a mixture of 4,5-diazafluorenone **1** and phenol to result in a low yield of **N-BPF** (40%). After considerable efforts, it turned out that the use of methanesulfonic acid in place of HCl gas afforded 82% yield of **N-BPF** in the presence of 3-mercaptopropionic acid (Scheme 1).

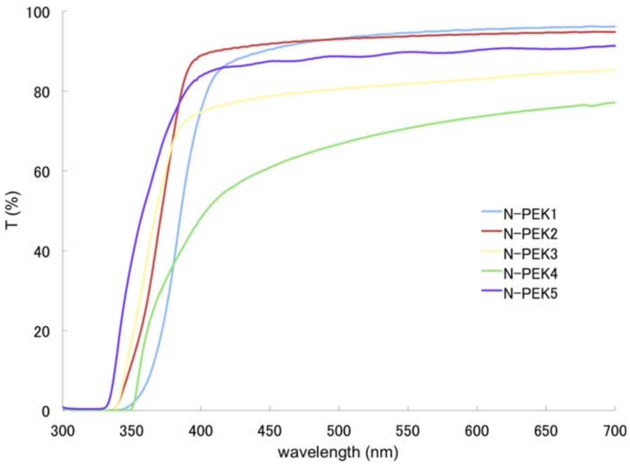


FIGURE 4 Transmittance of **N-PEKs** films measured by a UV-vis spectrometer (thickness 6–24 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of N-BPF-Based Cardo Polymer (N-PEK)

We have previously reported the synthesis of **DAF**-containing poly(ether ketone) (**PEK**) to the main chain and its excellent chemical and thermal stability.[2] Building on the previous work,[2] the polymerizations of **N-BPF** and difluoroarenes **2a–e** were examined (Scheme 2), and the results were summarized in Table 1.

At first, the polycondensation condition of **N-BPF** was investigated by using **2a** as a coupling partner (Entries 1–3). During polymerization in *N*,*N*-dimethylacetamide (DMAc) that is a good solvent of both **N-BPF** and **2a** (Entry 1), the polymers with low molecular weights deposited soon as white solids. Thus, we decided to use NMP or diphenylsulfone as the solvent, because these solvents show high solubility for not only **N-BPF** and **2a** but also the precipitated polymer. As a result, **N-PEK1** with high viscosity was obtained in both cases (Entries 2 and 3), in which it found that diphenylsulfone was the best solvent to afford a high yield of the polymer. Figure 2 shows the ^{1}H NMR spectra of **N-BPF**, **2a**, and **N-PEK1**. No terminal signal was observed in the ^{1}H NMR spectrum of **N-PEK1**, suggesting the formation of high-molecular weight polymer. On the other hand, the molecular weight of the polymer could be not estimated by an SEC measurement, probably because of the strong interaction between the nitrogen atoms in the 4,5-diazafluorene moieties of polymer and the SEC filler gel.

According to the same manner, the polycondensation reactions of **N-BPF** with various difluoroarenes **2b–e** were preformed to give the corresponding polymers with high viscosity in high yields (Entries 4–7). Copolymerization of **BPF** and **N-BPF** (90:10) with **5e** was also performed to give the corresponding copolymer (***co*-N-PEK5**) quantitatively. Through the integral ratio of the ^{1}H NMR spectrum of ***co*-N-PEK5** (Supporting Information Fig. S15), the composition of **BPF** and **N-BPF** was determined as 88:12. The structures of

TABLE 4 Optical Properties of **N-PEKs**

	Refractive Index (n)			Birefringence
Polymer	484 nm	588 nm	656 nm	(Δn_{p-s})[a]
PEK1	1.6962	1.6719	1.6621	–[b]
N-PEK1	1.6871	1.6618	1.6521	–[b]
N-PEK2	–[b]	–[b]	–[b]	–[b]
N-PEK3	1.6982	1.6719	1.6640	–[b]
N-PEK4	1.6947	1.6674	1.6570	–[b]
N-PEK5	1.6845	1.6559	1.6452	0.0009

[a] Retardation was measured by polarizing optical microscopy under crossed Nicols with a light wavelength of 588 nm.

[b] Not determined.

