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# Isomeric Poly(benzophenone)s: Synthesis of Highly Crystalline Poly(4,4'-benzophenone) and Amorphous Poly(2,5-benzophenone), a Soluble Poly(*p*-phenylene) Derivative

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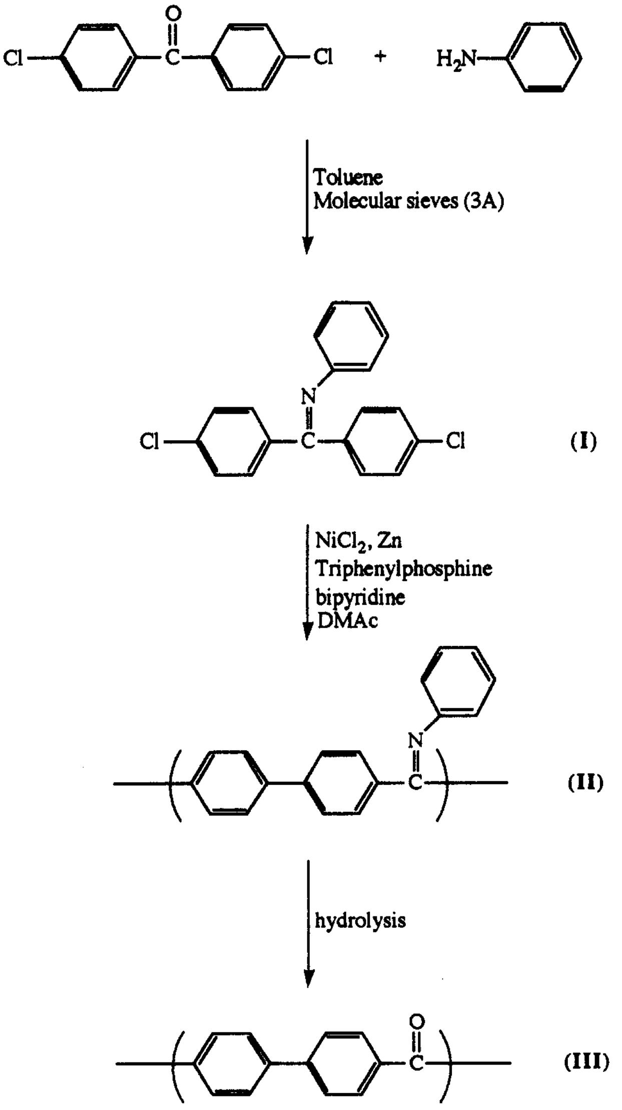
Herein we describe a nickel-catalyzed polymerization which employs the coupling of bis(aryl halide)s as the polymer-forming reaction in a step-growth polymerization of isomeric dichlorobenzophenones. The reaction utilized has general applicability to the synthesis of new processable engineering resins of superior thermal stability. The synthetic approach was first demonstrated by Colon *et al.*[1] in the synthesis of biphenyl. They found that a Ni(0)-catalyzed system would quantitatively convert chlorobenzene to biphenyl in short times at mild temperatures. It was thought that since the coupling of aryl chlorides could be achieved in high yields, the possibility existed for the use of this catalyst as a route to high polymer by coupling difunctional monomers. Poly(ether ether sulfone)s[2] were chosen by Colon as the first system to be studied because they are generally amorphous and soluble in dipolar aprotic solvents such as *N,N*-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) at the relatively low temperatures (70 °C) required to produce high polymer. In addition to poly(arylene ether sulfone)s,[3] Ueda has also investigated the use of the Ni(0) catalyst system for the synthesis of poly(arylene ether ketone)s.[4] This method proved to be advantageous relative to conventional methods because of the high rates and the mild conditions of the reaction.

Recently, Percec extended the use of this catalyst system in an attempt to synthesize soluble poly(phenylene)s.[5] Percec's efforts in the design of soluble materials were focused on the polymerization of "crankshaft" type monomers. Specifically, they reported the synthesis of Ni(0)-catalyzed oligomerization of 4,4'''-dichloroquaterphenyls. In spite of the fact that the kink was introduced, molecular weight was still limited to oligomers due to poor solubility ($\langle M_n \rangle = 9.0 \times 10^2$).

