

Synthesis and Crosslinking Reaction of Polyacetylenes Substituted with Benzoxazine Rings: Thermally Highly Stable Benzoxazine Resins

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Received 18 March 2018; accepted 25 May 2018; published online in Wiley Online Library DOI: 10.1002/pola.29076

ABSTRACT: Novel polyacetylenes, poly(1) and poly(2) substituted with benzoxazine rings were synthesized by the polymerization of the corresponding acetylene monomers 1 and 2 using Rh catalysts, [(nbd)RhCl]₂, and (nbd)Rh⁺B⁻Ph₄ (nbd = 2,5-norbornadiene). The polymers were heated at 250 °C under N₂ to obtain the corresponding polybenzoxazine resins, poly(1)' and poly(2)' possessing polyacetylene main chains via the ring-opening polymerization of the benzoxazine moieties. The polyacetylene backbones were maintained after crosslinking reaction at 250 °C, which were confirmed by Raman spectroscopy. The benzoxazine resins were thermally highly stable as evidenced by

INTRODUCTION Benzoxazines are easily synthesized by dehydration of phenolic compounds, amines, and formaldehyde. Benzoxazines undergo ring-opening polymerization/crosslinking without catalyst to afford polybenzoxazine resins, in which the crosslinked networks are constructed by phenolic moieties linked with Mannich bridges (-CH2-NR-CH2-) and six-membered intramolecular OH-N hydrogen bonding. Polybenzoxazines are focused as promising thermosetting resins, which show fine heat resistance, dimensional stability due to the near-zero volumetric properties and low electric constant, and so forth.¹ On the other hand, π -conjugated polymers are extensively investigated as photonics, nonlinear optical materials, electrical semiconductors, and organic lightemitting diodes.² Substituted polyacetylenes, representative π -conjugated polymers, possess carbon–carbon alternating double bonds at the main chain, in which the extent of the conjugation depends on the number, type, and bulkiness of substituents. Substituted polyacetylenes feature high gas permeability/separation ability, stimuli response, and chiral recognition as well as photoelectric functions.³ Substituted polyacetylenes are commonly synthesized by the polymerization of the corresponding monomers with early transition

differential scanning calorimetry and thermogravimetric analysis. The surface of poly(1)' film became hydrophilic compared to that of poly(1), while the surfaces of poly(2) and poly(2)' films showed almost the same hydrophilicity judging from the water contact angle measurement. Poly(1)' and poly(2)' exhibited refractive indices smaller than those of poly(1) and poly(2). © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *56*, 1884–1893

KEYWORDS: phenol resin; polyacetylene; polybenzoxazine; ringopening polymerization; thermosetting resin

metal catalysts such as Mo and W,⁴ late transition metal catalysts such as Rh and Ir, and recently with Ru and Pd.⁵ Rh catalysts⁶ are most widely used for the polymerization of monosubstituted acetylene monomers such as phenylacetylenes.⁷ It is possible to synthesize cis-stereoregulated acetylene polymers by Rh catalysts because the polymerization takes place via the coordination-insertion mechanism, which is satisfactorily supported by the DFT calculations.⁸ It is also possible to control the molecular weights of the formed monosubstituted acetylene polymers by employing welldefined Rh catalysts such as $[(nbd)Rh(C \equiv CPh)(PPh_3)]^9$ and [(nbd)Rh{C(Ph)=CPh₂}(PPh₃)].¹⁰ Substituted linear polyacetylenes prepared with Rh catalysts are transformed into crosslinked polymers by the postpolymerization reactions of pendant functional groups,¹¹ including crosslinking by subsequent UV irradiation to poly(pentafluorophenyl ethynylbenzoate)s modified with mono o-nitrobenzyl-protected diamine,12 salicylaldiminemetal ionic crosslinking reactions of salicylidene Schiff-basecontaining polyacetylenes,13 and interchain crosslinking of poly(4-ethynyl)phenylacetylne by heating.¹⁴ o-Diethynylbenzene gives crosslinked polymers, whose network structures are dependent on polymerization catalysts (Rh, Ta).¹⁵ On the other

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SCHEME 1 Synthesis of monomers 1 and 2.

