Synthesis and Evaluation of High-Molecular Weight Diphenyl Oxide and Diphenyl Sulfide Novolacs

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ABSTRACT: The preparation and characterization of high-molecular weight diphenyl oxide- and diphenyl sulfide-novolacs are described. The polymerization of diphenyl oxide with 2 equivalence of formaldehyde proceeded to give the corresponding polymer (**2**) (M_n: 160,000, M_w/M_n: 29.1) in good yield. Further, an ultra high-molecular weight fraction ($M_w > 1,000,000$) was observed in the GPC trace of **2**. The developed polymers can be considered as a new class of aromatic polymers that exhibit both novolac-like and engineering plastic properties and are thus promising compounds for material-engineering applications. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1651–1657, 2010

Key words: novolac; phenolic resin; diphenyl oxide; diphenyl sulfide; formaldehyde; addition-condensation

INTRODUCTION

Phenol-formaldehyde condensation is one of the simplest methods for the preparation of heat-resistant aromatic polymers.[1–6] The advantages of phenol-formaldehyde condensation are as follows: (1) polymerization can be carried out under mild conditions, (2) purification is easy, because water is the only by-product, and (3) high cost-performance, because phenol and formaldehyde are used. A large number of the phenolic-compound-based novolacs have been synthesized from various electron-rich aromatic compounds. However, majority of the reported novolacs have been synthesized by only two phenolic compounds, namely, phenol, and cresol.[1–23]

Heteroatom-containing aromatic compounds are a desirable component of engineering plastics. Heteroatom-containing poly(p-phenylene)s such as poly(phenylene oxide) (PPO),[24–29] poly(phenylene sulfide) (PPS),[30–33] polyaniline,[34,35] and poly(phenylene borane),[36,37] are extensively used for industrial purposes. These polymers exhibit excellent mechanical properties, high-thermostability, and several other beneficial properties. A majority of the abovementioned polymers are thermoplastic resins, and therefore, they are excellent for use in fabrications or processes. Heteroatom-containing poly(p-phenylene)s consist of electron-rich components are expected as novel novolacs with excellent properties as engineering plastics.[38,39]

Previously, Imoto prepared diphenyl oxide[40,41] and diphenyl sulfide[42] novolacs by the p-toluenesulfonic acid-catalyzed addition-condensation of diphenyl oxide or diphenyl sulfide with formaldehyde in a propionic acid solution. However, only oligomers (average degree of polymerization: ca. 4) were obtained because many ester bonds derived from methylol moieties and propionic acid were formed during the polymerization process. Furthermore, ^{13}C-NMR, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), thermal analyzes, etc. did not characterize the polymers adequately.

These results, although imperfect, have stimulated our interest in the development of a novel method to produce high-molecular weight heteroatom-containing novolacs without the formation of by-products. In our previous study, we showed that chloroform is an effective medium for the preparation of high-molecular weight novolacs.[43,44] Therefore, we hypothesized that it would be possible to prepare diphenyl oxide- and diphenyl sulfide-based novolacs with high-molecular weights using chloroform.

In this study, the synthesis and characterization of high-molecular weight diphenyl oxide-formaldehyde and diphenyl sulfide-formaldehyde copolymers (novolacs) are described. These polymers were characterized, and their properties were compared with those of PPO and PPS.

EXPERIMENTAL

Instruments

All the ^{1}H-NMR and ^{13}C-NMR spectra were measured in CDCl$_3$ and recorded by using a 270 MHz JEOL JNM-EX270. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the polymers were estimated by using gel permeation chromatography (LC-6A (TOSOH) with TSK$_{gel}$ GMH$_{HR}$ or Shodex LF804 columns) with tetrahydrofuran (THF) as an eluent after calibration with polystyrene standards. The FTIR spectra were recorded on a JASCO FTIR 460 plus spectrometer. The DSC analyzes were performed by using a Perkin-Elmer Diamond DSC with a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analyzes (TGA) were carried out by using a SII TG/TDA6200 with a heating rate of 10°C/min under air or nitrogen. The solution properties of the polymers were examined by using a Viscotek SEC-VISC-RALLS analysis system (Viscotek TDA302 & OmniSEC Software) by using THF as an eluent, according to the literatures.[45,46]

