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Synthesis and Characterization of Poly(benzoyl-1,4-phenylene)s. 2. Catalyst Coligand Effects on Polymer Properties

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ABSTRACT: High molecular weight, soluble poly(benzoyl-1,4-phenylene)s (η_{inh} = 0.99–1.6 dL/g) have been prepared by nickel-catalyzed polymerization of 2,5-dichlorobenzophenone in the presence of excess zinc and triphenylphosphine (PBP-A). Polymerization with 2,2′-bipyridine as coligand produces a soluble polymer (PBP-B) which exhibits a higher glass transition temperature of 217 °C (versus 149 °C for comparable PBP-A), a UV–vis λ_{max} at 352 nm (versus 328 nm for PBP-A), and only two ^{13}C NMR peaks in the carbonyl region at 196–198 ppm (versus an additional peak at 196.3 ppm for PBP-A). It has been proposed that these two polymers differ in the regiochemical placement of the lateral benzoyl groups along the chain, with PBP-B exhibiting more regular head-to-tail structures. These soluble polymers show no evidence for crystallinity by DSC or by WAXD and exhibit high thermal stability (only 3% weight loss in air or N_2 on heating to 500 °C). Film samples show tensile moduli of 6.4 GPa and tensile breaking strengths in the range of 0.9 GPa.

Introduction

Poly(*p*-phenylene)s are of interest because of their thermal and thermooxidative stability and because they can be converted from an insulator into an electrically conducting polymer by doping with electron donors or electron acceptors.[1–6] Unfortunately, because poly(*p*-phenylene) is highly crystalline, insoluble, and infusible, the potentially unique and useful properties of poly(*p*-phenylene)s as stable, rigid-rod polymers have not been realized. A number of recent methods have been developed to synthesize substituted poly(*p*-phenylene)s bearing lateral substituents to improve their solubility. These coupling reactions of aromatic compounds include the reaction between dihaloaromatic compounds and Mg metal in the presence of various low-valent Ni catalysts (Yamamato condensation),[4,5,7,8] the palladium-mediated coupling of aromatic bromides with aromatic boronic acids (Suzuki coupling),[5,9–11] nickel-catalyzed coupling of bis[[(trifluoromethyl)sulfonyl]oxy] derivatives of substituted hydroquinones,[12–14] the polymerization of *in-situ* generated *p*-lithiobromobenzenes,[15,16] and the nickel-catalyzed coupling of aromatic dihalides in the presence of zinc.[4,17–20] It is noteworthy that Phillips, Sheares, Samulski, and DeSimone[20] have reported the application of the nickel-catalyzed dihalide coupling for the preparation of soluble, amorphous poly(2,5-benzophenone), a polymer first disclosed by chemists at Maxdem, Inc.[21] Herein we report our results on the development of efficient nickel-catalyzed syntheses of poly(benzoyl-1,4-phenylene) (PBP) and on the dramatic effects of coordinating ligands on the properties of these polymers.[22]

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Experimental Section

Materials. *N,N*-Dimethylformamide (DMF; Fisher Scientific) was dried over 4-Å molecular sieves for 2 days with occassional stirring, followed by vacuum distillation and storage over 4-Å molecular sieves under dry N_2. Triphenylphosphine (Aldrich) was recrystallized from Et_2O [mp 82–83 °C (lit.[23] mp 80–81 °C)]. Zn powder (Aldrich) was washed with acetic anhydride, filtered, washed with dry Et_2O, and dried under high vacuum at 150 °C. Sodium iodide (Fisher Scientific) was recrystallized from acetone, dried under vacuum at 60 °C, recrystallized from dilute aqueous NaOH, and dried under vacuum at 100–110 °C.[23] 2,2′-Bipyridine (BPY; Aldrich) and nickel(II) chloride (Aldrich) were used as received.

2,5-Dichlorobenzoyl chloride. 2,5-Dichlorobenzoic acid (Aldrich; 97%, 142 g, 0.74 mol) and 69 mL (Fisher; 110 g, 0.95 mol) of thionyl chloride were added into a 500-mL flask and heated at 63 °C for 24 h. Excessive thionyl chloride was removed under reduced pressure by gradually increasing the temperature; light yellow 2,5-dichlorobenzoyl chloride (90–95%) was obtained by distillation at 76–79 °C (5–6 mmHg).