hand, 1-ethynyl-2-phenylethynylbenzene gives a linear poly (phenylacetylene) derivative bearing phenylethynyl groups by the selective polymerization of the terminal ethynyl group with Rh catalysts, while gives a polymer mainly consisting of trisubstituted benzene rings by the polymerization with W and Mo catalysts.¹⁵ π -Conjugated poly(high internal phase emulsion) foams are synthesized using poly(1,3-diethynyl benzene) skeleton as a crosslinker.¹⁶ Poly(propargyl ether) derivatives bearing benzoxazine groups undergo irreversible cis-trans isomerization and thermally activated curing without catalyst.¹⁷ We have designed novel acetylene monomers substituted with a benzoxazine ring in the course of our study on substituted polyacetylenes, aiming at the development of highly thermally stable resins based on the synergistic effect by the rigid polyacetylene backbone and high performance of bezoxazine. In this article, we disclose the synthesis and crosslinking reaction of novel poly(phenylacetylene) derivatives substituted with benzoxazine rings, which have no spacers between the poly(phenylacetylene) backbone and benzoxazine moieties.

EXPERIMENTAL

Measurements

¹H (400 MHz) and 13C (100 MHz) NMR spectra were recorded on JEOL ECA-400 and ECS-400 spectrometers. Number-average molecular weight (M_n) and dispersity (D) values of polymers were determined by SEC eluted with THF (columns: Shodex KF-805L × 3, JASCO RI-4030, UV-4075, PU-4180, DG-980-50, CO-4060, LC-NetII/ADC, AS-2055 Plus) and SEC eluted with LiBr solution (10 mM) in *N*,*N*-dimethyl-formamide (DMF) (columns: TSK gel α -M, GMHXL, JASCO RI-930, UV-2075 Plus, PU-980, DG-980-50, CO-965) calibrated by

polystyrene standards. Melting points (mp) were measured on a Yanaco micro melting point apparatus. Elemental analysis was done at the Analytical Center, Faculty of Engineering, Osaka University. ESI-MS spectra were recorded on a THERMO FISHER Q mass spectrometer. IR spectra were measured on a JASCO FT/IR-4100 spectrophotometer. IR spectra (ATR method) were measured on a Thermoscientific iS-50 FT-IR equipped with a Specac Golden Gate ATR unit. Raman spectra were recorded on a TOKYO INSTRUMENTS 3D Laser Raman Microspectroscopy System Nanofinder 30 and a JASCO NRS-5100 series of Raman spectrometer. UV-vis absorption spectra were recorded on a JASCO V-550 spectrophotometer. Diffuse reflectance UV-vis spectra were recorded on an Ocean Optics USB4000 UV-VIS-NIR equipped with a DH-2000-BAL as a light source. Thermogravimetric analysis (TGA) was performed on an SHIMADZU TGA-50 thermogravimetric analyzer. Differential scanning calorimetry (DSC) was performed on a Seiko Instruments DSC7020. Static water contact angles were measured on a Kyowa Interface Science DropMaster 100 and AUTO DISPENSER AD-31. Refractive indices were measured on a HORIBA smart SE Spectroscopic Ellipsometer.

Monomer Synthesis

The monomers **1** and **2** were synthesized according to Scheme 1. The synthetic procedures are described below.

4-(Trimethylsilylethynyl)Phenol (1a)

Into a reaction vessel, 4-iodophenol (5.50 g, 24.0 mmol), CuI (0.182 g, 0.96 mmol), and Pd(PPh₃)₄ (0.554 g, 0.48 mmol) were charged. THF (60 mL), trimethylsilylacetylene (3.38 mL, 24.0 mmol), and Et₃N (8.0 mL, 108 mmol) were fed to the vessel, and the resulting mixture was stirred in the dark at



Run	Monomer	Rh cat.	[M] ₀ /[Rh]	Solvent	Yield ^b (%)	Mn	Ð
1	1	[(nbd)RhCl] ₂	100	THF	46	12,000 ^c	2.4 ^c
2	1	[(nbd)RhCl] ₂	100	CHCl ₃	33	19,000 ^c	2.7°
3	1	(nbd)Rh ⁺ B ⁻ Ph ₄	100	THF	71	10,000 ^c	2.9 ^c
4	1	(nbd)Rh ⁺ B ⁻ Ph ₄	100	CHCl ₃	60	14,900 ^c	2.3 ^c
5	2	[(nbd)RhCl] ₂	100	THF	87	7,100 ^c	1.7°
6	2	[(nbd)RhCl] ₂	100	CHCl ₃	90	_e	_e
7	2	[(nbd)RhCl] ₂	50	DMF	Quant.	25,000 ^d	1.8 ^d
8	2	[(nbd)RhCl] ₂	100	DMF	Quant.	_e	_e
9	2	(nbd)Rh ⁺ B ⁻ Ph ₄	100	THF	Quant.	_e	_e
10	2	(nbd)Rh ⁺ B ⁻ Ph ₄	100	CHCl ₃	80	_e	_e
11	2	(nbd)Rh ⁺ B ⁻ Ph ₄	50	DMF	83	_e	_e
12	2	(nbd)Rh ⁺ B ⁻ Ph ₄	100	DMF	Quant.	_e	_e