Materials

Unless otherwise noted, all chemicals and solvents were obtained from commercial suppliers and used without further purification. Diphenyl oxide (1) and concentrated sulfuric acid (98%) Wako Pure Chem (Osaka, Japan), diphenyl sulfide (4) (TCI) and paraformaldehyde Nacarai Tesque (Kyoto, Japan) were purchased. Tetrahydrofuran (THF) was freshly distilled prior to its usage.

Diphenyl oxide novolac (2)

Acetic acid (15 mL) and chloroform (5 mL) were added to a mixture of diphenyl oxide 1 (3.60 g, 20 mmol) and paraformaldehyde (1.26 g, 40 mmol as formaldehyde). After stirring the mixture for 5 min at 4°C, 1.5 mL of conc. sulfuric acid was added to it dropwise at the same temperature. The mixture was stirred again at the same temperature for 20 min. Then, the stirring was carried out at 60°C for 6 h. After cooling the mixture to room temperature, it was poured into methanol (200 mL), and the crude polymer formed was collected. The crude polymer was dissolved in THF and reprecipitated with methanol to obtain the desired polymer 2 in the form of a colorless precipitate in 98% yield. In **run 1**, the molar ratio of diphenyl oxide:paraformaldehyde was found to be 1 : 3.

^{1}H-NMR (270 MHz, δ (ppm), CDCl$_3$): 3.75–4.00 (Ar—CH_2—Ar), 5.04–5.20 (Ar—CH_2—OCOCH$_3$), 6.60–7.20, 7.27–7.60 (Ar—H); ^{13}C-NMR (67.8 MHz, δ (ppm), CDCl$_3$): 21.1 (Ar—CH$_2$—OCOCH_3), 40.3 (p,p'-

Ar—CH_2—Ar), 61.4 (Ar—CH_2—OCOCH$_3$), 118–136 (aromatic C), 155 (aromatic C—O—Ar); FTIR (KBr, cm^{-1}): 3000 (aromatic C—H stretch), 2903 (methylene C—H stretch), 1763 (C=O stretch), 1250, 1033 (C—O—C); GPC (THF, polystyrene standards): M_n = 3,300, M_w = 56,000, M_w/M_n = 17.0.

Diphenyl sulfide novolac (5)

Diphenyl sulfide 4 (3.72 g, 20 mmol) and paraformaldehyde (1.26 g, 40 mmol as formaldehyde) were dissolved in a solution mixture of acetic acid (10 mL) and chloroform (10 mL). After stirring the solution for 5 min, 1.5 mL of conc. sulfuric acid was added to it for 1 min at 4°C. Then, the mixture was stirred for 1 min at 4°C. And then, the mixture was stirred at this temperature for 20 min. Next, the resultant mixture was stirred at 60°C for 3 h. After cooling the mixture to room temperature, it was poured into methanol (200 mL), and the crude polymer formed was collected. The crude polymer was dissolved in THF and reprecipitated with methanol to obtain the desired product 5 in the form of a colorless precipitate in 82% yield.

^{1}H-NMR (270 MHz, δ (ppm), CDCl$_3$): 3.70–4.15 (Ar—CH_2—Ar), 6.80–7.20 (Ar—H); ^{13}C-NMR (67.8 MHz, δ (ppm), CDCl$_3$): 39.0 (o,p'-Ar—CH_2—Ar), 40.3 (p,p'-Ar—CH_2—Ar), 125–140 (aromatic C), 139.2 (aromatic C—S—Ar); FTIR (KBr, cm^{-1}): 3,000 (aromatic C—H stretch), 2,900 (methylene C—H stretch); GPC: M_n = 2,600, M_w/M_n = 4.6.

