Bio-based Poly(Schiff-Base) Composed of Bifurfural

Yuya Tachibana, †‡§ Senri Hayashi, † and Ken-ichi Kasuya*†‡§

*Division of Molecular Science, Faculty of Science and Technology, Gunma University, 1-5-1 Tenjin, Kiryu, Gunma 376-8515, Japan
†Gunma University Center for Food Science and Wellness, 4-2 Aramaki, Maebashi, Gunma 371-8510, Japan

Supporting Information

ABSTRACT: In this study, bifurfural, an inedible biobased chemical and a second-generation biomass, was polymerized with several diamines using an environmentally benign process, and the chemical structures of the resulting poly(Schiff base)s were analyzed. Because furan rings, which are only produced from biomass and not from fossil resources, endow polymers with unique properties that include high rigidity and expanded π-conjugation, bifurfural, which contains two furan rings, is of significant interest as a biobased building block. 1H NMR, IR, and matrix assisted laser desorption ionization-time of flight mass spectra of the poly(Schiff base)s reveal that they are composed of mixtures of linear and cyclic structures. The UV–Vis spectroscopy and molecular orbital theory confirm the extended π-conjugation in the bifurfural/p-phenylenediamine poly(Schiff base) system. Poly(Schiff base)s composed of bifurfural and 1,3-propanediamine, 1,4-butanediol, 1,5-pentanediame, and 1,6-hexanediame were molded at 120 °C into films that exhibited good strengths and were tough to bend. These results indicate that bifurfural-based poly(Schiff base)s are promising biobased materials.

INTRODUCTION

Biomass is a critical alternative to fossil resources that combat carbon dioxide emissions and address the issue of dwindling fossil-fuel reserves. Although synthetic polymers are mainly produced from fossil resources, some commercially available polymers have shifted their resources to biomass. †‡ § Biobased polyethylene (PE) †‡ § and poly(lactic acid) † are manufactured from edible biomass, such as sugar and starch, which are defined as being “first-generation” biomass resources. On the other hand, inedible biomass, including cellulose, hemicellulose, and lignin, are gaining attention as sources of “second-generation” biomass resources. To prevent competition between food and material (or energy) uses of crops, second-generation biomass provides an alternative to fossil resources and first-generation biomass. †‡ §

Furfural, which is manufactured from inedible biomass, has been gaining attention as a second-generation biomass resource. †‡ § We have produced a range of biobased chemicals for polymer synthesis, including 1,4-butanediol, †‡ § succinic acid, † oxalic acid, †‡ § and terephthalic acid, † from furfural alone. Because the first step in their syntheses involves the oxidation of furfural to afford a mixture of fumaric acid and maleic acid, these products are devoid of furan rings. On the other hand, chemicals containing furan rings, such as furfural, furfuryl alcohol, 5-(hydroxymethyl)furfural, 2,5-dimethyl furan, and 2,5-furandicarboxylic acid (FDCA), are produced industrially only from biomass and never from fossil resources due to the high costs involved. † In the last decade, poly(ethylene furanoate) (PEF), which is composed of ethylene glycol and FDCA, has been produced commercially as an alternative to poly(ethylene terephthalate) (PET). † Because PEF exhibits several superior properties that are associated with the furan ring, such as gas permeability, the biobased PEF may replace PET in the future. PEF highlights the potential of the furan ring in next-generation biobased polymers.

To enhance the characteristic properties of the furan ring, we have focused on the bifurfural group, which consists of two furan rings connected through their 2-positions. The biphenyl group, which is an analogue of the bifurfural group, consists of C–C bonded benzene rings and possesses several characteristic properties, including extended π-conjugation, liquid crystallinity, and rigidity. The bifurfural group has been used in many functional applications, such as electrical devices, † liquid crystals, † and high-performance polymers. † Park et al. synthesized polyamides containing bifuryl groups as organic electroluminescent materials; † however, they did not consider the bifurfural group to be a biobased moiety even though it is potentially produced from biobased furfural. The first synthesis of bifurfural was reported by Grigg et al. in 1966 and involved the Ullman coupling of furfural derivatives through their 5-positions. † In 1976, Kozhevnikov et al. reported the direct oxidative homocoupling of furfural to give bifurfural. † Methods for the synthesis of compounds containing bifurfural groups have improved infrequently. In 2014, Li et al. reported a practical method for the production of some bifurfural-containing compounds, † whereas in 2017, Miyagawa et al. synthesized...
polyesters of bifurandicarboxylic acid, which is composed of one bifuryl and two carboxylic acid groups.\(^{27}\)