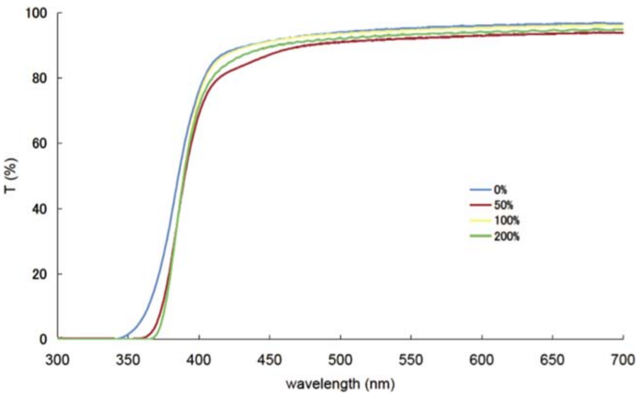


FIGURE 5 Transmittance of **N-PEK1·TsOH** network films measured by a UV-vis spectrometer (thickness: 14–55 μm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

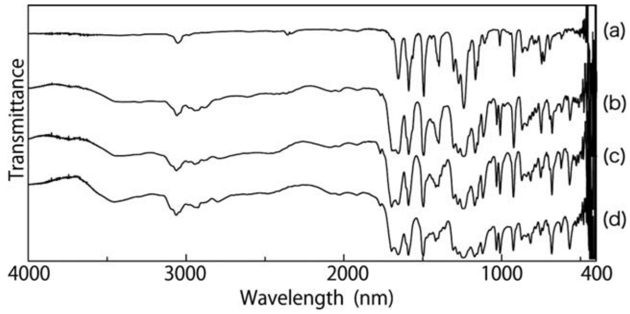


FIGURE 6 IR spectra (NaCl) of (a) **N-PEK1**, and the network polymers of **N-PEK1** with (b) 50 mol %, (c) 100 mol %, and (d) 200 mol % of TsOH.

N-PEKs were characterized by IR and ^{1}H NMR spectroscopy. The IR spectra of **N-PEKs** except for **N-PEK4** showed carbonyl absorption peaks at 1653–1663 cm^{-1}, while the absorption band attributed to the —C=N— (diazafluorene) stretching at 1590–1593 cm^{-1} appeared at all IR spectra of **N-PEKs**. The structure of **N-PEK4** was confirmed by the presence of the characteristic peak at 1013 cm^{-1} based on =C—O—C= stretching of the oxadiazole ring. In the spectrum of **N-PEK4**, the absorption band at 1598 cm^{-1} attributable to the —C=N— (oxadiazole) stretching was overlapped with that of the —C=N— stretching on the diazafluorene moiety.

Solubility

Solubility of **N-PEKs** in various solvents was evaluated by dissolving 3 mg polymer in 1 mL solvent and is summarized in Table 2. All **N-PEKs** showed *cardo* structure-specific high solubility in $CHCl_3$, DMAc, and NMP, which is a good contrast with the low solubility of typical poly(ether ketone) such as PEEK-HT® in common organic solvents. In addition, **N-PEKs** were partially soluble even in conc. aq. HCl, which is probably caused by the protonation of diazafluorene moieties on the polymer. Such solubility of **N-PEK1** was hardly different to that of 9,9-diarylfluorene-type polymer (**PEK1**, Fig. 3) except for the column of conc. aq. HCl in Table 2.

Thermal Stability

Thermal properties of **N-PEKs** were evaluated by TGA and differential scanning calorimetry (DSC) (Table 3). The weight loss temperatures (T_ds) of **N-PEKs** were in a range of 448–528 °C in air atmosphere, and the glass transition temperatures (T_gs) were in a range of 220–294 °C, respectively. The high thermal stability would come from the rigid backbone of polymer containing *cardo* moieties in the main chain. On