TABLE 1 Polymerization of 1 and 2^a

^a Conditions: $[1]_0 = [2]_0 = 0.05$ mol/L in THF, CHCl₃, or DMF at 30 °C for 1 h under Ar. Ten equivalents of Et₃N was added in the polymerization with [(hbd)RhCl]₂.

^b MeOH-Insoluble part.

room temperature under Ar for 24 h. The solvent was distilled off on a rotary evaporator, and diethyl ether was added to the residue. The resulting solution was washed with water, and the organic layer was separated and dried over anhydrous MgSO₄. It was concentrated on a rotary evaporator, and benzene (15 mL) and ethylenediamine (3 mL) were added to the residue. The resulting mixture was stirred at 60 °C for 20 min, and diethyl ether was added to the mixture. The resulting solution was washed with 0.5 M HCl, and the organic layer was separated and dried over anhydrous MgSO4, and concentrated on a rotary evaporator to obtain a brown viscous liquid. It was purified by silica gel column chromatography eluted with ethyl acetate/hexane = 1/1 (v/v) to give **1a** as a brownish white solid (2.50 g, 13.1 mmol). Yield = 54%. ¹H NMR (400 MHz, CDCl₃): δ 0.21 (s, 9H, TMS), 4.90 (s, 1H, – OH), 6.74 (d, *J* = 8.8 Hz, 2H, Ar), 7.35 (d, *J* = 12.0 Hz, 2H, Ar).

6-(Trimethylsilyl)Ethynyl-3-Phenyl-3,4-Dihydro-1,3-Benzoxazine (1b)

A mixture of **1a** (0.95 g, 5.0 mmol), 1,3,5-trioxane (0.30 g, 3.33 mmol), aniline (0.46 mL, 5.0 mmol), and toluene

 $^{\rm c}$ Determined by SEC eluted with THF calibrated by polystyrene standards. $^{\rm d}$ Determined by SEC eluted with DMF calibrated by polystyrene standards. The polymer was insoluble in THF and CHCl₃.

^e Could not be determined due to insolubility in THF, CHCl₃, and DMF.

(15 mL) was stirred at 90 °C for 5 h. The solvent was distilled off, and diethyl ether was added to the residue. The resulting solution was washed with 0.5 M NaOH aqueous solution. The organic layer was separated, dried over anhydrous MgSO₄, and concentrated on a rotary evaporator to obtain **1b** as a brown solid (1.19 g, 3.8 mmol). Yield = 77%. ¹H NMR (400 MHz, CDCl₃): δ 0.23 (s, 9H, TMS), 4.56 (s, 2H, Ar-CH₂-N), 5.36 (s, 2H, O-CH₂-N), 6.70-7.25 (m, 8H, Ar). 13C NMR (100 MHz, CDCl₃): δ 0.16, 50.2, 80.1, 92.6, 105.0, 115.4, 117.0, 118.6, 120.8, 121.9, 129.4, 130.7, 131.9, 148.1, 154.8.

6-Ethynyl-3-Phenyl-3,4-Dihydro-1,3-Benzoxazine (1)

Compound **1b** (0.40 g, 1.30 mmol) was dissolved in THF (5 mL), and then 1 M tetrabutylammonium fluoride solution in THF (15.6 mL, 15.6 mmol) was added dropwise to the solution. The resulting mixture was stirred at room temperature for 1 h. Diethyl ether was added to the mixture, and the resulting mixture was washed with water. The organic layer was separated and dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator to obtain a yellowish brown

[2] ₀ /[Rh]	[PA] ₀ /[Rh]	Yield ^b (%)	<i>M</i> _n ^c	D^{c}
0	100	Quant.	12,300	5.2
5	95	Quant.	16,700	4.5
25	75	Quant.	6,100 ^d	6.3 ^d
50	50	78	10,000 ^d	1.6 ^d
100	0	Quant.	_e	_e

TABLE 2 Copolymerization of **2** with Phenylacetylene (PA)^a

^a Conditions: $[2]_0 + [PA]_0 = 0.2 \text{ mol/L}$ in THF at 30 °C for 1 h under Ar. $[Et_3N]/[Rh] = 10$.