Bifurfural, which is composed of one bifuryl and two formyl groups, is the basic structure of biobased bifuran derivatives because other bifuryl compounds can be prepared from it. For example, bifurancarboxylic acid can be synthesized through the oxidation of bifurfural. On the other hand, the dialdehyde is setup to form poly(Schiff base)s with diamines. As several diamines are synthesized from biomass, poly(Schiff base)s composed of bifurfural are potentially fully biobased polymers. The polymerization process that forms the poly(Schiff base) is environmentally benign because it does not rely on a catalyst. As the imine bonds in poly(Schiff base)s are readily hydrolyzed by acid, they revert to their monomeric forms. In addition, these bonds can be reformed by the removal of water. As a consequence, Fukuda et al. demonstrated that such poly(Schiff base)s are environmentally degradable polymers.\(^{28}\) In 1992, Hui et al. demonstrated that a poly(Schiff base) composed of furan and \(p\)-phenylenediamine units exhibited good thermal stability, and that the \(\pi\)-conjugation extended over the two furan rings and the phenylene group.\(^{29}\)

In this study, we polymerized bifurfural with several diamines, in the presence of \(m\)-cresol or in the absence of solvent, to yield poly(Schiff base)s; their chemical structures were determined by \(^1\)H NMR and IR spectroscopies, size exclusion chromatography (SEC), and matrix-assisted laser-desorption-ionization-time-of-flight mass spectrometry (MALDI-TOF-MS). Thermal and optical properties were examined by thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and UV–vis spectroscopy; the UV–vis spectra were also simulated by computational methods. In addition, physical properties were examined by tensile strength testing using melt-molded films.

## RESULTS AND DISCUSSION

### Synthesis and Properties of Bifurfural

Scheme 1 shows the pathway used to synthesize the poly(Schiff base)s from bifurfural. Bifurfural was prepared from furfural by oxidative homocoupling following a literature procedure.\(^{26}\) To prevent side reactions and increase the electron density of the furan ring, the aldehyde was converted into the corresponding 1,3-dioxolane through protection as an acetal. Figure S2 shows the \(^1\)H NMR spectrum of 2-(2-furyl)-1,3-dioxolane. The oxidative homocoupling reaction of 2-(2-furyl)-1,3-dioxolane was carried out with palladium acetate as the catalyst under an atmosphere of oxygen, after which the acetal group was removed by treatment with hydrochloric acid, to give bifurfural. The direct homocoupling product from 2-(2-furyl)-1,3-dioxolane was not isolated because it became partially deprotected under the oxidative homocoupling reaction conditions to afford the monoprotected and unprotected bifurfurals. Sublimation of the resulting mixture at 130 °C at a pressure below 1 Pa gave purified bifurfural in an overall yield of 39%. Bifurfural is slightly soluble in chloroform, dichloromethane, and tetrahydrofuran, but insoluble in water, methanol, dimethyl sulfoxide, \(N,N\)-dimethylformamide, ethyl acetate, and diethyl ether. In general, \(\pi\)-conjugated compounds are poorly soluble due to strong \(\pi\)–\(\pi\) interactions. Bloom et al. used ab initio calculations to investigate the geometry and energy of dimeric 2,2′-bifuran.

They observed that the most stable conformation of bifuran occurs when the torsional angle between the two furan groups is 180°; the two furan rings are coplanar in this conformation, and the overall group is remarkably \(\pi\)-conjugated. On the other hand, the two phenyl rings of the biphenyl group prefer to be twisted.\(^{30}\) To evaluate the geometry and the extended \(\pi\)-conjugation of bifurfural, the molecular orbitals of bifurfural were calculated using density functional theory (DFT) at the B3LYP/6-311++G(d,p) level. Figure 1 reveals that the most stable geometry of bifurfural is of \(C_{2h}\) symmetry, with an

![Figure 1](https://example.com/figure1.png)
antiparallel arrangement of the furan rings; other geometries and their associated energies are shown in Figure S1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are clearly extended over the two furan rings and both formyl groups (Figure 1), confirming that π-conjugation extends through bifurfural; strong intermolecular π–π interactions between the furan rings and formyl groups results in its low solubility.