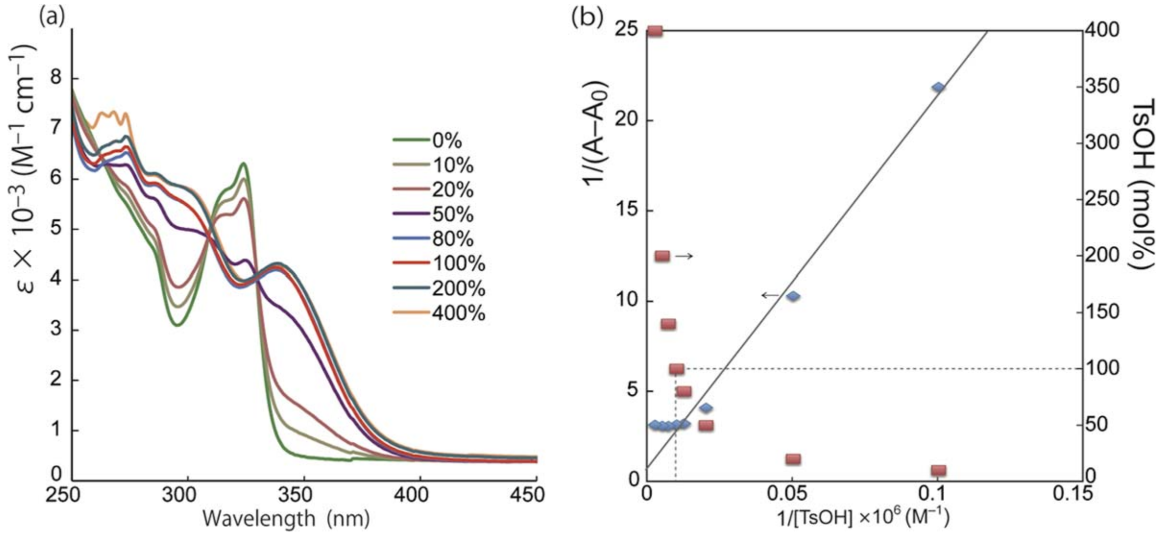


FIGURE 7 (a) UV-vis spectral change of **3** on addition of TsOH (CH_2Cl_2, 0.1 mM, 298 K); and (b) Benesi-Hildebrand plot of absorbance at 337 nm (blue, $(A–A_0)^{-1}$ versus $[TsOH]^{-1}$ plot; red, mol % of TsOH versus $[TsOH]^{-1}$ plot). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the other hand, no melting point was observed in all **N-PEKs**, which indicated the amorphous nature of **N-PEKs**.

Transparency

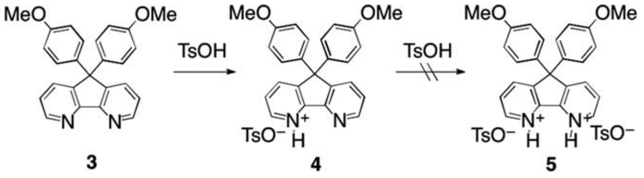
The transparency of the casting films of **N-PEK1**, **N-PEK2**, and **N-PEK5** reached over 80% at 400 nm (Fig. 4). This high transparency can be attributed to their amorphous nature of **N-PEKs**. On the other hand, the films of **N-PEK3** and **N-PEK4** showed relatively low transparency, probably because of the aggregation between the polymer chains of **N-PEK3** and **N-PEK4** with rigid spacer moieties.

Refractive Index and Birefringence

Optical properties were summarized in Table 4. Refractive indices were sufficiently high (1.65–1.67 at 588 nm), which would be attributed to the high content of aromatic groups. Intriguingly, the refractive index of **N-PEK1** was nearly same as **PEK1** with the same spacer, despite **N-PEK** has C=N bonds with high atom refraction.[44] **N-PEK5** exhibited very low birefringence attributed to the structural property of *cardo* skeleton, although birefringence values of other polymers could not be measured, because of the poor film forming properties of **N-PEKs**.

Preparation of Hydrogen-Bond Network Polymer

To prepare the chemically stable network polymer of **N-PEK**, *p*-toluenesulfonic acid (TsOH) was used as a proton source, because of the nonvolatility and low pK_a constant of TsOH. Several network polymer films were prepared at 100 °C by a drop cast using an NMP solution of **N-PEK1** with arbitrary amounts of TsOH. It was found that no precipitation of TsOH was observed, even when 200 mol % of TsOH per the repeating unit was added to the polymer. After the removal of solvent, the swelling ability of the polymers was examined to evaluate a network formation. The polymers were swollen without any degradation in $CHCl_3$ and NMP that are good solvents for the original polymers (Supporting Information Fig. S21). These results strongly indicate the formation of network polymer.



SCHEME 3 Protonation of model Compound **3**.

TABLE 5 Optical Properties of Network Polymers

Network Polymer	TsOH (mol %)	Refractive Index (n)[a]	Birefringence (Δn_{p-s})[b]
N-PEK1	0	1.6618	–[c]
	10	1.6746	0.0038
	50	1.6530	–[c]
	100	1.6077	–[c]
N-PEK3	0	1.6719	–[c]
	10	1.6716	0.0035
	50	1.6509	0.0006
	100	1.6193	0.0001
N-PEK5	0	1.6674	–[c]
	50	1.6670	0.0003
	100	1.6640	0.0003

[a] Refractive index was measured at 588 nm.