^b Insoluble part in MeOH.

 $^{\rm c}$ Determined by SEC eluted with THF calibrated by polystyrene standards.

^d THF-soluble part.

 $^{\rm e}$ Could not be determined due to insolubility in THF, $\rm CHCl_3$ and DMF.

TABLE 3 Static Water Contact Angles of Poly(1), Poly(1)', Poly(2), and Poly(2)'

Sample	Spin Speed upon Preparing the Sample (rpm)	Static Water Contact Angle θ (°)
Poly(1)	800	81.6 ± 0.6
Poly(1)	900	78.5 ± 0.7
Poly(1)	1000	87.2 ± 1.6
Poly(1)'	800	$\textbf{33.2}\pm\textbf{0.1}$
Poly(1)′	900	27.2 ± 0.3
Poly(1)'	1000	$\textbf{32.8} \pm \textbf{1.9}$
Poly(2)	_ ^a	81.0 ± 0.3
Poly(2)'	_a	80.5 ± 0.6
Glass plate	_	71.7 ± 1.4

^a Prepared by drop cast method.

viscous liquid. It was purified by silica gel column chromatography eluted with CHCl₃ to obtain **1** as a brownish white solid (0.20 g, 0.85 mmol). Yield = 65%, mp = 92-94 °C. IR (KBr disk): 3269, 3036, 2913, 2101, 1671, 1599, 1576, 1494, 1416, 1368, 1323, 1233, 939, 758, 694, 669, 603, 572 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.96 (s, 1H, CH=C), 4.58 (s, 2H, Ar-CH₂-N), 5.36 (O-CH₂-N), 6.73-7.30 (m, 8H, Ar). 13C NMR (100 MHz, CDCl₃): δ 50.3, 76.0, 80.0, 83.5, 114.3, 117.2, 118.6, 121.0, 121.9, 129.4, 130.8, 132.0, 148.1, 155.0. ESI-MS (*m*/*z*): [M + H]⁺ calcd for C₁₆H₁₃NO, 236.1031; found, 236.1070.

3-(4-Ethynyl)Phenyl-3,4-Dihydro-1,3-Benzoxazine (2)

The title compound was synthesized from 4-ethynylaniline (2.25 g, 19.1 mmol), 1,3,5-trioxane (1.20 g, 12.8 mmol) and phenol (1.80 g, 19.1 mmol) in a manner similar to **1b**. The product was purified by recrystallization with CH₂Cl₂ to obtain **2** as a brown solid (2.10 g, 8.9 mmol). Yield = 46%, mp = 96–99 °C. IR (KBr disk) = 3262, 2100, 1606, 1511, 1455, 1373, 1297, 1252, 1225, 1183, 1159, 1086, 1033, 948, 858, 832, 767, 744, 678, 626, 547 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.98 (s, 1H, CH=C), 4.63 (s, 2H, Ar-CH₂-N), 5.35 (O-CH₂-N), 6.80–7.39 (m, 8H, Ar). 13C NMR (100 MHz, CDCl₃): δ 50.1, 76.1, 78.6, 83.9, 114.3, 117.1, 120.7, 121.1, 126.8, 128.1, 133.4, 148.5, 154.3. ESI-MS (*m*/*z*): [M + H]⁺ calcd for C₁₆H₁₃NO, 236.1031; found, 236.1070.

TABLE 4 Thickness and Refractive Indices of Poly(1), Poly(1)', Poly(2), and Poly(2)'^a

Sample	Thickness (nm)	Refractive Index
Poly(1)	31.2 ± 0.17	1.68
Poly(1)'	23.3 ± 0.07	1.72
Poly(2)	41.3 ± 0.12	1.80
Poly(2)'	$\textbf{28.3} \pm \textbf{0.11}$	1.79

^a Measured by ellipsometry.