**Polymerizing Bifurfural.** Bifurfural was polymerized with five aliphatic diamines, namely, 1,2-ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, and 1,6-hexanedi-amine, as well as an aromatic diamine, p-phenylene diamine, to give poly(Schiff base)s; these polymers are referred to as “PSE”, “PSPr”, “PSB”, “PSe”, “PSH”, and “PSPh”, respectively. The reaction conditions used to prepare these materials are summarized in Table 1. In the absence of

| poly(Schiff base) | solvent | yield/% | $M_n$ × $10^{-4}$ | color |
|------------------|---------|---------|-----------------|-------|
| PSE              | non-cresol | 76      | light brown     |       |
| PSE              | m-cresol | 28      | light brown     |       |
| PSPr             | non-cresol | 71      | 1.2 reddish brown |     |
| PSPr             | m-cresol | 32d     | redish brown    |       |
| PSB              | non-cresol | 70      | ochre           |       |
| PSB              | m-cresol | 12      | ochre           |       |
| PSPe             | non-cresol | 54      | 0.30 redish brown |     |
| PSPe             | m-cresol | 5d      | redish brown    |       |
| PSH              | non-cresol | 60      | 7.9 reddish brown |     |
| PSH              | m-cresol | 60      | reddish brown   |       |
| PSPh             | non-cresol | trace   | red orange      |       |
| PSPh             | m-cresol | 67      | 0.74 dark red   |       |

*The number average molecular weight was calculated from $^1$H NMR spectra. The reaction was carried out at 140 °C for 6 h. The yield was calculated by $^1$H NMR due to the residual m-cresol.

solvent, the polymerization reaction was carried out at 140 °C for 6 h. Because m-cresol has often been used as the solvent in polymerizations to form poly(Schiff base)s, we carried out the polymerization at 30 °C for 1 h in m-cresol. The formation of the imine bond proceeded in the absence of a catalyst, and the color of the reaction mixture gradually changed from yellow to orange and then became yellowish-brown or reddish-brown. Poly(Schiff base)s could be prepared either without solvent or in m-cresol when aliphatic diamines were used, whereas PSPh could not be prepared in the absence of solvent. In vacuo removal of m-cresol, as the solvent, from the poly(Schiff base)s prepared using the aliphatic diamines was difficult; these polymers were purified by double reprecipitation and extraction with methanol and ethanol. Mélares et al. also reported that it was difficult to remove m-cresol from poly(Schiff base)s prepared from 2,5-furandicarboxaldehyde because m-cresol has a strong affinity for furan rings. Unfortunately, we were unable to remove m-cresol from PSPr and PSPe; consequently, their yields were determined from their $^1$H NMR spectra. Polymerizations with 1,2-ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanediamine, and 1,6-hexanedi-amine, without solvent, gave PSE, PSPr, PSB, PSPe, and PSH in yields of 76, 71, 70, 54, and 60%, respectively. In addition, the analogous polymerizations in m-cresol provided PSE in 28%, PSPr in 32%, PSB in 12%, PSPe in 5%, PSH in 60%, and PSPh in 67% yield. Except for PSH and PSPh, the yields of poly(Schiff base)s in m-cresol were lower than those in the absence of solvent. In the case of PSH, the yields in the absence and presence of solvent were the same, but the high molecular-weight fraction was produced when PSH was polymerized in the absence of m-cresol than in the presence of m-cresol, as shown in Figure S3. These results indicate that m-cresol is unsuitable as a solvent for polymerizing aliphatic diamines to poly(Schiff base)s. During the polymerization of PSPh, the precipitate obtained in the absence of solvent was mainly bifurfural, whereas that in m-cresol was PSPh, indicating that m-cresol is suitable as a solvent for the polymerization of PSPh. The color of the poly(Schiff base) depended on the diamine, as listed in Table 1. The bifurfyl-containing poly(Schiff base)s were soluble in some organic solvents, whereas previously reported poly(Schiff base)s were hard to dissolve in organic solvents and often became insoluble following reprecipitation. Polymer solubility is important for electric-device applications because wet processes are used to fabricate these devices. The poly(Schiff base)s were slightly soluble in halomethane solvents, namely chloroform and dichloromethane, and amid-base aprotic polar solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide, and N-methylpyrrolidone, but they were insoluble in other polar solvents, including water, methanol, dimethyl sulfoxide, ethyl acetate, diethyl ether, and tetrahydrofuran. PSPh was completely soluble in chloroform and dichloromethane under reflux.