[b] Retardation was measured by polarizing optical microscopy under crossed Nicols with a light wavelength of 588 nm.

[c] Not determined.

Figure 5 shows the transparency of the films. The obtained films were remarkably flexible and transparent. In the case of a mixture of 9,9-diarylfluorene-type polymer **PEK1** and TsOH, opaque film was obtained (Supporting Information Fig. S20), indicating that the diazafluorene moieties of **N-PEK** behave as a dispersant of TsOH. In IR spectra of the network polymer **N-PEK·TsOH**, stretching modes of pyridine and pyridinium ring were observed at 1590 and 1698 cm^{-1}, respectively (Fig. 6). Interestingly, the former band remained as a broaden peak even upon the addition of excess amount of TsOH, which indicates that all pyridine moieties are not protonated. We evaluated a UV-vis spectral change of monomer **3** by a manipulation of feed ratio of TsOH. The UV-vis spectra of **3** substantially changed on the addition of TsOH. The UV-vis titration results are shown in Figure 7(a). It turned out that the spectral change reached ceiling on the addition of more than 100 mol % TsOH. In addition, clear one isobestic point was observed. The reciprocals of the absorbance at around 337 nm were calculated and plotted against $[\mathrm{TsOH}]^{-1}$ to make the Benesi-Hildebrand plot [Fig. 7(b)].[45] These plots were fitted well with a straight line ranging from the point of 0 to 100 mol % of TsOH added, indicating that only one nitrogen atom was protonated and the other was not (Scheme 3). The binding constant was determined to be 1.5×10^3 M^{-1}. These results could strongly support the formation of hydrogen bonds between pyridinium and pyridine ring to give the network structure.

Refractive Index and Birefringence

Table 5 summarizes the optical properties of the network films. As the feed ratio of TsOH increased, the refractive indices (n) of the polymer decreased, probably because of the

FIGURE 8 Bent film of network polymer (**N-PEK5** with 1 mol % TsOH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

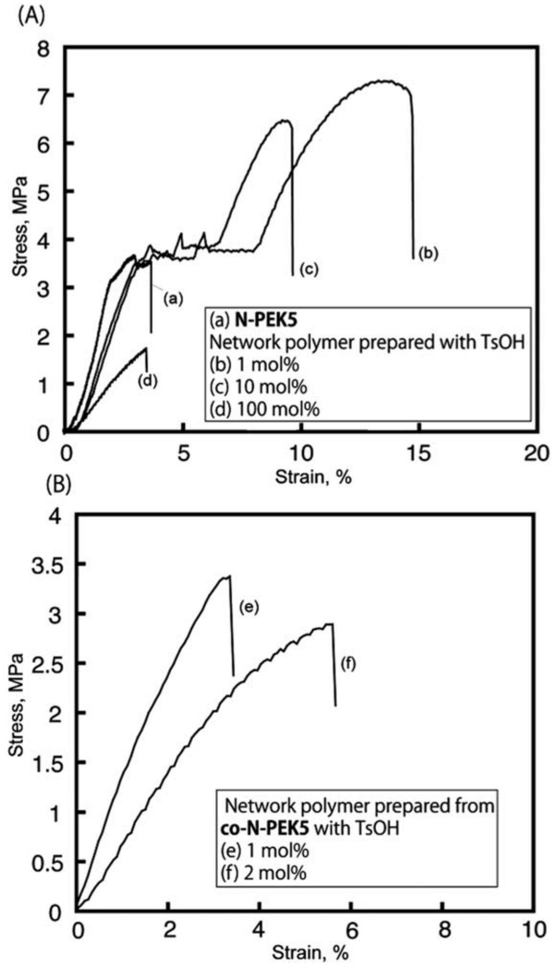


FIGURE 9 Stress–strain curves (thickness 10 μm, 10 mm min^{-1}) of (a) **N-PEK5** and network polymer prepared with TsOH; (b) network polymer prepared from ***co*-N-PEK5** with TsOH.

low refractive index of TsOH (n 1.56 at 589 nm) and the decrease in the polymer density attributed to the introduction of ionic bonds with long distance between atoms. On the other hand, the birefringence value (Δn) also decreased along the increase of the feed ratio of TsOH, which would be attributed to the defect of ordered aggregation of polymer chain by the formation of hydrogen bonds and/or the existence of TsOH as a dorpant.[36]