Polymerization

Typical procedure: $[(nbd)RhCl]_2$ (4.58 mg, 0.99 × 10⁻² mmol) was dissolved in CHCl₃ (9.8 mL) in a 50 mL Schlenk tube under Ar. Then a solution of **1** (234 mg, 0.99 mmol) in CHCl₃ (10 mL) and Et₃N (0.01 mL) were fed into the tube, and the resulting solution was stirred at 30 °C for 1 h ([**1**]₀/ [Rh] = 100, [**1**]₀ = 0.05 mol/L, [Et₃N]/[Rh] = 10). The polymerization mixture was poured into CH₃OH (200 mL) to precipitate a solid mass. It was separated from the solution with a membrane filter (ADVANTEC H100A047A), and dried *in vacuo* to obtain a polymer [poly(**1**)] as a brownish solid (79.1 mg, yield = 33%).

Thermal Curing

A powdery sample of poly(1) was fed in a glass tube. It was placed on a glass petri dish, and heated in a Nitto black MINI SH-OMT oven at 250 °C for 2 h under N_2 to obtain poly(1)'. Poly(2)' was obtained by thermal curing of poly(1) in the same fashion. Film samples of poly(1) and poly(2) were prepared by casting solutions in THF (4 or 10 mM) on a glass plate or a silicon wafer. The samples were submitted to thermal curing as described later. The polymer films on a glass plate and a silicon wafer were used for water contact angle and refractive index measurements, respectively.

Spectroscopic Data of the Polymers

Poly(1) IR (KBr disk): 3393, 3026, 2892, 1600, 1559, 1554, 1494, 1452, 1415, 1375, 1321, 1301, 1230, 1152, 1029, 997, 970, 943, 754, 693, 616, 520 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 4.07 (s, Ar-CH₂-N), 4.84–5.01 (s, O-CH₂-N), 5.71 (s, CH=CH), 6.32–7.20 (m, Ar). **Poly(2)** IR (KBr disk): 3398, 3027, 2957, 2918, 2835, 1605, 1583, 1559, 1507, 1488, 1455, 1375, 1336, 1251, 1226, 1189, 1159, 1111, 1034, 970, 820, 751, 586 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 4.08–4.14 (s, Ar-CH₂-N), 4.86 (s, O-CH₂-N), 5.71 (s, CH=CH), 6.32–7.22 (m, Ar). **Poly(1)**' IR (KBr disk): 3393, 2958, 2919, 2368, 1773, 1734, 1718, 1700, 1696, 1685, 1653, 1647, 1617, 1559, 1554, 1534, 1522, 1507, 1490, 1165, 820, 750, 692 cm⁻¹. **Poly(2)**' IR (KBr disk): 3393, 2918, 2368, 1617, 1559, 1554, 1507, 1458, 1169, 818, 751, 515 cm⁻¹.

Preparation of Samples for Water Contact Angle Measurement

The samples were prepared by drop cast or spin-coating from a polymer solution in THF (4 mol/L) on a glass plate at 800, 900, or 1000 rpm for 30 s. The samples after thermal curing were prepared by heating the aforementioned samples in a Nitto black MINI SH-OMT oven at 250 °C for 2 h under N_2 .

Samples Used for Spectroscopic Measurement, TGA, and DSC

The samples obtained by runs 1 and 5 in Table 1 were used for the measurements depicted in Figures 5–10 and Tables 3 and 4. Poly(1)' and poly(2)' samples in Figure 7 and Tables 3 and 4 were prepared by drop cast or spin-coating from a polymer solution in THF (10 mM) on a glass plate at 1000 rpm for 30 s followed by heating at 250 °C for 2 h under N₂.



SCHEME 2 Polymerization of 1 and 2 followed by crosslinking reaction.