RESULTS AND DISCUSSION

Diphenyl oxide novolac (2)

When the addition-condensation reaction of diphenyl oxide (1) with formaldehyde was started at room temperature, the diphenyl oxide novolac with a high-molecular weight (3) was obtained (Table I, run 1) (Scheme 1). The weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of the obtained novolac were 160,000 and 29.1, respectively. Both M_w and polydispersity index were found to increase when an excess amount of paraformaldehyde was used (Table I, run 1). The ^{1}H-NMR spectrum of 3 shows that the methylene protons of acetoxymethyl groups appeared at 5.00–5.40 ppm, and the protons of acetyl groups, those might be from ester groups or surviving acetic acid appeared at 1.80–2.20 ppm (Fig. 1). The acetoxymethyl group was formed by the condensation of acetic acid and methylol intermediate, as described in our previous report (Scheme 2).[43] This result indicated that the reactivity of the methylol moiety was extremely high; therefore, both the formation of the ester group and the addition-condensation reaction proceeded

TABLE I
Addition-Condensation of Diphenyl Oxide (1) with Formaldehyde

Run	Feed ratio (mmol) (1 : aldehyde)	Solvent (mL)	Temp (°C)	Time (h)	Yield[b] (%)	M_w[c]	M_w/M_n[c]
1	1 : 3	AcOH (5) / CHCl$_3$ (15)	60	6	87	160,000	29.1
2	1 : 2	AcOH (5) / CHCl$_3$ (15)	60	6	98	56,000	17.0
3	1 : 2	AcOH (20)	60	0.5	28	1,700	1.4
4	1 : 1.2	bulk	80	12	82	7,400	8.2
5[a]	1 : 2	AcOH (5) / CHCl$_3$ (15)	60	6	trace	–	–

[a] Catalyzed by 12 N HCl aq.
[b] Isolated yield after precipitation in methanol.
[c] Determined by GPC (eluent: THF, polystyrene standards).

competitively under these reaction conditions, and (**3**) with ester groups was obtained (Table I, run 1).

The results of polymerization under various reaction conditions are summarized in Table I. To suppress the esterification side reaction, the addition-condensation of **1** with formaldehyde was started at 4°C (Table I, run 2). The mixture was then heated at 60°C. The polymerization of **1** with formaldehyde was achieved by the limited catalyst; conc. sulfuric acid (Table I, runs 2–4). Polymerization did not proceed when 12 mol/L hydrochloric acid was used as a catalyst (Table I, run 5). Therefore, we concluded that a strong acid is required for polymerization to take place to compensate for the poor reactivity of **1**, which is less as compared with that of phenol.

The resulting polymer (**2**) was highly soluble in common organic solvents such as chloroform, THF, toluene, and acetone; however, it was insoluble in methanol. Furthermore, an ultra high-molecular weight fraction ($M_w > 1,000,000$) was observed in the gel permeation chromatography (GPC) trace (Table I, run 2) (Fig. 2). The structure of polymer **2** (Table I, run 2) was confirmed from the FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra.

The FTIR spectrum of **2** (supporting information: Figure S1) showed absorption at 3000 and 2903 cm^{-1}, which was due to the stretching of aromatic and methylene C—H bonds and also at 1763 cm^{-1}, which was due to C=O bonds.

The ^{1}H-NMR spectrum of **2** showed the characteristic signals of aromatic protons at 6.60–7.20 and 7.27–7.60 ppm, and peaks attributable to methylene protons (o,p'- or p,p'-Ar—CH_2—Ar') at 3.85–4.10 ppm were also observed (Fig. 3). Minimal signals of the methylene protons of methylol esters at 5.04–5.20 ppm indicated that some esterification between the methylol moieties and acetic acid did occur; however; the extent of the reaction was much larger than that of **3**. The peaks at 1.12–1.38 and 1.81–2.19 ppm appeared to be from the contaminations and surviving acetic acid.