As is well-known, poly(*p*-phenylene) (PPP) exhibits remarkable thermal stability. They have been considered for use in numerous thermally robust organic materials including composites, lubricant additives, and thermoset precursors for high-performance aerospace material applications. The improvement of the solubility of poly(phenylene) has been attempted by attaching lateral substituents.[6,7] Appropriately substituted materials should be soluble and yet exhibits thermal properties comparable to that of PPP. Several researchers have examined the substitution of PPP via polymerization techniques other than Ni(0) catalysis to vary polymer properties. Schluter *et al.*[8,9] have described the palladium-catalyzed polymerization of alkyl-substituted poly(*p*-phenylene) derivatives. In some cases, degrees of polymerization of 30–50 could be achieved and solubility maintained. Tour *et al.* has also investigated the substitution of a PPP backbone, but with the goal of making thermoset precursors.[10] Specifically, they reported the functionalization of brominated PPP with several alkynes. A tetrahydrofuran-promoted polymerization of bromolithiobenzene gave the polymer, and subsequent replacement of the bromines with alkynes led to the target materials. Novak has focused on the synthesis of water-soluble poly(*p*-quaterphenylene-2,2'-dicarboxylate) via the palladium-mediated, cross-coupling of aryl halides and arylboronic acids.[11] The resulting polymers[12] are rodlike polyelectrolytes that have the unusual properties of water solubility, conformational rigidity, and charged character similar to biopolymers. More recently, Morrocco reported the physical properties of soluble poly(*p*-phenylene) derivatives.[13] The synthetic details were not disclosed, but it was suggested that the "route involves relatively inexpensive materials". These substituted poly(*p*-phenylene)s were reported to be soluble in common organic solvents and exhibit numerous interesting properties which make them candidates for high-performance applications. Herein, we report the synthesis of isomeric poly(benzophenone)s using Ni(0) catalysts for the polymerization of inexpensive, readily available monomers, 4,4'-dichlorobenzophenone (4,4'-DCBP) and 2,5-dichlorobenzophenone (2,5-DCBP).

The first polymerization was attempted using 4,4'-dichlorobenzophenone in *N,N*-dimethylacetamide (DMAc). Realizing that the 4,4'-DCBP would give a rigid, insoluble material, polymerization was accomplished through an imine derivative—a methodology derived by McGrath *et al.*[14] for the synthesis of amorphous poly(arylene ether ketone)s. For our purposes, the required imine-functionalized dichloride monomer (I) was synthesized by the



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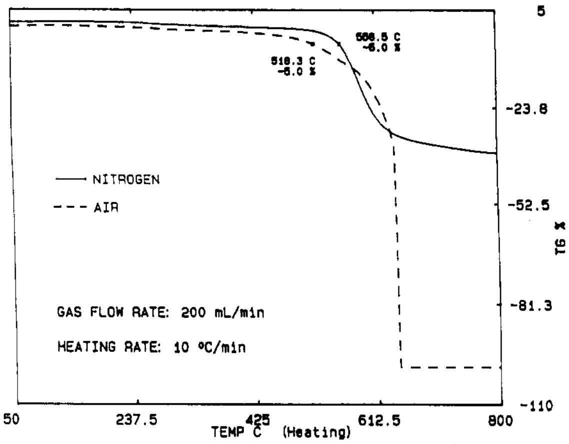
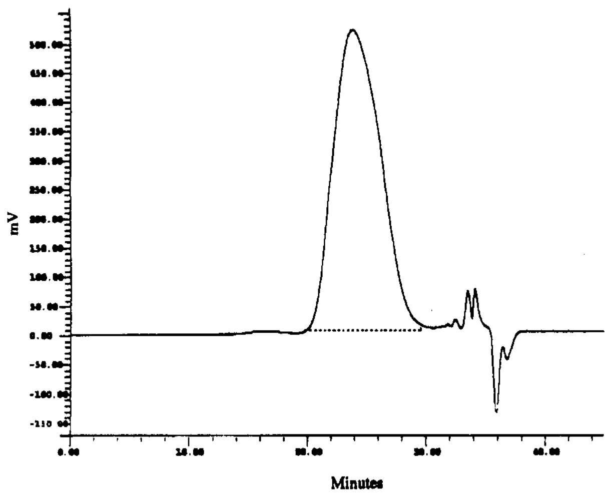