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2,5-Dichlorobenzophenone. 2,5-Dichlorobenzoyl chloride (34 g, 0.16 mol) was added dropwise via an addition funnel to a suspension of $AlCl_3$ (24 g, 0.18 mol) in 80 mL of dry (CaH_2) benzene in a 250-mL flask fitted with a reflux condenser followed by heating at 63 °C for 12 h. The reaction mixture was quenched by pouring onto acidified, ground ice and then extracted with toluene. The organic layer was washed with water, aqueous $NaHCO_3$, and water and then dried with anhydrous Na_2SO_4. After removal of the toluene, the resulting yellow–red residue was first recrystallized from ethanol/water (90/10, v/v) and then from hexane/toluene (50–80 vol % hexane): mp 88–90 °C (lit.[20] mp 88.9 °C); 94% yield; FTIR 1661 cm^{-1} (s, C=O); ^1H NMR δ 7.81 (m), 7.77 (m), 7.65 (t), 7.62 (t), 7.58 (t), 7.50 (m), 7.47 (m), 7.43 (m), 7.38 (m), 7.35 (m); ^{13}C NMR δ 194.4 (C=O), 140.46 (C_1), 136.38 ($C_{1'}$), 134.6 (C_4), 133.5 (C_2), 131.8 and 131.6 (C_3, C_6), 130.6 ($C_{2'}$), 130.1 (C_5), 129.4 and 129.3 ($C_{4'}$) and ($C_{3'}$). Only one peak was observed by HPLC analysis. Calcd for $C_{13}H_8Cl_2O$: C, 62.18; H, 3.21; Cl, 28.26. Found: C, 62.3; H, 3.3; Cl, 28.5.

Polymerization. Preparation of PBP-B by Polymerization in the Presence of 2,2′-Bipyridine (BPY). 2,5-Dichlorobenzophenone (2.5 g, 10 mmol), Zn powder (2 g, 30.6 mol), $NiCl_2$ (0.13 g, 1 mmol), $(C_6H_5)_3P$ (1.04 g, 4 mmol), and BPY (0.16 g, 1.01 mmol) were added inside an argon atmosphere drybox into a 100-mL long-neck flask with a side tubing capped by a rubber septum. After removal from the drybox, the flask was connected to a N_2 bubbler through the neck and set in an oil bath. While heating the oil bath, 30 mL of DMF was added by syringe through the septum. The solution was stirred magnetically. When temperature reached to 40 °C, a brown color formed; at 50–60 °C, the color became deep red–brown. At 70 °C the solution became dark brown and then gelled at about 40 min after addition of DMF. After terminating the reaction by dispersing the gel, or solution, into acetone, the resulting solid was filtered and washed with aqueous HCl (5 vol %) (three times), water (three times), and acetone. The polymer was isolated in quantitative yield as a yellowish powder.

Preparation of PBP-A by Polymerization in the Absence of 2,2′-Bipyridine (BPY). Polymerizations without BPY were carried out similarly to PBP-B, except the amount of $(C_6H_5)_3P$ was increased to 5–6 mol equiv relative to $NiCl_2$. A brown color generally formed at 70 °C 2–3 h after addition of DMF. The purified polymer had a light-yellowish color.

Polymerizations with NaI in the absence of BPY were carried out as described for PBP-A, except for the addition of 1 mol equiv of NaI relative to $NiCl_2$. The brown color of the active catalyst was generally formed when temperature was gradually increasing to 40 °C. The final purified polymer had a light-yellowish color.

Thin polymer films were prepared by first dissolving about 1 g of polymer powder in 8–15 mL of chloroform by heating. The clear solution was poured onto clean mirror glass, followed by spreading with a piece of glass tubing; each end of the tubing was wrapped with a ring of copper wire to control the thickness of the film. The film was cut into ribbon shapes (5 × 60 mm).

Characterization. Size-exclusion chromatographic (SEC) analyses of polymers were performed at 30 °C with flow rates of 0.4 mL min^{-1} in tetrahydrofuran (THF) or 0.4 mL min^{-1} in chloroform using a Waters HPLC component system (RI or Hewlett Packard 1040 diode array detector) equipped with ultra-μ-Styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) (THF) or two mixed-bed columns ($CHCl_3$) after calibration with standard polystyrene samples (Polymer Laboratories). FTIR spectra were performed on a Bomem MB100 instrument. Both ^1H NMR (200 MHz, Varian Gemini-200) and ^{13}C NMR (100.4 MHz, Varian XL-400) spectra were measured in $CDCl_3$. UV–vis absorption spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer with 1.0-cm quartz cells.

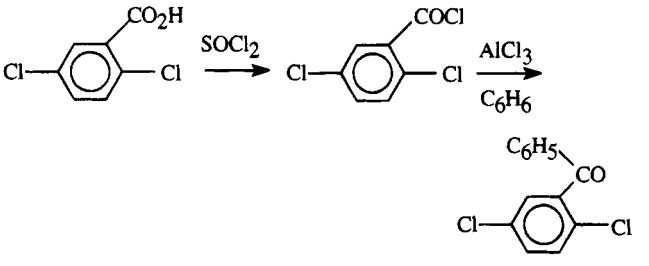
Wide-angle X-ray diffraction (WAXD) experiments were carried out using a 12-kW Rigaku rotating-anode generator. Linear coefficients of thermal expansion of polymer film were determined using a Seiko stress–strain thermal mechanical analyzer (TMA/SS 100) at a heating rate of 10 °C/min under flushing N_2 of 50 mL/min. Dynamic mechanical spectroscopy (DM) and mechanical properties (stress–strain) of polymer films were measured on a Rheometrics solid-state analyzer (RSA II); for DM measurements, the instrument was in the temperature/frequency sweeping mode with an applied frequency of 0.05–1 Hz. Storage (E') and loss (E'') moduli were measured, and tan δ was derived from the two moduli. Polymer film thicknesses were determined from the average of eight measurements by thickness gauge, which could read to 0.001 mm.