Mechanical Properties

All network polymer films were flexible compared with the original polymers before the addition of TsOH (Fig. 8). Stress–strain curves of **N-PEK5** and the network polymer with arbitrary amounts of TsOH are shown in Figure 9(a). **N-PEK5** exhibited a rigid and brittle feature originating from the inherence of *cardo* polymer. On the other hand, on the addition of less than 10 mol % TsOH, clear strain hardening region was observed, which means a ductile feature of the polymer. Young's moduli of network polymers remarkably decreased as the feed ratio of TsOH increased; 155 MPa (**N-PEK5**), 122 MPa (1 mol % TsOH), 135 MPa (10 mol % TsOH), and 54 MPa (100 mol % TsOH). Such results were in good agreement to the increase of weak hydrogen bonds between pyridine and pyridinium moieties in the network polymer. It is noted that the network polymers prepared from ***co*-N-PEK5** also showed the increase of flexibility and elongation at rupture; Young's modulus: 110.9 MPa (1 mol % TsOH) and 64.7 MPa (2 mol % TsOH) [Fig. 9(b)], strongly suggesting that only a few composition of **N-BPF** is crucial to modify the mechanical properties of the polymer.

CONCLUSIONS

A new series of N-BPF-based *cardo* polymer (**N-PEKs**) were synthesized in high yields by polymerization of a new *cardo* monomer (**N-BPF**) with various difluoroarenes (**2**), and the network polymers were prepared by the addition of TsOH. **N-PEKs** exhibited high thermal properties and high solubility in various organic solvents. These excellent properties come from *cardo* structure of **N-BPF**. The network polymer films showed not only high flexibility and transparency but also low birefringence. Additionally, ***co*-N-PEK5** copolymerized by **BPF** and **N-BPF** with **2** exhibited the increase of flexibility on the addition of TsOH. This study demonstrated that the hybridization of heteroaromatics to *cardo* structure enables the creation of new *cardo* monomer for the production of high-performance polymers with excellent properties. Because 4,5-diazafluorene skeleton has been widely exploited as a ligand similar to 1,10-phenanthlorine, directed toward electron injection layers, electron transporting layers, organic light emitting materials, dye sensitizers, and so forth, **N-BPF** and the related polymers would become a good candidate of these materials.

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REFERENCES AND NOTES

1 K. Sakurai, M. Fuji, *Polym. J.* **2000**, *32*, 676–682.

2 S. Kawasaki, M. Yamada, K. Kobori, F. Jin, Y. Kondo, H. Hayashi, Y. Suzuki, T. Takata, *Macromolecules* **2007**, *40*, 5284–5289.

3 S. Seesukphronrarak, S. Kawasaki, K. Kobori, T. Takata, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 3073–3082.

4 S. Seesukphronrarak, S. Kawasaki, K. Kobori, T. Takata, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2549–2556.

5 H. Hayashi, M. Takizawa, T. Arai, K. Ikeda, W. Takarada, T. Kikutani, Y. Koyama, T. Takata, *Polym. J.* **2009**, *41*, 609–615.

6 H. Hayashi, S. Kawasaki, K. Kobori, Y. Koyama, S. Asai, T. Takata, *Polym. J.* **2009**, *41*, 272–278.

7 M. Aguilar-Vega, D. R. Paul, *J. Polym. Sci. Part B: Polym. Phys.* **1993**, *31*, 1599–1610.

8 Z. Wang, T. Chen, J. Xu, *J. Appl. Polym. Sci.* **2002**, *83*, 791–801.

9 S. Kazama, T. Teramoto, K. Haraya, *J. Membr. Sci.* **2002**, *207*, 91–104.

10 S. Kawasaki, M. Yamada, K. Kobori, T. Kakumoto, F. Jin, A. Tarutani, T. Takata, *Polym. J.* **2007**, *39*, 115–117.

11 K. Matsukawa, Y. Matsuura, A. Nakamura, N. Nishioka, H. Murase, S. Kawasaki, *J. Photopolym. Sci. Technol.* **2007**, *20*, 307–308.

12 K. Fujishiro, N. Yokoyama, K. Kitamura, T. Teramoto, Proceeding of the 3rd International Display Workshop, Kobe, Vol. 2, p 385, **1996**.