**Structural Analyses of the Poly(Schiff Base).** Although the yields of the poly(Schiff base)s prepared from the aliphatic diamines were higher in m-cresol than in the absence of solvent, it was difficult to remove the residual m-cresol from the resulting precipitate; PSPh from p-phenylenediamine was not obtained in the absence of solvent. To analyze the chemical structures of the poly(Schiff base)s, we examined PSE, PSPr, PSB, PSPe, and PSH samples that were polymerized without solvent, whereas PSPh polymerized in m-cresol was used.

Figure 2 displays the partial $^1$H NMR spectra of bifurfural and the poly(Schiff base)s; full spectra are shown in Figure S4. Peaks corresponding to iminyl protons (H$_J$) at around 8 ppm were observed, whereas the peak corresponding to the formyl proton (H$_L$) at around 9.7 ppm became comparatively weaker following polymerization. Although peaks at around 9.7 ppm were visible in the spectra of PSPr, PSPe, PSH, and PSPh, they appeared at higher magnetic fields compared with that of bifurfural, indicating that they are derived from terminal formyl groups (H$_J$'). The separated peaks at around 9.7 and 8.3 ppm, which correspond to H$_L$' and H$_J$ in PSPh, are the result of syn- and anti-conformations about the imine/carbonyl and imine/ imine bonds, respectively, because the p-phenylene unit inhibits the free rotation of the imine bond. The peaks corresponding to the amine-derived terminal group were not observed in the spectra of PSE, PSPr, PSB, PSPe, and PSPh, indicating that these polymers are terminated at each end with bifurfyl groups. On the other hand, peaks corresponding to formyl and amino terminal groups are observed in the spectrum of PSH. The number average molecular weights of PSPr, PSPe, PSH, and PSPh were calculated from their $^1$H NMR spectra; the integrated H$_J$-to-H$_J$ signal ratios led to values of 1.2 × 10$^4$, 0.30 × 10$^4$, 7.9 × 10$^4$, and 0.74 × 10$^4$, respectively. The peaks corresponding to H$_J$' in PSE and PSB were not observed, suggesting that their molecular weights are very high.

Figure 3 displays the IR spectra of bifurfural and the poly(Schiff base)s. Peaks corresponding to the C==N double
bonds are visible at 1635 cm$^{-1}$, whereas peaks due to C=O double bonds, at around 1660 cm$^{-1}$, were observed to be weaker following polymerization. The residual C=O peaks in the spectra of PSPr, PSPe, PSH, and PSPh were observed at 1670 cm$^{-1}$, indicating that the proportions of terminal formyl groups in PSPr, PSPe, PSH, and PSPh were relatively high; the high proportions of terminal groups indicate that the molecular weights of these polymers were not high. On the other hand, C=O peaks were not observed in the spectra of PSE and PSB, suggesting that the proportions the terminal formyl groups in PSE and PSB were low, and that the molecular weights of PSE and PSB were higher than those of the other polymers. These results are consistent with those obtained by $^1$HNMR spectroscopy.

The molecular weights of the poly(Schiff base)s were evaluated by SEC, the profiles of which are shown in Figure 4; the x-axis in this figure displays the logarithm of the molecular weight determined against a polystyrene standard. The SEC traces conflict with the $^1$HNMR and IR data. As discussed above, the number average molecular weights calculated by $^1$HNMR spectroscopy exceeded $3.0 \times 10^3$, especially those of PSE and PSB, which are expected to be high-molecular-weight polymers. However, the molecular weights of the main fractions of all poly(Schiff base)s were between 100 and 1000, whereas a slightly higher-molecular-weight fraction was observed in the SEC profiles of PSPe, PSH, and PSPh.

To gain an insight into the origins of this conflict, the poly(Schiff base)s were subjected to MALDI-TOF-MS. Figure 5 displays the MALDI-TOF-MS spectra of PSH and PSPh as representative spectra of the poly(Schiff base)s, whereas Figure 5S displays the spectra of the remaining polymers. As depicted in Figure 5a, the small repeating peaks observed for PSH are assigned to silver-ion-coordinated linear structures terminated...
with bifurcral at both ends, whereas the large repeating peaks were assigned to silver-ion-coordinated cyclic structures. Figure S5 reveals that similar repeating peaks were also observed in the spectra of PSE, PSPr, PSB, and PSPe, indicating that both linear and cyclic structures were formed during Schiff-base polymerizations with aliphatic diamines, with the cyclic structures preferred over the linear structures. In the case of PSPh, the repeating peaks corresponding to cyclic structures were less intense than those corresponding to linear structures (Figure S5b). These results indicate that the formation of smaller cyclic structures was sterically restricted, whereas the formation of larger cyclic structures was entropically restricted as a result of the rigid p-phenylenediamine structure, whereas aliphatic diamines, especially 1,6-hexanediame, facilitated the easy formation of both cyclic and linear poly(Schiff base)s due to their flexibilities.