Differential scanning calorimetry (DSC) measurements of 10-mg samples of polymer were performed using a DuPont 910 DSC controlled by a 9900 thermal analyzer at a heating rate of 10 °C/min under nitrogen flushing at a rate of 50 mL/min. Each sample was run two times; after the first run (20–380 °C), the sample was quenched with liquid N_2. The glass transition temperature (T_g) was assigned from the second run as the intersection of the base line with the tangent at the inflection point of the curve due to the change in heat capacity. This procedure gave reproducible results. Thermogravimetric analysis (TGA) measurements were performed using a DuPont 9900 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen or air flushing at a rate of 50 cm^3/min with 10-mg samples.

Solution viscosities were measured in $CHCl_3$ at 25 °C using an Ubbelohde-type viscometer. Elemental analyses were performed by Midwest MicroLab.

Results and Discussion

Monomer Synthesis. 2,5-Dichlorobenzophenone was synthesized by aluminum chloride-catalyzed, Friedel-Crafts acylation of benzene with 2,5-dichlorobenzoyl chloride as shown in eq 1. The acid chloride could be



(1)

directly used from the first reaction for the second step, by simply degassing under vacuum to remove excess thionyl chloride. In this way, the yield of the final product was about 84% based on the acid. If purified (distillation) acid chloride was used, the overall yields were 90–95%.

Phillips, Sheares, Samulski, and DeSimone[20] have independently prepared this monomer utilizing the Friedel–Crafts benzoylation of 1,4-dichlorobenzene. Their reported mp and ^{13}C NMR spectral data are in good agreement with the data reported herein except for their reversed assignments of C_4 versus $C_{4'}$, which are listed at 128.9 and 134.1 ppm, respectively.

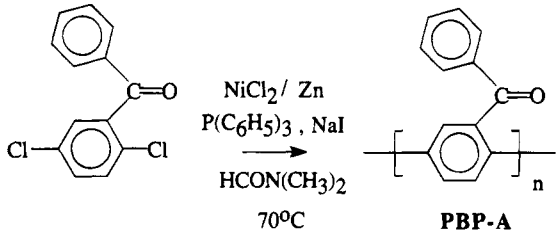
Polymer Synthesis. PBP-A. Colon and Kelsey[24] have reported detailed general procedures for the efficient synthesis of biaryls from aryl chlorides utilizing a coupling reagent composed of a mixture of a catalytic amount of an anhydrous nickel salt and triphenylphosphine in the presence of an excess of a reducing metal (Zn, Mg, or Mn). Variables investigated included the effects of the reducing metal, added coligands, halide salts, and substituents on the aromatic ring. From the results of Kaeriyama and co-workers[17] and the requirements for high molecular weight, step-growth (conden-

Table 1. Effects of Polymerization Conditions on the Molecular Weight and Thermal Properties of Poly(benzoyl-1,4-phenylene)

polymzn syst	reaction time (h)	temp (°C)	η_{inh} (dL/g)[a]	M_w(SEC) ($\times 10^4$)[b]	T_g (°C)[c]
procedure A[d]	11	70	1.1		149
	60	70	1.39	8.9	164
	10[e]	70	1.6		
procedure B[f]	2	70	0.94		
	20	130[g]	0.99	5.0	217[h]
	20	70	1.1	5.8	205[i]
	25	120	1.14	5.95	209[i]
	20	70	1.09	4.4	170[j]

[a] 0.1 g in 1 dL of $CHCl_3$. [b] M_w relative to polystyrene standards. [c] Scanning rate of 10 °C/min. [d] Triphenylphosphine as ligand. [e] Triphenylphosphine and 1 equiv of NaI relative to Ni as ligands. [f] Triphenylphosphine and 2,2′-bipyridine as ligands. [g] Polymerization at 70 °C for 120 min formed gel; heating continued for 20 h at 130 °C. [h] DSC analysis of as-formed polymer after washing with acetone and water (no reprecipitation). [i] DSC analysis of polymer after dissolution in THF and precipitation into methanol. [j] DSC analysis of polymer after precipitation into acetone, filtration, and washing three times each with aqueous HCl (5 vol %) and with water followed by acetone washing (unpublished work of Jianxin Kuang and Yungai He).

sation) polymerizations,[25] it was apparent that the use of high-purity, dry reagents were required for the preparation of high molecular weight, substituted poly(*p*-phenylene)s. An efficient synthesis of relatively high molecular weight, soluble poly(benzoyl-1,4-phenylene) (PBP-A) has been achieved using reaction conditions based on the work of Colon and Kelsey[24] as shown in eq 2 and in Table 1, procedure A. Thus, sodium iodide