From the ^{13}C-NMR spectrum of **2**, it can be observed that the two signals around 30–40 ppm were from the carbons of methylene bridges between two aromatic rings.[1] The sharp peak at 40 ppm and the weak peak at 35 ppm were attributable to p,p'-diphenylmethane-type methylene carbons and o,p'-diphenylmethane-type methylene carbons, respectively. On the basis of the peak intensities in this region, the abundance ratio of the o,p'- to p,p'- linkage patterns at the methylene units was estimated to be less than 5%. This result suggested that the p,p'-linkages were formed predominantly during the polymerization of **1** with formaldehyde. The carbocation intermediate derived from formaldehyde reacted mainly with phenyl rings at the para-position. This reaction can be explained by the steric hindrance at the ortho-position of **1**. Several peaks observed at 118–136 ppm were attributable to methylene-substituted and nonsubstituted aromatic carbons (Fig. 4). Phenoxy carbon (a carbon attached to an oxygen atom) signals were observed at 155.0–
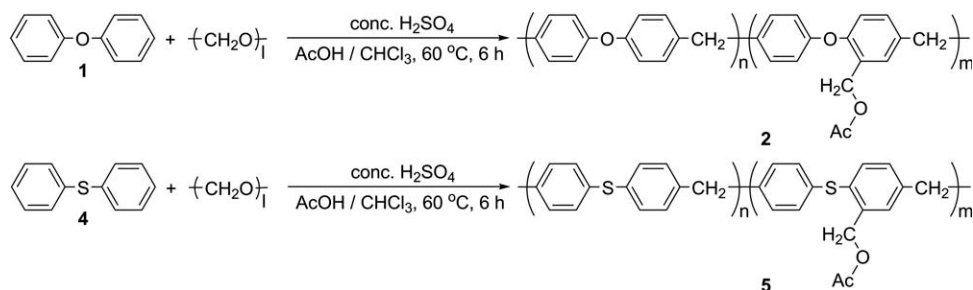
Scheme 1 Addition-condensation of diphenyl oxide (**1**) or diphenyl sulfide (**4**) with formaldehyde (typical units).
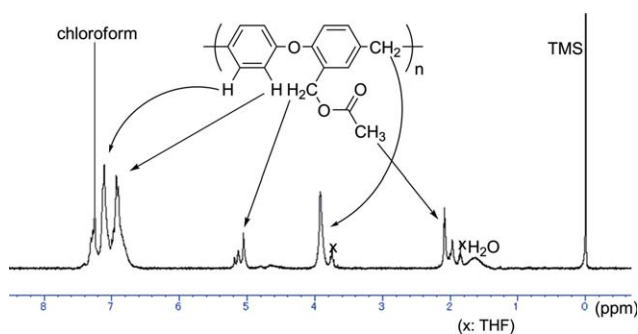
Figure 1 ^{1}H-NMR spectrum of **3** in CDCl$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

156.1 ppm (Figure 4, inset). In our previous study, on phenol novolacs, phenoxy carbon signals at the terminal phenolic unit (one reacted site), linear phenolic unit (two reacted sites), and branched phenolic unit (three reacted sites) were observed at 157–159 ppm, 154–157 ppm, and 151–154 ppm, respectively. From the phenoxy carbon region of **2**, it can be observed that only when the upfield shift (γ-substituent effect) was considered, the peaks attributable to linear phenolic units appeared at 155.0–156.1 ppm. This suggests that **2** might consist of linear phenolic units only. From this result, it can be concluded that **1** acts as a bifunctional monomer, despite the presence of six possible reaction sites (4 ortho- and 2 para-positions). However, the ^{13}C-NMR spectrum showed that the methyl carbons of acetyl groups and methylene carbons of ester groups appeared at 21.1 ppm and 61.4 ppm, respectively. This result suggests that polymer **2** also consists of the ester formations derived from methylol moieties and acetic acid. The obtained polymer 2 (Table I, run 2) had large polydispersity index. In an acid-catalyzed phenol-formaldehyde condensation process, although a bifunctional phenol monomer such as o-cresol, a high-molecular weight polymer with large polydispersity index is obtained as a linear polymer.[47]
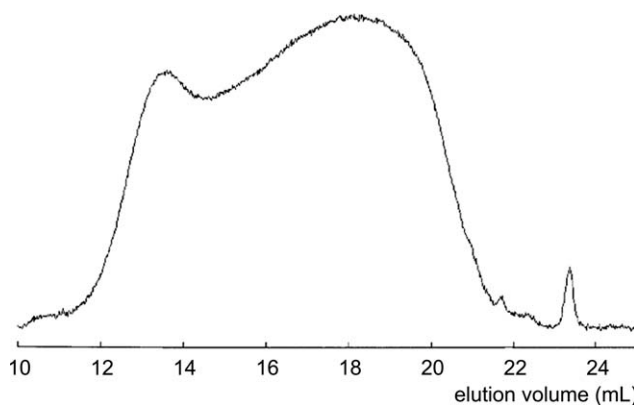