The reaction of an amine with an aldehyde to form an imine is an equilibrium process under acidic conditions. Because the condition in chloroform is weakly acidic condition due to its decomposition to form hydrochloric acid, a poly(Schiff base) in chloroform would decompose into the diamine and bifurcral, and then followed by reconstruction to form the thermally stable cyclic structure. To investigate the decomposition of the poly(Schiff base)s, PSH was subjected to time-dependent SEC

![Figure 4. SEC traces of the poly(Schiff base)s.](image)

![Figure 5. MALDI-TOF-MS positive ion spectra of (a) PSH and (b) PSPh. Color code: Black corresponds to cyclic structures, red corresponds to linear structures terminated at both end with bifurcral groups, blue corresponds to linear structures terminated at both ends with amines, and green corresponds to linear structures terminated with both amines and bifurcral moieties.](image)
analysis following the dissolution in chloroform (1.0 mg mL$^{-1}$), the results of which are displayed in Figure 6. The high-
molecular-weight fraction containing linear structures was observed to decrease, whereas the low-molecular-weight fraction containing cyclic structures was observed to concomitantly increase over a 2 h period. This result indicates that a poly(Schiff base) in chloroform exists in equilibrium, with the linear structures formed in the absence of solvent decomposing and reforming as the thermally more stable cyclic structures in dilute chloroform solution.

**Thermal Properties.** TGA and DSC traces of various poly(Schiff base)s are shown in Figure 7. The weight loss temperatures, residual weights at 1000 °C, and glass transition temperatures ($T_g$s) of the poly(Schiff base)s are summarized in Table 2. The 5% weight-loss temperatures ($T_{d5\%}$) of PSE, PSPr, PSB, PSPe, and PSH were in the 260–280 °C range, whereas that of PSPh was 339 °C. The residual weights of the poly(Schiff base)s were above 40% following heating to 1000

**Figure 6.** Time-dependent molecular weight profiles in chloroform of PSH prepared without solvent.

**Figure 7.** (a) TGA traces of the poly(Schiff base)s at a rate of 10 °C min$^{-1}$. (b) DSC curves of the poly(Schiff base)s during the second heating cycle at rates of 10 °C min$^{-1}$.

**Table 2.** Thermal Properties, $\lambda_{\text{max}}$, and Mechanical Properties of Bifurcal and the Poly(Schiff Base)$^a$

| poly(Schiff base) | $T_{d5\%}$/°C | $T_{d10\%}$/°C | $T_{d20\%}$/°C | $T_{d50\%}$/°C | weight b/% | $T_g$/°C | $\lambda_{\text{max}}$/nm | Young's modulus/GPa | tensile strength/MPa | strain at breaking point/% |
|------------------|---------------|----------------|----------------|----------------|------------|--------|----------------|-----------------|------------------|----------------------|
| bifurcal         | 205           | 234            | 255            | 284            | 909        | 47     | 909           | 1.01            | 5.2              | 2.6                  |
| PSE$^g$          | 263           | 317            | 435            | 494            | nd         | 394    | 348, 368      | 0.85            | 22.1             | 0.8                  |
| PSPr$^g$         | 279           | 333            | 447            | 494            | nd         | 394    | 348, 368      | 0.90            | 49.4             | 7.2                  |
| PSB$^g$          | 258           | 275            | 392            | 494            | nd         | 394    | 348, 368      | 1.19            | 7.2              | 0.9                  |
| PSPe$^g$         | 264           | 284            | 379            | 494            | nd         | 394    | 348, 368      | 1.52            | 49.4             | 7.2                  |
| PSH$^g$          | 281           | 306            | 417            | 494            | nd         | 394    | 348, 368      | 0.85            | 22.1             | 0.8                  |
| PSPh$^g$         | 339           | 395            | 439            | 494            | nd         | 394    | 348, 368      | 0.85            | 22.1             | 0.8                  |

$^a$Polymerized without solvent.