(2)

accelerated the rate of polymerization and also produced the highest molecular weight, as deduced by the η_{inh}, in a relatively short period of time. In the absence of sodium iodide catalyst, color formation was observed over a period of 2–3 h, while with sodium iodide the color developed in a matter of minutes. The molecular weight increased only slowly, and long reaction times were required in the absence of sodium iodide also. Using procedure A, the polymer PBP-A was obtained in quantitative yield after 60 h and was soluble in $CHCl_3$ and in mixed solvents of 5–10% phenol in CH_2Cl_2 or in *sym*-tetrachloroethane. The apparent molecular weights (M_w) by SEC (in $CHCl_3$, relative to polystyrene calibration standards) were in the range of 90×10^3 with a polydispersity (M_w/M_n) of ≈2.3.

PBP-B. Colon and Kelsey[24] observed that the nickel-catalyzed coupling reaction of aryl chlorides in the presence of zinc is accelerated dramatically by addition of 1 equiv of 2,2′-bipyridine (BPY). It was also reported that bipyridine effectively suppresses the principal side reaction of phenyl transfer from triphenylphosphine which would limit the polymer molecular weight. The effect of 2,2′-bipyridine on the polymerization of 1,5-dichlorobenzophenone was investigated using the same conditions as described previously (eq 2), i.e., $NiCl_2$, Zn, and 4–7 equiv of triphenylphosphine, with the addition of 1 mol equiv of 2,2′-bipyridine relative to nickel (eq 3). As expected, the rate of polymerization for procedure B was faster in the presence of 2,2′-bipyridine compared to procedure A in the absence of sodium iodide as shown in Table 1. The red–brown color of the catalyst formed within 5 min after addition of solvent and at a temperature of ≈40 °C. Another difference observed for polymerizations in the presence of bipyridine was the fact that gel formation was observed after approximately 40 min at 70 °C (η_{inh} = 0.94 dL/g). The gel disappeared upon increasing the temperature to 130 °C; however, the molecular weight did not increase significantly upon raising the temperature and continued heating as shown in Table 1 (η_{inh} = 0.99 dL/g).

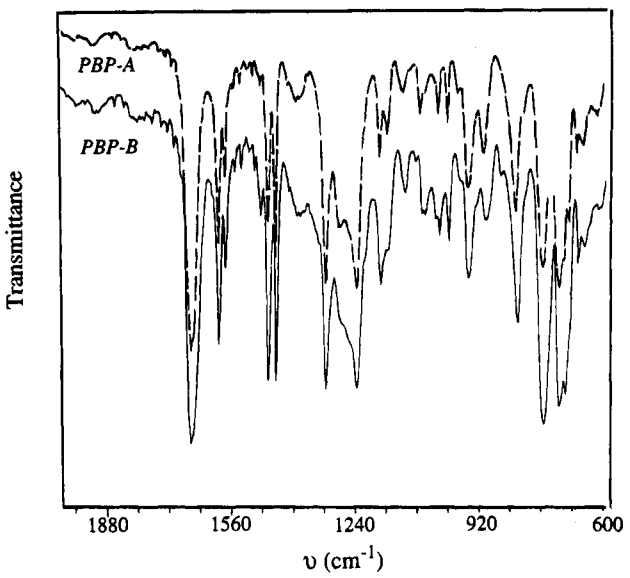
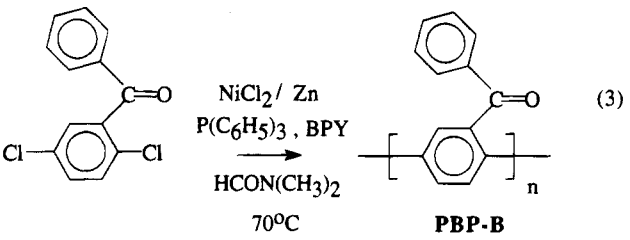


Figure 1. FTIR spectra of PBP-A and PBP-B films.



(3)

DeSimone and co-workers[20] have reported results similar to those of procedure B using the procedures of Colon and Kelsey[24] in the presence of sodium bromide and 2,2′-bipyridine in NMP; i.e., M_n (SEC, polystyrene calibrations) = 26.7×10^3 and η_{inh} = 0.87 dL/g (NMP, 30 °C).

Quite unexpectedly, it was found that PBP-B was soluble not only in the same solvents as PBP-A but also in tetrahydrofuran (THF). PBP-A was not soluble in THF. In addition, purified PBP-B had a deeper yellow color than PBP-A. These observations suggested that the two polymers prepared using procedures A and B might have different microstructures. A variety of characterization methods were utilized to determine the microstructural basis for these dramatic differences.

Characterization. As shown in Figure 1, PBP-A and PBP-B have almost identical IR spectra, except for small differences around 710 and 1173 cm^{-1}. This is consistent with the expectation that the differences between these two polymers are due to subtle microstructural effects.