RESULTS AND DISCUSSION

Polymerization

The polymerization of **1** and **2** was carried out using [(nbd)RhCl]₂-Et₃N and (nbd)Rh⁺B⁻BPh₄ as catalysts in THF, CHCl₃, and DMF as solvents at 30 °C for 1 h under Ar (Scheme 2). The corresponding polymers [poly(1) and poly(2)] with M_n and D values of 7,100–25,000 and 1.7–2.9 were obtained in 33%-quantitative yields as listed in Table 1. All the samples of poly(1) obtained by the polymerization of 1 were soluble in THF, $CHCl_3$ and DMF. The polymerization of **1** in CHCl₃ afforded poly(**1**) with an M_n higher than that in THF both with [(nbd)RhCl]₂ and (nbd)Rh⁺B⁻BPh₄. The polymer yields by the polymerization in CHCl₃ were lower than those in THF (runs 1-4).¹⁸ Poly(2) samples obtained by the polymerization with [(nbd)RhCl]₂ in THF (run 5, $[M]_0/[Rh] = 100$) and that in DMF (run 7, $[M]_0/$ [Rh] = 50) were soluble in THF, CHCl₃ and DMF just after isolation, while the polymers became insoluble in the solvents during storing. The other samples of poly(2) were insoluble in the solvents even just after isolation. All the polymerization took place homogenously, and no precipitation or gelation was observed during the polymerization. It is therefore likely that the crosslinking by the ring-opening of the benzoxazine moieties partly took place during acetylene polymerization and/or after isolation. The copolymerization of 2 with phenylacetylene (PA) was also carried out with various feed ratios using $[(nbd)RhCl]_2-Et_3N]$ catalyst in THF to obtain the corresponding copolymers with M_n and D values of 6,100–16,700 and 1.6–6.3 in good yields as listed in Table 2. The copolymer was completely soluble in THF when the feed ratio of **2** was 5%. On the other hand, the copolymers were partly insoluble in THF when the feed ratios of **2** were 25% and 50%.

Thermal Curing of the Polymers

Poly(1) and poly(2) were heated at 250 °C under N₂ for 2 h to obtain polymers with ring-opened benzoxazine moieties. Brownish poly(1) turned into black after heating as shown in Figure 1, while poly(2) exhibited no apparent color change. Figure 2 shows the IR spectra of monomers 1, 2 and the polymers before and after heating. Monomers 1 and 2 exhibited a stretching vibration peak of C=C of the ethynyl group around 2100 cm⁻¹, while poly(1) and poly(2) did not, indicating the successful acetylene polymerization. The monomers and polymers exhibited stretching vibration peaks assignable to the trisubstituted benzene ring around 1490–1510 cm⁻¹ and 940–970 cm⁻¹, and that of C–O–C around 1230 cm⁻¹. These peaks almost disappeared after thermal curing, indicating that the ring-opening reaction of the benzoxazine moieties took place to give poly(1)' and poly(2)' as



SCHEME 3 Copolymerization of 2 with phenylacetylene (PA).



FIGURE 1 Appearance of the polymer samples before and after heating at 250 °C for 2 h under N₂: (a) Poly(1), (b) Poly(1)', (c) Poly(2), (d) Poly(2)'. The samples were obtained by runs 4 and 5 in Table 1. [Color figure can be viewed at wileyonlinelibrary. com]

shown in Scheme 2. Rh catalysts commonly polymerize monosubstituted acetylene monomers via the coordinationinsertion mechanism to give the corresponding *cis*-stereoregular substituted polyacetylenes.^{5,6} The solid state Raman spectra of the polymers were measured before and after heating at 250 °C to obtain information on the structures. Poly(**1**) and poly(**2**) exhibited Raman scattering peaks around 1560 cm⁻¹ assignable to the vibration of C=C at the main chain and benzene ring, and around 1330 cm⁻¹ assignable to the vibration of cis C-C at the main chain as shown in Figure 3. The Raman scattering peaks around 1200– 1280 cm⁻¹ are assignable to the vibration of trans C-C at the main chain. It is therefore considered that poly(**1**) and poly(**2**) consist both of cis and trans stereostructures.¹⁹

It should be noted that the cis polyacetylene backbone possibly isomerizes into trans due to the heat caused by laser light irradiation during Raman spectroscopic measurement.²⁰ In fact, the cis contents of poly(1) and poly(2) were almost quantitative judging from the integration ratio of the cis vinyl protons at the main chain appeared around 5.7 ppm in the ¹H NMR spectra as shown in Figure 4. Poly($\mathbf{1}$)' exhibited broad Raman scattering peaks around 1600 and 1350 cm⁻¹, indicating the existence of polyacetylene backbone after thermal curing at 250 °C. The stereostructure of poly(1)' was unclear due to the broadness of the absorption peaks. The Raman spectroscopic measurement of poly(2)' was unsuccessful due to the emission of luminescence from the sample. Figure 5 shows the UV-vis absorption spectra of 1 and poly(1) measured in THF. Poly(1) exhibited absorption peak assignable to the π - π ^{*} transition of the conjugated polyacetylene backbone at 350-530 nm, while 1 did not show such