Figure 2 GPC trace of **2** detected by UV detector (254 nm) (eluent: THF, polystyrene standards).

The polymerization reaction did not proceed effectively when it was carried out with acetic acid (Table I, run 3). Although the bulk polymerization (Table I, run 4) proceeded to give the product in high-yield, its M_w value was lower than that of **2** and **3**. These results indicated that both acetic acid and chloroform played critical roles in the preparation of the high-molecular weight polymer. Acetic acid can activate a carbocation intermediate from formaldehyde.[2,40–42] Chloroform can add solubility to the polymer in the polymerization process.

Diphenyl sulfide-formaldehyde novolac (5)

Polymerization did not occur when the addition-condensation reaction was catalyzed by 12 mol/L HCl (aqueous); however, the concentrated-H$_2$SO$_4$-catalyzed addition-condensation reaction of **4** with formaldehyde proceeded efficiently (Scheme 1). The results of the polymerization are summarized in Table II. The polymerization behavior of **4** was quite similar to that of **1**. The solubility of the resulting polymer (**5**) (Table II, run 1) was also similar to that of **2**. The weight-average molecular weights (M_w) and the polydispersity index of **5** were found to be
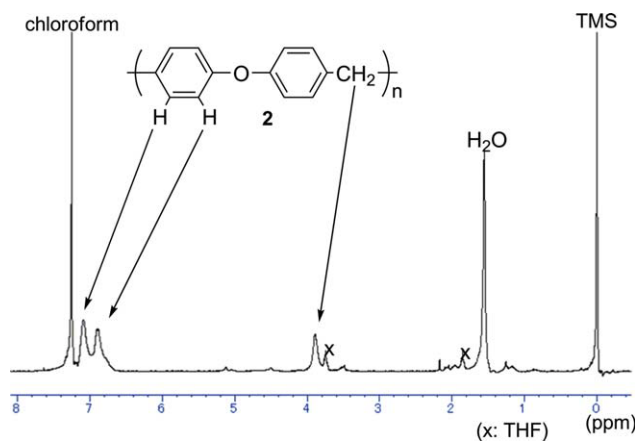

Scheme 2 Polymerization and esterification mechanism (typical units).
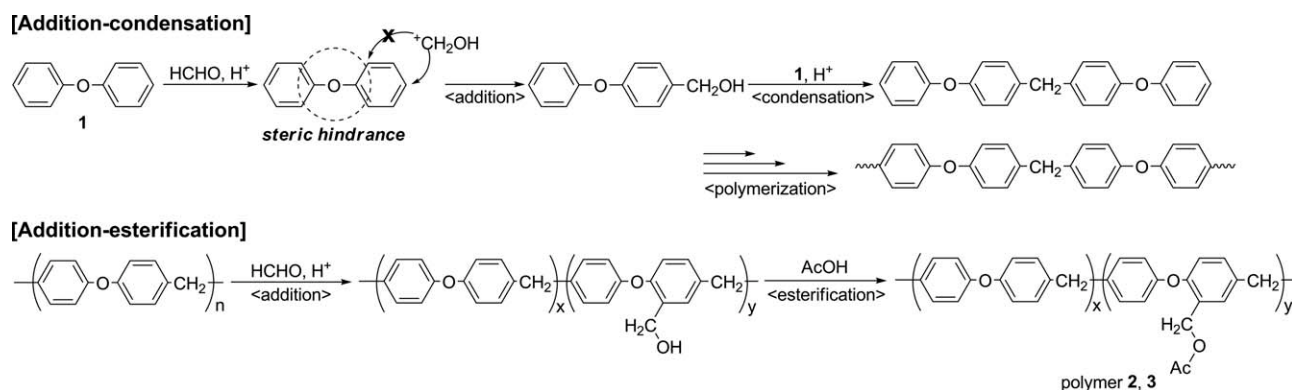
Figure 3 ^{1}H-NMR spectrum of **2** (Table I, run 2) in CDCl$_3$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Addition-Condensation of Diphenyl Sulfide (4) with Formaldehyde