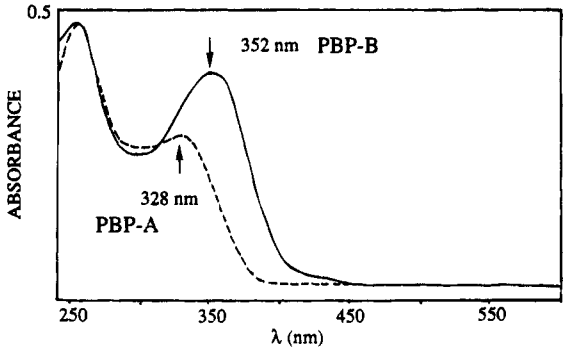
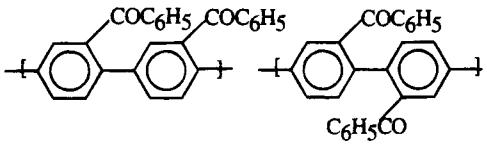
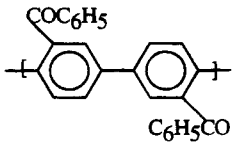


Figure 2. UV–vis absorption spectra of PBP-A and PBP-B in $CHCl_3$.

The UV–vis spectra of PBP-A and PBP-B are significantly different as shown in Figure 2. PBP-A exhibits an absorption maximum at 328 nm, whereas the absorption maximum for PBP-B is at 352 nm. DeSimone and co-workers[20] reported that the PBP sample obtained in the presence of coligands 2,2′-bipyridine and sodium bromide exhibited a λ_{max} at 354 nm, in good agreement with the absorption maximum observed for PBP-B which was also prepared in the presence of bipyridine. It has been well-established that the wavelength of maximum absorbance in the *p*-phenylene series increases (bathochromic shifts) as the number of conjugated phenyl rings increases.[26] The absorption maxima for terphenyl and sexiphenyl are 320 and 345 nm, respectively.[26] Although a theoretically calculated limiting value of λ_{max} = 339 nm has been predicted,[27] experimental values as high as 395 nm have been reported.[1,6,26] Thus, the differences in UV absorption maxima for PBP-A versus PBP-B suggest that the conjugation length of consecutive substituted phenylene rings is different in these two polymers. Since PBP-B exhibits a longer wavelength absorption maximum than PBP-A, it is suggested that PBP-B has structural sequences which are more conjugated. As described in our preliminary report,[22] it is proposed that these differences are due to different regiochemical regularities in the placement of the lateral benzoyl groups along the polymer backbone. For example, if PBP-B has a more regular structure, i.e., more head-to-tail structures (**1**) and fewer head-to-head structures (**2**), then



1. head-to-tail 2. Head-to-head



3. Tail-to-tail

the conjugation length along the chain would be expected to be longer since the *o*-biphenyl-type substitution in the head-to-head units would be expected to lead to out-of-plane rotation and decreased conjugation. For example, biphenyl itself is not planar; the rings are twisted by about 45° in the gas phase[28] and approximately 23° in the melt.[29,30] Furthermore, it is known that ortho-substituted biphenyls exhibit steric inhibition of resonance which is manifested in their UV–vis spectra[32] and in increased barriers to rotation which permit the isolation of stereoisomers (atropisomers).[33]

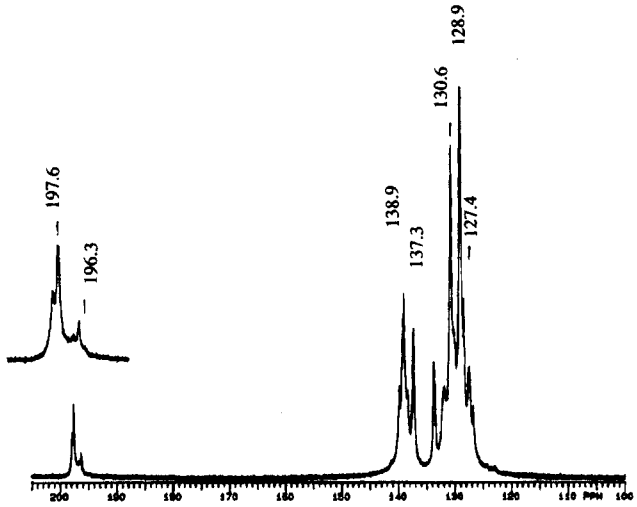


Figure 3. ^{13}C NMR spectra for PBP-A in $CDCl_3$.

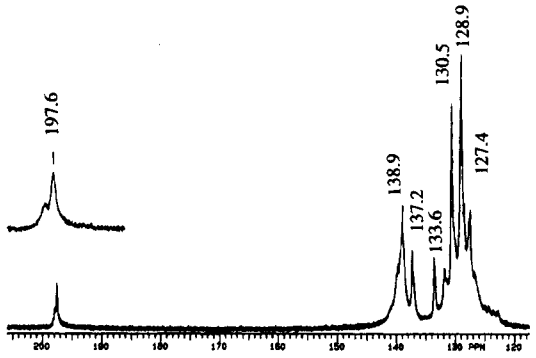


Figure 4. ^{13}C NMR spectra for PBP-B in $CDCl_3$.