$^b$Polymerized with m-cresol. Specimens could not be obtained.

$^c$Specimens could not be obtained.

$^d$Residual weight at 1000 °C.

$^e$Measured by DSC.

$^f$Measured by UV−vis spectrometry.

$^g$Measured by tensile strength testing.
°C, and the samples following testing were shiny and black, indicating that the poly(Schiff base)s are readily carbonized. As listed in Table S1, elemental analyses of the black residues reveal that about half of the original nitrogen atoms remain in the carbonized residues, which suggests that carbon nitride-like residues had formed. A carbon electrode is prepared from furan resin because furan rings readily form graphite in general, half of the nitrogen atoms in the furan resin remain in the carbonized residue following this process. Therefore, the high residual weights of these poly(Schiff base)s reflect the properties of the furan ring. The \( T_g \) of PSPr, PSB, PSPe, and PSH decreased with increasing length of the alkyl chain in the starting aliphatic diamine, whereas PSE and PSPh did not exhibit \( T_g \)s during the DSC measurements in the second heating and first cooling processes. Endothermic and exothermic peaks derived from melting and crystallization were not observed in any poly(Schiff base). On the other hand, weak crystalline peaks were observed in the wide-angle X-ray diffraction (WAXD) patterns of melt-molded samples of PSE, PSB, and PSPh films, whereas only a halo peak was observed in those of the PSPr, PSPe, and PSH films, as shown in Figure S6. These results indicate that PSE, PSB, and PSPh are crystalline polymers. Moreover, PSPr, PSPe, and PSH are also crystalline polymers that exhibit low crystallization speeds because of the chromophores in these poly(Schiff base)s correspond to imine–bifuryl–imine bonds that are not affected by chain length. In addition, their solid-state colors (Table 1) are consistent with the experimentally observed values. The \( \lambda_{\text{max}} \) derived from the \( \pi-\pi^* \) transitions did not depend on the length of the aliphatic diamine because the chromophores in these poly(Schiff base)s correspond to imine–bifuryl–imine bonds that are not affected by chain length. In addition, their solid-state colors (Table 1) do not coincide with the UV–vis spectra because they appear yellow in solution. This suggests that the color in the solid state is the result of charge-transfer complexes formed between the bifuryl group and imine double bond.

**Mechanical Properties.** The mechanical properties of the polymers were assessed using melt-molded films. PSPr, PSB, PSPe, and PSH could be molded at 120 °C into self-standing films; however, PSE and PSPh formed powders after molding at 150 °C. Figure 9 displays the stress–strain curves of PSPr, PSB, PSPe, and PSH. Bending the PSPr film

![Figure 9](Image)

Figure 9. (a) Stress–strain curves for PSPr, PSB, PSPe, and PSH. (b) Bending the PSPr film.

PSE, and PSH. The Young’s moduli, tensile strengths, and strains at breaking point are summarized in Table 2. All the films were reddish-brown, those of PSPr, PSPe, and PSH were transparent, whereas unmelted particles remained in the PSB film. As shown in Figure 9b, the PSPr film was tough to bend; the Young’s moduli of all the films were around 1 GPa, with strains at the breaking point below 10%, indicating that PSPr, PSPe, and PSH are tough polymers. The cyclic structures act as plasticizers that affect the mechanical properties differently. On the other hand, PSB was relatively fragile due to residual particles in the specimen, and its tensile strength and strain at breaking point were lower than those of others.

**CONCLUSIONS**

Furfural is a promising biobased chemical for the production of polymers. We successfully synthesized biobased poly(Schiff base) by the reactions of a variety of dianimes with bifurfural obtained from furfural, using an environmentally benign process devoid of both solvent and catalyst. The cyclic structures act as plasticizers that affect the mechanical properties differently. On the other hand, PSB was relatively fragile due to residual particles in the specimen, and its tensile strength and strain at breaking point were lower than those of others.

Bifurfural and PSH completely dissolved in dichloromethane at concentrations of 5 \( \mu \)g mL\(^{-1}\), whereas an insoluble component remained for PSE, PSPr, PSB, PSPe, and PSPh; consequently, quantitative evaluations are difficult. Optical Properties. Figure 8 displays the UV–vis spectra of the poly(Schiff base)s acquired in dichloromethane.