absorption, which also confirmed that the acetylene polymerization of **1** successfully took place. The UV-vis absorption spectra of poly(**2**) could not be measured because the samples of poly(**2**) became insoluble in organic solvents during storing after isolation as mentioned above. The UV-vis absorption spectra of the monomers and polymers were therefore measured by the KBr pellet method (Supporting Information, Fig. S15), and diffuse reflectance UV-vis spectra of the polymers as well (Supporting Information, Fig. S16). Poly(**1**)' and poly(**2**)' exhibited UV-vis absorption/reflection peaks at longer wavelength regions compared with poly(**1**) and poly(**2**), respectively, suggesting the extension of conjugation by thermal treatment presumably accompanying the isomerization of the polyacetylene backbone from cis to trans.

Figure 6 shows the DSC thermograms of the monomers and polymers. Monomer **1** exhibited the first endothermic peak at 93 °C corresponding to the mp, and exothermic peak at 145–245 °C corresponding to the ring-opening reaction of the benzoxazine moieties [Fig. 6(a)]. Monomer **2** exhibited



FIGURE 2 IR spectra of (a) **1**, poly(1), and poly(1)'; (b) **2**, poly(2), and poly(2)'. [Color figure can be viewed at wileyonlinelibrary.com]



the endo and exothermic peaks at 97 °C and 150–280 °C corresponding to the mp and ring-opening reaction, respectively [Fig. 6(c)]. Poly(**1**) exhibited exothermic peaks around 140– 180 °C possibly assignable to the glass transition, and 200– 280 °C assignable to the ring-opening reaction of benzoxazine rings [Fig. 6(a,b)] Poly(**1**)' exhibited a exothermic peak around 290–370 °C, which may be attributable to thermal decomposition behavior [Fig. 6(a,b)].^{1f} Poly(**2**) poly(**2**)' exhibited the exothermic peaks [Fig. 6(c,d)] in a manner similar to poly(**1**) poly(**1**)'.

Figure 7 shows the TGA traces of the polymers before and after heating at 250 °C. Poly(1)' and poly(2)' were thermally more stable than poly(1) and poly(2) judging from the 5% weight loss temperatures (T_{d5}) and weight residues at 500 °C. It is likely that the weight loss at the first stage was caused by the cleavage of the unreacted side chains from the polyacetylene backbone. At higher temperatures, the polymers underwent decomposition irrespective of prior thermal treatment at 250 °C. The polymers kept their weights 78–87% at 500 °C, indicating the enhancement of thermal



FIGURE 3 Raman spectra of (a) **1**, poly(1), and poly(1)'; (b) **2** and poly(2). [Color figure can be viewed at wileyonlinelibrary. com]



FIGURE 4 ¹H NMR (400 MHz) spectra of (a) poly(1) and (b) poly(2) measured in $CDCI_3$. [Color figure can be viewed at wileyonlinelibrary.com]

stability compared with poly(PA) derivatives without benzoxazine moieties.²¹ It is reported that aniline is eliminated from benzoxazine moiety upon curing in some cases.²² The



FIGURE 5 UV-vis spectra of **1** and poly(**1**) measured in THF (c = 0.04 mM). [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 6 DSC thermograms of (a, b): **1**, poly(**1**), and poly(**1**)'; (c, d): **2**, poly(**2**), and poly(**2**)' measured at a heating rate = 10 °C/min. [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 7 TGA traces of (a) 1, poly(1), and poly(1)'; (b) 2, poly(2) and poly(2)' (heating rate = 10 °C/min, under N₂). [Color figure can be viewed at wileyonlinelibrary.com]

nitrogen contents of poly(1) and poly(1)' were 5.79% and 5.55%, slightly lower than the theoretical value (6.00%). It is therefore considered that aniline was eliminated only slightly during the curing process of the present polymers.