Run	Feed ratio (mmol) (4 : aldehyde)	Solvent (mL)	Yield[a] (%)	M_w[b]	M_w/M_n[b]
1	1 : 2	CHCl$_3$ (10)/ AcOH (10)	82	12,000	4.6
2	1 : 2	CHCl$_3$ (15)/ AcOH (5)	80	8,100	2.7
3	1 : 2	AcOH (10)	66	1,100	1.4
4	1 : 2	CHCl$_3$ (10)	40	2,800	1.9

[a] Isolated yield after precipitation in methanol.
[b] Determined by GPC (eluent: THF, polystyrene standards).

12,000 and 4.6, respectively. The structure of polymer **5** was confirmed from FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra. From the ^{1}H-NMR spectrum of **5** (supporting information: Figure S2), the signals of the methylene protons of the p,p'-methylene bridges (p,p'-Ar—CH$_2$—Ar—) it can be observed that signals of the methylene protons of the p,p'-methylene bridges (p,p'-Ar—CH$_2$—Ar—) appeared at 3.70–4.15 ppm. However, the peaks of the methylene protons that formed ester moieties with acetic acid were also detected at 4.95–5.24 ppm. The structure of **5** can be studied from the ^{13}C-NMR spectrum (supporting information: Figure S3); all the peaks were in good agreement with those of the expected structure. The peak at 40 ppm was attributed to the p,p'-methylene bridge carbons, that is, the p,p'-linkage formed in **5**. This result indicates that **4** predominantly reacted at the para-positions because a sulfur atom is bigger than an oxygen atom. Moreover, the peaks from the methyl carbons of ester moieties were detected at 63–66 ppm. These results suggest that polymer **5**
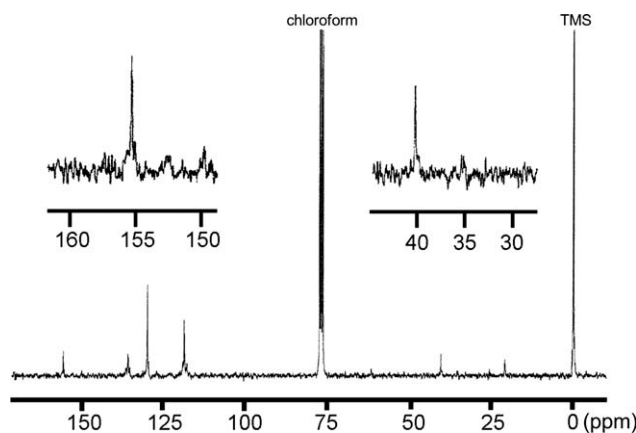
had an approximately linear main chain structure with partial esterified moieties.

Thermal properties

Differential scanning calorimetric (DSC) and TG analyzes were carried out to determine the thermal transition and degradation behavior of the polymers. The DSC analyzes (supporting information: Figure S4) indicate that neither well-defined glass-transition temperatures (T_g) nor melting points (T_m) were observed. All the DSC thermograms did not show any clear base-line shifts and exothermic peaks attributable to glass-transition and melting, respectively.