![Figure 8](Image)

Figure 8. UV–vis spectra of bifurfural and the poly(Schiff base)s in dichloromethane.
poly(Schiff base)s in chloroform are in equilibria and form thermally stable cyclic structures. The DSC traces reveal that the $T_g$ of poly(Schiff base)s composed of aliphatic diamines depended on the length of the alky1 chain. The UV−vis spectroscopy and DFT calculations reveal the expanded π-conjugation in PSPI. PSPR, PSB, PSp, and PSH were moldable at 120 °C, and the molded films were tough to bend and strong. Therefore, we demonstrated that a poly(Schiff base) composed of bifurural is a novel biobased polymer with good mechanical properties and extended π-conjugation. We are currently evaluating the environmental benignness and photovoltaic properties of these materials for use in green electrical devices.

**EXPERIMENTAL SECTION**

**Reagents.** Furfural, toluene, dimethyl sulfoxide, acetic acid, anhydrous tetrahydrofuran, hydrochloric acid, ethylene diamine, dichloromethane, m-cresol, and deuterated chloroform were purchased from Kanto Kagaku Co., Inc. (Tokyo, Japan). p-Toluenesulfonic acid, 1,3-propanediamine, 1,4-butanediamine, 1,5-pentanedi amine, and 1,6-hexanedi amine were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Palladium dicarboxylic acid was isolated from Sigma-Aldrich Japan Co., LLC. (Tokyo, Japan). Furfural was used after distillation from Na2CO3 under reduced pressure. Acetic acid was distilled, and m-cresol was distilled under reduced pressure. Toluene, dichloromethane, dimethyl sulfoxide, and ethylene glycol were distilled from calcium hydride before use. Ethylenediamine, 1,3-propanediamine, 1,4-butanedi amine, and 1,5-pentanedi amine were distilled under reduced pressure. All the other chemicals were of reagent grade and used without further purification.

**Synthesis of 2-(2-Furyl)-1,3-dioxolane.** p-Toluenesulfonic acid monohydrate (53 mg, 0.28 mmol) was added to a solution of furfural (11.4 mL, 138 mmol) and ethylene glycol (8.9 mL, 158 mmol) in toluene (35 mL). The reaction mixture was refluxed with Dean−Stark apparatus under N2 for 12 h, and the resulting solid was removed by filtration. The solution was concentrated in vacuo and washed with saturated NaHCO3 (20 mL) and saturated brine (20 mL), followed by extraction with dichloromethane (20 × 2 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. Then, the solvent removed in vacuo to give a mixture of a solid and a viscous liquid.

**Synthesis of Bifurural.** Palladium acetate (372 mg, 1.66 mmol), dimethyl sulfoxide (32 mL), acetic acid (8 mL), and 2-(2-furyl)-1,3-dioxolane (2 mL, 16.6 mmol) were added to a 100 mL two-necked flask. The flask was flushed with O2, after which the reaction mixture was heated at 50 °C for 24 h under O2 (3 L rubber balloon). The resulting mixture was washed with saturated NaHCO3 (50 mL) and saturated brine (30 mL), followed by extraction with dichloromethane (20 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate and filtered. Then, the solvent was removed in vacuo at room temperature to give a mixture of a solid and a viscous liquid. The crude product was dissolved in tetrahydrofuran (10 mL) and 1 M aqueous HCl (12.5 mL) was added dropwise to the solution. After stirring at room temperature for 5 min, the resulting precipitate was collected by filtration and dried under vacuum at room temperature to give the crude product as a brown solid. The crude product was purified by sublimation at 130 °C/1 Pa to afford bifurural (0.47 g, 60%) as a yellow solid.

**General Procedure for the Preparation of Poly(Schiff Bases) in the Absence of Solvent.** A mixture of bifurural (0.526 mmol) and the diamine (0.526 mmol) was stirred at 140 °C for 3 h in a 25 mL two-necked flask under N2. After the reaction mixture was heated under vacuum at 140 °C for 3 h, the resulting solid was washed with methanol and heated under vacuum at 80 °C to remove the residual methanol. The resulting solid was collected as a yellowish-brown solid or a reddish-brown material.