Further support for the proposal that the differences between PBP-A and PBP-B are due to microstructural differences resulting from different regiochemical placements of benzoyl groups along the polymer chain has been obtained from ^{13}C NMR spectra of these two polymers as shown in Figures 3 and 4. The observed chemical shifts of poly(2-benzoyl-1,4-phenylene) and the calculated values for a model compound (2,5-diphenylbenzophenone, **4**) are listed in Table 2.[33] Polymer PBP-B (Figure 4) shows only two peaks in the carbonyl region of the spectrum (196–198 ppm) with the main peak at 197.6 ppm, while polymer PBP-A (Figure 3) shows an additional distinct peak at 196.3 ppm. Therefore, the polymer prepared in the presence of 2,2′-bipyridyl (PBP-B) seems to generate carbonyl groups which are in a more regular environment, i.e., in fewer different regiochemical environments, than the polymer prepared in the absence of 2,2′-bipyridyl (PBP-A). The proposed structural differences between these polymers are sche-

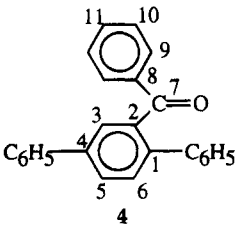


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Table 2. Calculated and Observed ^{13}C NMR Chemical Shifts for Poly(4-benzoyl-1,4-phenylene)

carbon atom[a]	chemical shift (ppm) calcd	obsd
C_1	142.1	139
C_2	137.1	137.3
C_3	129.4	128.9
C_4	140.2	139
C_5	131.5	131.9
C_6	127.5	127.3
C_7	196.6	197.6
C_8	137.8	137.3
C_9	130.1	130.6
C_{10}	128.2	128.9
C_{11}	132.2	133.6

[a] See structure **4** for carbon assignments.

matically represented in Figure 5. It is proposed that more of the triad repeat units are in the regular, H–T, H–T type of arrangement in PBP-B, which was prepared in the presence of 2,2′-bipyridyl as coligand, while a more random distribution of the four possible triad units is formed in PBP-A, which was prepared only in the presence of triphenylphosphine as ligand. The ^{13}C NMR data are consistent with the conclusion based on the differences in UV–vis spectra that PBP-B, prepared in the presence of 2,2′-bipyridyl, possesses a more regular regiochemical arrangement of the lateral benzoyl substituents along the polymer backbone which results in longer sequences of conjugated phenylene rings as manifested in a longer wavelength UV–vis absorption maximum and fewer different stereochemical environments for the carbonyl groups as evidenced by observation of fewer resonances in the carbonyl region of the ^{13}C NMR spectra.

Polymerization Mechanisms. Several mechanisms have been proposed for the nickel-catalyzed coupling of aryl halides to form biphenyls;[4,12,24,34–36] however, it is generally agreed that there are two steps which are important components. The first step is oxidation addition of an aryl halide to nickel(0) to form an arylnickel(II) intermediate (eq 4). The last step involves reductive elimination from the diaryl product (eq 5). Unfortunately, the intermediate steps, the rate-

$$\text{X-Ar-X} + \text{Ni(0)L}_m \xrightarrow[\text{addition}]{\text{oxidative}} \text{L}_m\text{Ni(II)X(Ar-X)} \quad (4)$$

$$\text{Ni(Ar-X)}_2\text{L}_m \xrightarrow[\text{elimination}]{\text{reductive}} \text{X-Ar-Ar-X} + \text{NiL}_m \quad (5)$$

determining step, and the valences of nickel intermediates remain controversial and probably vary with the reaction conditions. Two types of reactions are generally considered for formation of the diarylnickel intermediate; (a) oxidative addition of an aryl halide with an arylnickel intermediate leads to the formation of the diaryl nickel (eq 6) or (b) in the absence of aryl halide, the diarylnickel complex can be formed by metathesis of two arylnickel complexes (eq 7).

$$\text{L}_m\text{Ni(II)X(Ar-X)} + \text{X-Ar-X} \longrightarrow \text{Ni(Ar-X)}_2\text{L}_m \quad (6)$$

$$2\ \text{L}_m\text{NiX(Ar)} \xrightarrow{\text{disproportionation}} \text{Ni(Ar)}_2\text{L}_m + \text{NiX}_2\text{L}_m \quad (7)$$

With respect to the regiochemistry of the biaryl coupling reaction and its dependence on ligands, Yamamoto[4] has noted that tertiary phosphine ligands like