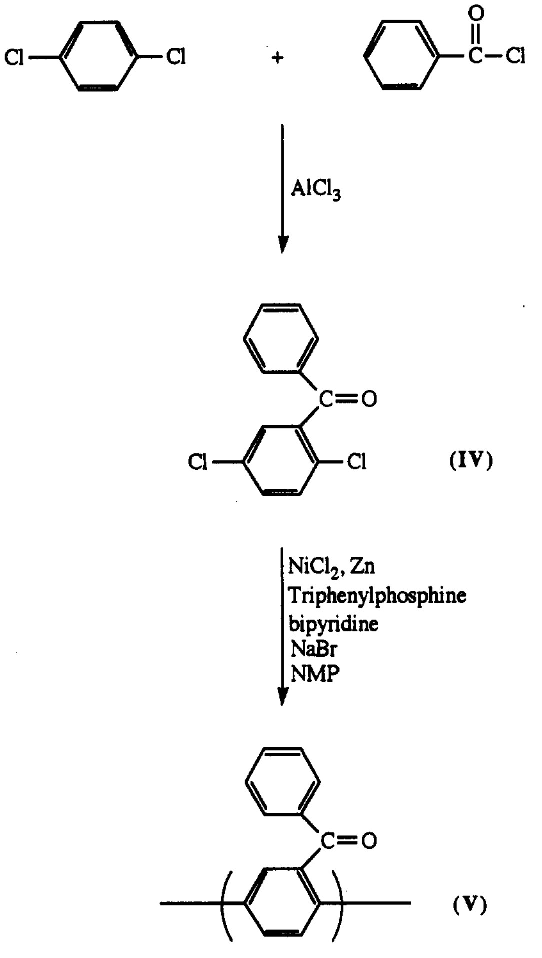
**Figure 1.** Thermal gravimetric analysis (TGA) thermograms of poly(4,4′-benzophenone) (III) using a heating rate of 10 °C/min.

treatment of 4,4′-DCBP with aniline in the presence of molecular sieves to give a bright yellow product in 50% yield. After two recrystallizations from toluene, the purity of **I** was >99.9% by gas chromatography. The polymerization was then performed using the Ni(0) catalyst prepared from $NiCl_2$ (0.3125 mol), triphenylphosphine (0.0093 mol), bipyridine (0.3886 mol), and zinc dust (0.0495 mol) in DMAc. The monomer was dissolved in DMAc and added to the active catalyst (as evidenced by the deep red color), and the resulting solution was stirred at 80 °C for 24 h. The resulting polymer (**II**)[15] was soluble in DMAc and gave an inherent viscosity of 0.25 dL/g (NMP, 30 °C). When this polymerization was repeated in 1-methyl-2-pyrrolidinone (NMP), an increase in the inherent viscosity was seen (0.36 dL/g; NMP at 30 °C) presumably due to the increased solubility in NMP. The amorphous polymer had a glass transition temperature of 225 °C with a 5% weight loss temperature in nitrogen at 558 °C. The amorphous prepolymer was hydrolyzed in 10% hydrochloric acid solution to generate poly(4,4′-benzophenone) (**III**) which is completely insoluble presumably due to high levels of crystallinity.[16] The 5% weight loss temperatures in air and nitrogen were 510 and 560 °C, respectively (Figure 1).



<Mn> = 26.7 x $10^3$ g/mol
MWD = 2.1

**Figure 2.** Size-exclusion chromatogram of poly(2,5-benzophenone) (V) in $CH_2Cl_2$ (1 mL/min) using a refractive index detector at 30 °C.



Synthesis of poly(2,5-benzophenone) not only increases the solubility of the polymer compared with the poly(4,4′-benzophenone) but also changes the polymer backbone to a substituted poly(*p*-phenylene). Synthesis of the monomer (**IV**) was accomplished by an aluminum chloride catalyzed acylation of *p*-dichlorobenzene with benzoyl chloride in a 1:1 ratio. The reaction was followed by TLC, and complete conversion was seen after 3 h. Recrystallization from ethanol gave polymer-grade monomer[17] (>99.9% purity by GC) that was analyzed extensively by a series of 2D NMR experiments to verify the correct isomer and rule out the possibility of halogen exchange during acylation. Once 2D NMR experiments confirmed the structure, the 13C could be utilized to identify subsequent reaction products.[18] For this polymerization, we referred to Colon's original paper in which he described the quantitative synthesis of biphenyl from chlorobenzene. It was noted that the addition of an alkali-metal salt to the reaction in 1–3 equiv decreased the total reaction time from 2 h to 20 min. Upon addition of 1 equiv of sodium bromide to the polymerization and the use of an overhead stirrer, high molar mass polymer was obtained (**V**). The resulting material was characterized by a number of techniques in order to confirm composition and molar mass. The number-average molar mass was 26.7 × $10^3$ g/mol[19] (Figure 2) by GPC with an inherent viscosity of 0.87 dL/g (NMP, 30 °C). Poly(2,5-benzophenone) has a $T_g$ = 206 °C (Figure 3) and 5% weight loss temperatures in air and in nitrogen of 496 and 495 °C, respectively (Figure 4). The reported Maxdem Poly-X material of similar composition of matter and number-average molar mass of (14.0–18.0) × $10^3$ g/mol has a $T_g$ of 140–150 °C.[20,21] The glass transition temperature of the poly(2,5-benzophenone) reported on herein is 50 °C higher than that reported by Maxdem and may be the result of a different sequence length distribution of regioisomers. The regiochemistry would be anticipated to be a function of the synthetic methodology (catalyst) utilized to make the polymer. In addition, Poly-X was reported to be a white polymer,[20]