The static water contact angle (θ) values of the polymers were measured in order to get information about the hydrophilicity before and after thermal curing. The θ values of poly(**1**)' samples were 48.4–54.4° smaller than those of poly(**1**) as listed in Table 3 and the photographs of the representative samples as shown in Figure 8. The θ values of the polymers carrying benzoxazine moieties are commonly not so different before and after curing (ring-opening of benzoxazine moieties), or rather increase after thermal curing, that is, the sample surface tends to become hydrophobic after ring-opening reaction of the benzoxaine moieties due to the formation intra- and intermolecular hydrogen bonding



FIGURE 8 Photographs of water droplets on the films of (a) poly(1) prepared by spin coating method, 1000 rpm; (b) poly(1)'; (c) poly(2) prepared by drop cast method; (d) poly(2)'.



between amino and hydroxy groups formed, leading to the decrease of surface energy.²³ On the contrary, the θ values of poly(1) decreased after thermal curing, indicating the hydrophilicity of the surface of poly(1)' larger than that of poly(1)[Fig. 8(a,b)]. It is speculated that the hydroxy groups of poly(1)' are orientated toward the film surface, and this orientation is not retarded by such hydrogen bonding so much. On the other hand, no remarkable difference was observed between the θ value of poly(2) and poly(2)' films, which is explainable by the formation of hydrogen bonding between the amino and hydroxy groups formed by ring opening of the benzoxazine moieties [Fig. 8(c,d)]. This is reasonable because the hydroxy groups of poly(1)' are located at the benzene rings directly connected to the rigid polyacetylene backbone, while those of poly(2)' are located at the benzene rings through phenylene-nitrogen-methylene spacer. It is therefore likely that the hydroxy groups of poly(2)' are more movable compared to those of poly(1)', and form hydrogen bonding more efficiently.

Table 4 lists the thickness and refractive indices of the polymer films before and after curing. The thickness and refractive indices of the four polymer films were in the ranges of 28–41 nm and 1.68–1.80. Poly(1) and poly(2) became thin after curing, while exhibited no remarkable difference of refractive indices with those of those of poly(1)' and poly(2)', respectively. It is considered that the free volumes of these polymers were intact after thermal curing.

CONCLUSIONS

cis-Stereoregulated polyacetylenes substituted with benzoxazine rings were successfully synthesized by the polymerization of the corresponding substituted acetylene monomers using Rh catalysts, $[(nbd)RhCl]_2$ and $(nbd)Rh^+B^-Ph_4$. The $M_{\rm n}$ s of the present poly(phenylacetylene) derivatives were one-order higher than those of poly(propargyl ether) derivatives substituted with benzoxazine rings,¹⁷ likely due to the high polymerizability of the triple bond conjugated with benzene rings. The present benzoxazine-substituted acetylene polymers underwent ring-opening reaction at 250 °C under N₂ to afford crosslinked polybenzoxazine resins. The polyacetylene backbone of poly(1) was maintained after ringopening reaction of the benzoxazine rings, which was confirmed by Raman spectroscopy. The benzoxazine resins, poly(1)' and poly(2)' were thermally more stable than the precursors, poly(1) and poly(2), presumably due to the rigid polyacetylene backbones. Poly(1)' and poly(2)' kept 78%-87% weights at 500 °C under N₂. The water contact angle measurement revealed that the surface of a film of poly(1)'was more hydrophilic than that of poly(1), likely because the hydroxy groups are oriented toward outside of the film surface. It is suggested that the rigid polyacetylene backbone disturbs the molecular motion of the ring-opened benzoxazine moieties, resulting in the unfavorable formation of hydrogen bonding between OH and N commonly observed in cured benzoxazine resins. In contrast, poly(2) and poly(2)'films exhibited almost the same hydrophilicities in a fashion

similar to common pre- and cured benzoxazine resins. Thus, we developed novel thermally highly stable benzoxazine resins bearing polyacetylene backbones. The refractive indices of the cured resins were rather smaller than those of the prepolymers, showing the possibility of the present polymers as nonvolume shrinkage thermosetting resins. Further study such as mechanical properties are now in progress.

ACKNOWLEDGMENT

The authors are grateful to Prof. Masashi Ishikawa, Prof. Masaki Yamagata, Mr. Hirofumi Yamamoto (Kansai University), and Prof. Kayo Terada (Nara Institute of Science and Technology) for measurement of Raman spectra, Prof. Hideya Kawasaki (Kansai University) for measurement of diffuse reflectance UVvis spectra, Prof. Miyuki Harada and Mr. Takuya Matsumoto (Kansai University) for measurement of DSC, Prof. Takashi Miyata and Mr. Takato Senzaki (Kansai University) for measurement of static contact angles, and Prof. Hiroto Kudoh (Kansai University) for measurement of refractive indices.

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