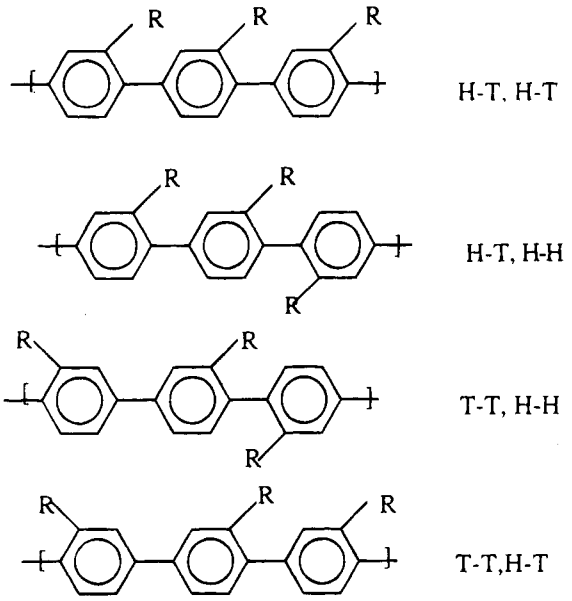
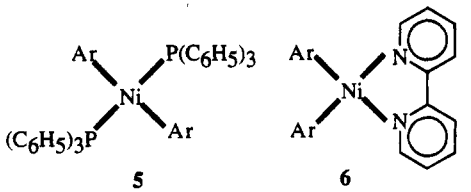


Figure 5. Structures for the four poly(4-benzoyl-1,4-phenylene) triads.

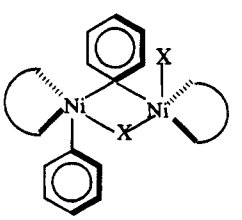
$P(C_6H_5)_3$ usually form the *trans*-Ni(II) complex (**5**), whereas the bidentate 2,2′-bipyridine ligand affords the *cis*-Ni(II) complex (**6**); furthermore, the reductive elimi-



5 **6**

nation usually proceeds more easily in the *cis*-type complex than the *trans*-type complex. Thus, it appears that the formation of the *cis*-type complex and the regiochemical requirements for formation of this complex ultimately control the variation in placement of lateral benzoyl substituents during polymerizations in the presence of 2,2′-bipyridine compared to polymerizations in the presence of only triphenylphosphine as coordinating ligand. One could envision that direct formation of the *cis*-complex, **6**, would have more selective steric requirements than formation of the *trans*-complex, **5**, and thus formation of the *cis*-complex would tend to promote more head-to-tail enchainment (**1**) rather than *head*-to-*head* structures (**2**).

During the PBP-B synthesis in the presence of BPY, physical gel formation was observed which disappeared on heating or on workup. This may be a consequence of the formation of dinuclear bridging structures of the type **7** proposed by Yamamoto and coworkers.[34]



7

Properties of PBP. As shown in Table 1, DSC analysis showed that the polymers obtained in the presence of both 2,2′-bipyridyl and triphenylphosphine exhibited higher glass transition temperatures than the

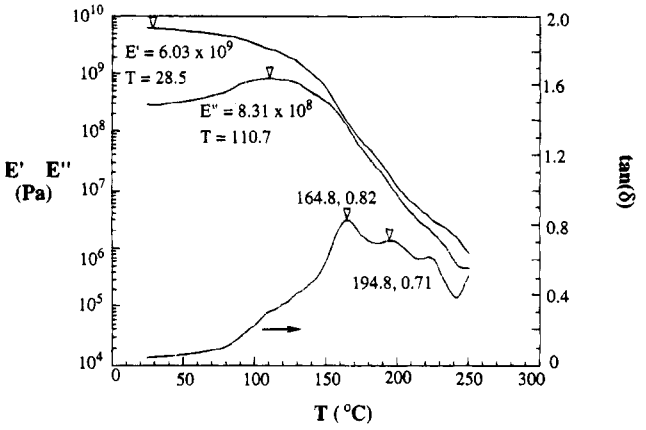


Figure 6. Dynamic mechanical analysis of PBP-A at an applied frequency of 1.0 s^{-1}.

polymers obtained in the presence of only triphenylphosphine. Polymer PBP-B exhibited a glass transition temperature which is 68 °C higher than a sample of polymer PBP-A with approximately the same inherent viscosity. For comparison, DeSimone and co-workers[20] reported that a PBP sample prepared in the presence of cocatalyst 2,2′-bipyridyl, analogous to polymer PBP-B reported herein, exhibited a glass transition temperature of 206 °C for a sample with M_n(SEC) = 26.7 × 10^3 and inherent viscosity (NMP, 30 °C) of 0.87 dL/g. The surprising result is that the glass transition temperature can be increased and varied over such a wide range by simply adding the coligand, 2,2′-bipyridyl.[37] It is also important to note that neither polymer PBP-A nor PBP-B showed any observable melting endotherm or crystallization exotherm in their DSC traces. Furthermore, WAXD investigation of these polymers provided no evidence for any long-range order characteristic of crystalline polymers. Thus, it is concluded that, even though PBP-A and PBP-B appear to differ in the regiochemical regularity of placement of the lateral benzoyl groups, neither polymer is crystalline.