**General Procedure for the Preparation of Poly(Schiff Bases) in m-Cresol.** m-Cresol (0.5 mL) was added to a mixture of bifurural (0.526 mmol) and the diamine (0.526 mmol) in a 25 mL two-necked flask under N2. After stirring at 30 °C for 1 h, the resulting solid was dissolved in dichloromethane (2 mL), and the solution was poured into methanol (40 mL). The resulting precipitate was collected by filtration and heated at 80 °C under vacuum to remove the residual m-cresol and methanol to give a red solid.

**Spectroscopy.** 1H NMR spectra were recorded at 400 MHz on a JNM-ECD400 NMR spectrometer (JEOL, Tokyo, Japan) in deuterated chloroform and with tetramethylsilane as the internal standard. IR spectra were acquired using a Nicolet iS50 FT-IR spectrophotometer (Thermo Fisher Scientific K.K., Yokohama, Japan) equipped with a single-reflection attenuated total reflectance system (Spectra-Tech Foundation Performer; Thermo Fisher Scientific K.K., Yokohama, Japan). The UV−vis spectra were recorded using a U-3000 UV−vis spectrometer (Hitachi, Tokyo, Japan). A dichloromethane solution of the sample (5 μL mL−1) was prepared and examined at room temperature using a quartz cell (10 × 10 × 20 mm3). The solubility proportions of low-solubility samples were examined after adding 25 μg of the sample to 5 mL of dichloromethane.

**Molecular Weights.** Molecular weights were determined by SEC with a refractive index detector using a combination of two TSKgel MultiporeHXL-M columns ( Tosoh Co., Tokyo, Japan) and a guard column (TSKgel guard column MP (XL); Tosoh Co., Tokyo, Japan). The columns were eluted with chloroform (1.0 mL min−1) at 40 °C and polystyrene standards were used for calibration. Mass spectra were recorded on an AXIMA Performance MALDI-TOF-MS (Shimadzu Co., Kyoto, Japan) equipped with a nitrogen laser (λ = 337 nm). The spectrometer was operated in linear and reflectron-positive ion modes with pulsed ion extraction. Polymer samples in dichloromethane (100 mg mL−1) and tetrahydrofuran solutions of sodium trifluoroacetate (100 mg mL−1) or silver trifluoroacetate (100 mg mL−1) were mixed (in equal volumes), and 2 μL aliquot of each mixture was deposited onto the sample target plate.

**Thermal Properties.** Thermal stabilities were determined using an STA-6000 thermal gravimetric analyzer (PerkinElmer Co., Ltd., Yokohama, Japan) to 1000 °C at a rate of 10 °C min−1 under N2. Glass transition temperatures ($T_g$) were determined by differential scanning calorimetry (DSC-4000; PerkinElmer Inc., Co., Ltd., Yokohama, Japan). After each sample was heated to 200 °C and cooled to −60 °C at a rate of 10 °C min−1, it was then heated from −60 to 200 °C at a rate of 10 °C min−1 during the second heating scan. The $T_g$ of each polymer was determined from the second heating scan.

**Tensile Strength Testing.** Each sample was compressed into a 10 × 20 × 0.1 mm3 film at 15 MPa using a Mini Press Test 10 hot-pressing machine (Toyo Seiki Seisaku-sho Ltd., Japan).

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conducted using X-ray diffractometer (RINT220; Rigaku Co., Tokyo, Japan). The radiation source was Cu Kα radiation with a wavelength of 0.154 nm. The voltage was set to be 40 kV and the current 20 mA. Each melt-pressed film was mounted on a sample holder and scanned from 0 to 60°.

DFT Calculations. DFT and TD-DFT calculations were carried out using the Gaussian-09 Revision C.01 WIN64 program package. The geometries of bifurcal and the model imines were optimized by DFT/B3LYP/6-311++G(d,p) and excited states were calculated by TD-DFT/B3LYP/6-311++G(d,p). The orbital interactions were evaluated using the natural bond orbital method, and the structures and orbitals were visualized using the GaussView ver. 5.0.9 program.

Decomposition Testing of PSH in Chloroform. PSH (50 mg) was dissolved in chloroform (50 mL) under N₂. The solution was stirred at room temperature, and the molecular weight profile of an aliquot of the solution was recorded by SEC after 0, 2, 4, 6, 24, and 72 h.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00466.

Author Contributions
Y.T. (e-mail: tachibana@gunma-u.ac.jp) and K.-i.K. designed this work and wrote the article. Y.T. and S.H. carried out the synthetic experiments and evaluated the properties. All the authors participated in the analysis and discussion of the results.

Notes
The authors declare no competing financial interest.

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