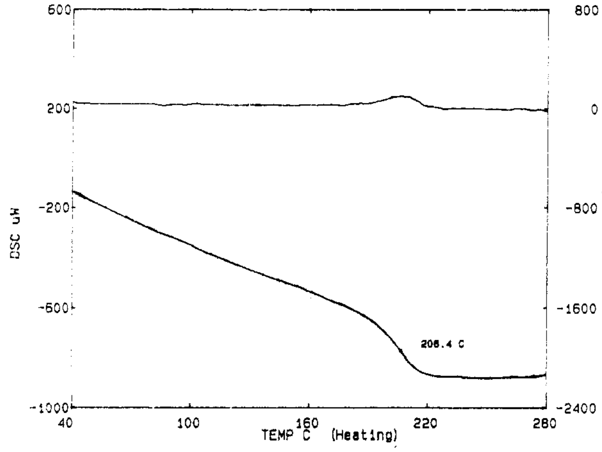


**Figure 3.** Differential scanning calorimetry of poly(2,5-benzophenone) (V) at a heating rate of 20 °C/min.

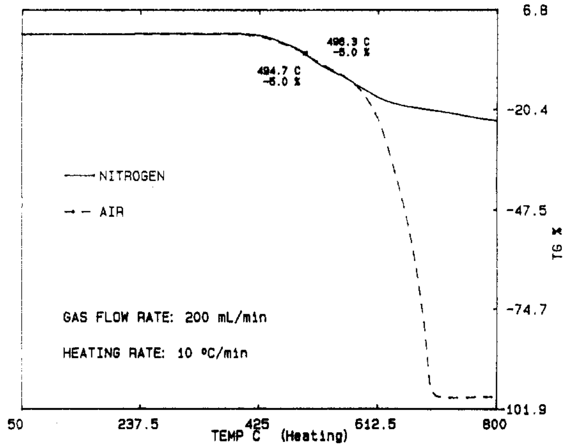


**Figure 4.** Thermal gravimetric analysis (TGA) thermograms of poly(2,5-benzophenone) (V) using a heating rate of 10 °C/min.

while the poly(2,5-benzophenone) reported on herein is slightly yellow with $\lambda_{max}$ = 354 nm.

In conclusion, it is apparent that use of the Ni(0) catalysts in polymerization of bis(aryl chloride)s leads to high molar mass polymers. In the case of poly(4,4′-benzophenone), the imine-derivatized monomer gave increased solubilities, resulting in higher molar mass. The successful polymerization of 2,5-DCBP yields a soluble derivative of poly(*p*-phenylene). Further work to increase the conversion, and therefore the molecular weight of the polymer, in addition to more in-depth thermal analysis is underway. This Ni(0)-catalyzed polymerization is a facile and economically feasible synthetic route and opens the way to a low-temperature, mild reaction for a large variety of heterocyclic and phenyl-based homopolymers. Moreover, the ability to make a wide range of copolymers enables one to tailor-make polymers that will be generally applicable for utilization in advanced materials.

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(15) The polymer was isolated by hot filtration to remove the zinc and precipitated into acetone to remove other remaining catalyst components.
(16) WAXS analysis of polymer III is currently underway.
(17) Mp: 88.9 °C. MS: 251 ($M^+$).
(18) $^{13}$C NMR of 2,5-DCBP: $\delta$ 140 (C-1), 133 (C-2), 131.1 (C-3), 128.9 (C-4), 129.2 (C-5), 131.3 (C-6), 136.2 (C-1′), 130.1 (C-2′), 128.8 (C-3′), 134.1 (C-4′), 128.8 (C-5′), 130.1 (C-6′), 190 (C-carbonyl).
(19) Determined by using a Waters 717 GPC in methylene chloride using polystyrene standards.
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