We performed the TG analyzes of **2** (Table I, run 2) in a nitrogen gas atmosphere and air. The weight loss of **2** at 600°C in the nitrogen atmosphere was roughly 55%. However, polymer **2** completely decomposed at 600°C in air [Fig. 5(a)]. The weight loss of polymer **5** (Table II, run 1) at 600°C was about 60% in the nitrogen atmosphere. However, the weight loss above 600°C in air was only 50% [Fig. 5 (b)].

Solution properties

The solution properties of the polymers were examined using a combination of SEC with an online viscometer (VISC) and a right-angle laser light-scattering (RALLS) detector. The high-molecular weight fractions of **2** (Table I, run 2) (**2′**) and **5** (Table II, run 1) (**5′**) were separated by HPLC. The weight-average molecular weights (eluent: THF; RALLS) of **2′** and **5′** were estimated to be 550,000 and 130,000, respectively. The parameters obtained by the Mark–Houwink–Sakurada equation ([η] = KM^a) are often used to characterize the morphology of polymers in a dilute solution. The a values of **2′** and **5′** were 0.38 and 0.41, respectively. These results suggest that the conformation of **2′** was an intermediate between a
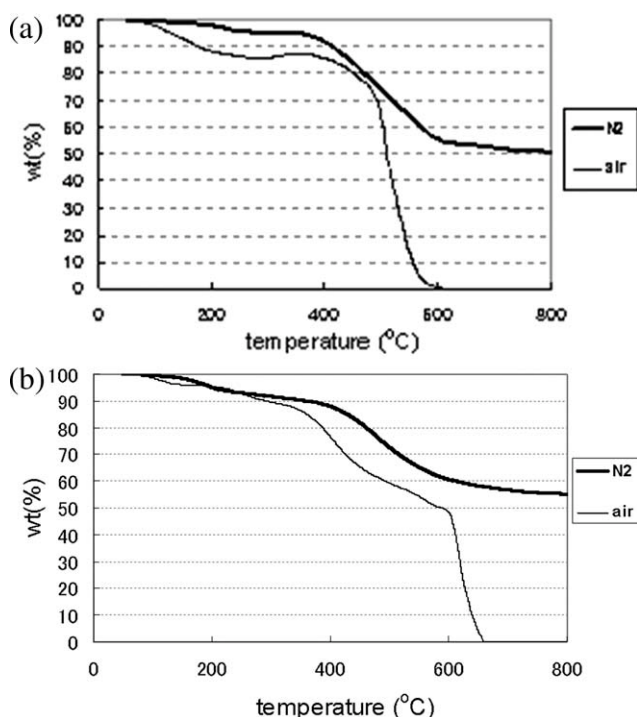

Figure 4 ^{13}C-NMR spectrum of **2** (Table I, run 2) in CDCl$_3$.

Figure 5 TG analyzes of (a) polymer **2** (Table I, run 2); and (b) polymer **5** under a nitrogen atmosphere or air.

spherical and a random coil. The abovementioned values were considered reasonable because the morphology of phenol novolacs in a dilute THF solution is usually spherical and compact. These measurements show that the properties of **2′** and **5′** were similar to those of phenolic resins rather than PPO or PPS. Furthermore, films were prepared from these polymers using the solvent-cast method; however, the transparency of the obtained films was low.

CONCLUSION

We successfully prepared diphenyl oxide- (**1**) and diphenyl sulfide (**4**)-based novolacs with high-molecular weights using chloroform as the halogenated cosolvent and acetic acid. When the addition-condensation reaction of **1** with formaldehyde was carried out under the favorable reaction conditions, formation of the esterified moieties derived from methylol groups and acetic acid was suppressed, and the main chains of the obtained polymer (**2**) formed approximately linear structures with a branching fraction of less than 5%. From the viewpoint of material science, a linear polymer is very useful for making films and polymer blends. The thermal and solution properties of **2** and **5** were similar to those of conventional phenolic resins rather than engineering plastics, that is, PPO or PPS. The high-molecular weight diphenyl oxide- and diphenyl sulfide-novolacs are a new class of promising aromatic polymers having the properties of both novolac and engineering plastics.

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