13 A. K. Salunke, M. Sharma, V. Kute, S. Banerjee, *J. Appl. Polym. Sci.* **2005**, *96*, 1292–1305.

14 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung, Y.-J. Lee, *Eur. Polym. J.* **2010**, *46*, 1355–1366.

15 S.-H. Hsiao, M.-H. He, *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 4014–4021.

16 A. A. Askadskii, *Polym. Sci. U.S.S.R.* **1967**, *9*, 471–487.

17 P. W. Morgan, *Macromolecules* **1970**, *3*, 536–544.

18 H. Ghassemi, A. S. Hay, *Macromolecules* **1993**, *26*, 5824–5826.

19 Y. Charlier, J. L. Hedrick, T. P. Russell, A. Jonas, W. Volksen, *Polymer* **1995**, *36*, 987–1002.

20 T. Teramoto, *Kogyo Zairyo* **1995**, *43*, 79–86.

21 S. Seesukphronrarak, T. Takata, *Polym. J.* **2007**, *39*, 731–736.

22 K. Tokumitsu, A. Tanaka, K. Kobori, Y. Kozono, M. Yamada, K. Nitta, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2259–2268.

23 R.-T. Chen, S.-H. Chen, B.-Y. Hsieh, Y. Chen, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 2821–2834.

24 K.-S. Lee, Y.-H. Kim, Y. Lee, J. Jang, S.-K. Kwon, *J. Polym. Sci. Part A: Polym. Chem.* **2005**, *43*, 2316–2324.

25 For reviews on Cardo polymers, see: (a) V. V. Korshak, S. V. Vinogradova, Y. S. Vygodskii, *J. Macromol. Sci. Rev. Macromol. Chem.* **1974**, *11*, 45.

26 S. V. Vinogradova, V. A. Vasnev, Y. S. Vygodskii, *Russ. Chem. Rev.* **1996**, *65*, 249–277.

27 Y. Koyama, K. Nakazono, H. Hayashi, T. Tataka, *Chem. Lett.* **2010**, *39*, 2–9.

28 B. Bae, S. Kawamura, K. Miyatake, M. Watanabe, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3868–3873.

29 H. Yeo, K. Tanaka, Y. Chujo, *J. Polym. Sci. Part A: Polym. Chem.* **2012**, *50*, 4433–4442.

30 S. Seesukphronrarak, T. Takata, *Chem. Lett.* **2007**, *36*, 1138–1139.

31 R. Seto, Takashi Sato, T. Kojima, K. Hosokawa, Y. Koyama, G. Konishi, T. Takata, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 3658–3667.

32 H. Hayashi, M. Takizawa, T. Arai, K. Ikeda, W. Takarada, T. Kikutani, Y. Koyama, T. Takata, *Polym. J.* **2009**, *41*, 609–615.

33 H. Okuda, R. Seto, Y. Koyama, T. Takata, *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4192–4199.

34 H. Okuda, R. Seto, Y. Koyama, T. Takata, *Polym. J.* **2010**, *42*, 795–798.

35 K. Ono, K. Saito, *Heterocycles* **2008**, *75*, 2381–2413.

36 K. Ono, T. Yanase, M. Ohkita, K. Saito, Y. Matsushita, S. Naka, H. Okada, H. Onnagawa, *Chem. Lett.* **2004**, *33*, 276–277.

37 T. Oyamada, C.-H. Chang, T.-C. Chao, F.-C. Fang, C.-C. Wu, K.-T. Wong, H. Sasabe, C. Adachi, *J. Phys. Chem. C* **2007**, *111*, 108–115.

38 Z. Liu, F. Wen, W. Li, *Thin Solid Films* **2005**, *478*, 265–270.

39 M. J. Plater, S. Kemp, E. Lattmann, *J. Chem. Soc. Perkin Trans. 1* **2000**, 971–979.

40 K. A. Walker, L. J. Markoski, J. S. Moore, *Macromolecules* **1993**, *26*, 3713–3716.

41 F. A. Bottino, G. D. Pasquale, L. Lucrezia, A. Pollicino, *Eur. Polym. J.* **1995**, *31*, 35–38.

42 S.-H. Jung, D. Y. Kim, H.-N. Cho, D. H. Suh, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1189–1198.

43 M. Ohno, T. Takata, T. Endo, *Macromolecules* **1994**, *27*, 3447–3448.

44 S. Shibata, In Chemical Handbook Basic II; K. Ishii, Eds.; Chemical Society of Japan, Maruzen: Tokyo, **2004**; pp 644.

45 H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.