The dynamic mechanical behavior of PBP-A (η_{inh} = 1.35 dL/g) was investigated using film samples cast from $CHCl_3$ as shown in Figure 6. It is noteworthy that dynamic mechanical analysis is indicated that T_g = 165 °C, which is in surprisingly good agreement with the T_g value determined by DSC for this sample (T_g = 164 °C). The high moduli of these polymers are also indicated by the data shown in Figure 6.

These soluble poly(benzyoyl-1,4-phenylene)s exhibit the stress–strain properties of high-performance polymers. For example, a representative stress–strain curve is shown in Figure 7, for a film sample of PBP-A cast from $CHCl_3$ solution (thickness 0.011–0.014 mm); other data are listed in Table 3. These soluble, noncrystalline polymers show tensile moduli of >6 GPa and tensile breaking strengths in the range of 0.9 GPa. It is anticipated that these soluble, rigid-rod polyphenylenes will find useful applications as high strength materials and as molecular reinforcing agents in nanocomposites.

These polymers also exhibit the high thermal stabilities expected for polyphenylenes as shown by the TGA thermograms exhibited in Figure 8. Thus, the polymer exhibits less than 3% weight loss upon heating in air or in nitrogen up to 500 °C. In nitrogen, there is only 20% weight loss upon heating to 650 °C. Isothermal heating at 350 °C in air for 15 h resulted in less than 1.9% weight loss. Similar data have been reported by

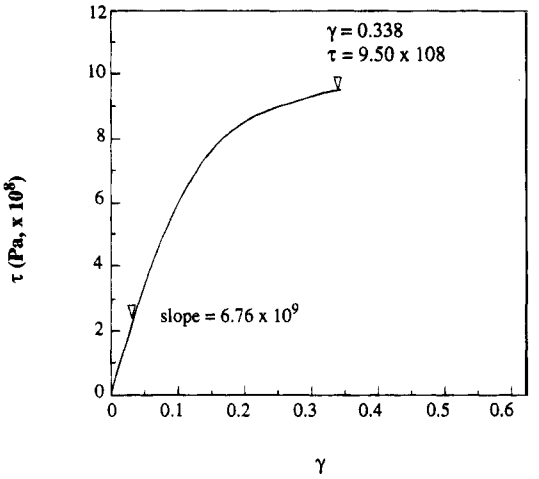


Figure 7. Stress–strain curve for PBP-A.

Table 3. Stress–Strain Properties of Poly(benzoyl-1,4-phenylene)[a]

sample	elongation (%)	tensile strength at break (MPa)	tensile modulus (MPa)
1[a]	23	1176	7380
2	14	710	6770
3	34	850	6760
4	32	965	6240
5	42	918	5520
6	32	1024	6610
7	57	1013	6270
average[b]	35	913	6362

[a] Strain rate of 0.002 in./s except for sample 1 for which the strain rate was 0.005 in./s. [b] Samples 2–7.

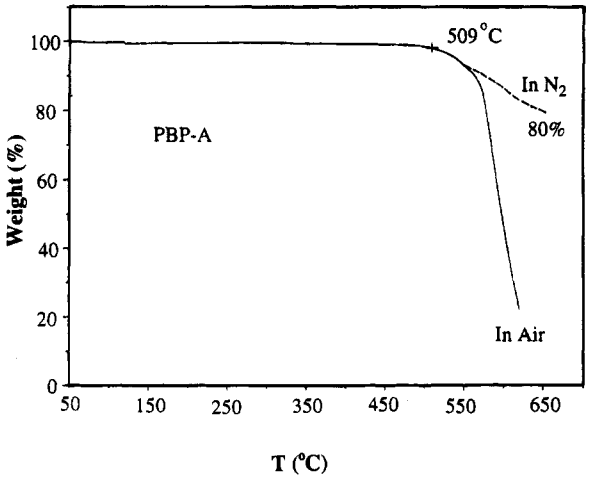


Figure 8. TGA thermogram for PBP-A.

DeSimone and co-workers[20] for their polymer prepared in the presence of the 2,2′-bipyridyl ligand.

Conclusions

High molecular weight, soluble poly(benzoyl-1,4-phenylene) (PBP-A) can be prepared by step-growth polymerization of 2,5-dichlorobenzophenone using a catalytic mixture of nickel chloride and triphenylphosphine in the presence of zinc metal as the reducing agent in DMF. It has been proposed that the regiochemical placement of lateral benzoyl groups along the backbone can be varied by addition of 2,2′- bipyridine as coligand (PBP-B). Thus, PBP-B exhibits a glass transition temperature which is 68 °C higher than an analogous polymer PBP-A. The UV–vis absorption maximum for PBP-B is observed at 352 nm versus 328

nm for PBP-A. ^{13}C NMR analyses suggest polymer PBP-B is more regular than polymer PBP-A based on the observation of fewer peaks in the carbonyl carbon region. Stress–strain measurements indicate that these polymers are high-performance, soluble materials with high tensile moduli and high tensile stress at break.

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