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High Molecular Weight Aromatic Polyamides from Aromatic Diiodides and Diamines

S. Richard Turner,* Robert J. Perry, and Richard W. Blevins

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2110

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Introduction. Imai[1] recently reported the coupling of aromatic dibromides and diamines under Pd-mediated carbonylation conditions as a new synthetic route to form aromatic polyamides. The molecular weight of the polymers in the reported examples was lower than those that can be readily obtained in the low-temperature coupling reaction of diacid chlorides and diamines commonly used to prepare aromatic polyamides.[2] Although the carbonylation and coupling reaction to aromatic polyamides offers potential advantages, such as the elimination of corrosive, moisture-sensitive acid chlorides, the relatively low degree of polymerization observed in the reported aromatic polyamides via this chemistry is a serious drawback. We report in this paper that *m*-diiodobenzene reacts differently than *m*-dibromobenzene under Pd-mediated carbonylation conditions when coupled with the same diamine and that significantly higher molecular weight aromatic polyamides can be readily obtained with the diiodoaromatic monomer.

Experimental Part. Materials. *m*-Diiodobenzene (Kodak), *m*-dibromobenzene (Kodak), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Aldrich) were purified by vacuum distillation. 4,4′-Diaminodiphenyl ether (Aldrich) was purified by bulb-to-bulb distillation. *N*-Methylpyrrolidinone (NMP; Aldrich, anhydrous) was used as received. Triphenylphosphine (Kodak) was recrystallized from hexane and bis(triphenylphosphine)palladium(II) chloride (Aldrich) was used as received.

Polymerization Procedure. A clean, dry 100-mL Fisher–Porter pressure bottle outfitted with a pressure gauge, a pressure release valve, a gas inlet, and a ball valve for sample withdrawal was charged under a helium atmosphere in a dry box with 4,4′-diaminodiphenyl ether (2.00 g, 10 mmol), *m*-diiodobenzene (3.20 g, 9.7 mmol), NMP (40 g), DBU (3.65 g, 24 mmol), triphenylphosphine (0.312 g, 1.2 mmol), and bis(triphenylphosphine)palladium(II) chloride (0.42 g, 0.6 mmol). A magnetic stirbar was added for agitation during the reaction. The reaction vessel and contents were purged three times with CO and then pressurized to the desired pressure. The reactor was placed into a stirred oil bath for heating. Samples of the reaction solution were removed at intervals with a syringe to monitor the growth of molecular weight. The polymer solution was filtered and then precipitated into methanol. The resulting polymer was then recovered by filtration, and, after thorough washing, it was dried under vacuum.

The polymerizations with *m*-dibromobenzene were done under identical conditions used for *m*-diiodobenzene.

Polymer Characterization. Approximate molecular weights were determined by size-exclusion chromatography in 0.01 M $LiNO_3$/DMF using three 10-μm Waters HT linear columns and one 300-Å HT column. Molecular weight values are reported in poly(methyl methacrylate) equivalents. Inherent viscosities were measured in DMF at 30 °C at a concentration of 0.25 g/dL.

Results and Discussion. We have compared the polymerization of *m*-dibromobenzene, *m*-diiodobenzene, and 4,4′-diaminodiphenyl ether under identical Pd-catalyzed carbonylation reaction conditions (eq 1). We have found that there is a large difference in the rate of increase in molecular weight and the ultimate molecular weight of the aromatic polyamide formed. The diiodoaromatic shows a much faster rate of reaction and a much higher ultimate molecular weight. At 1 atm of CO (Figure 1) the diiodoaromatic reacts faster to give a polymer of significantly higher molecular weight. After 2 h the iodo reaction is complete, giving an aromatic polyamide with a number-average molecular weight around 24 000 (PMMA equivalents) (η_{inh} = 0.75 dL/g). The bromo reaction is not complete after 6 h, and the maximum number-average molecular weight was around 14 000 (η_{inh} = 0.51 dL/g). This is in good agreement with the Imai[1] value of 0.55 dL/g for the same polymerization.

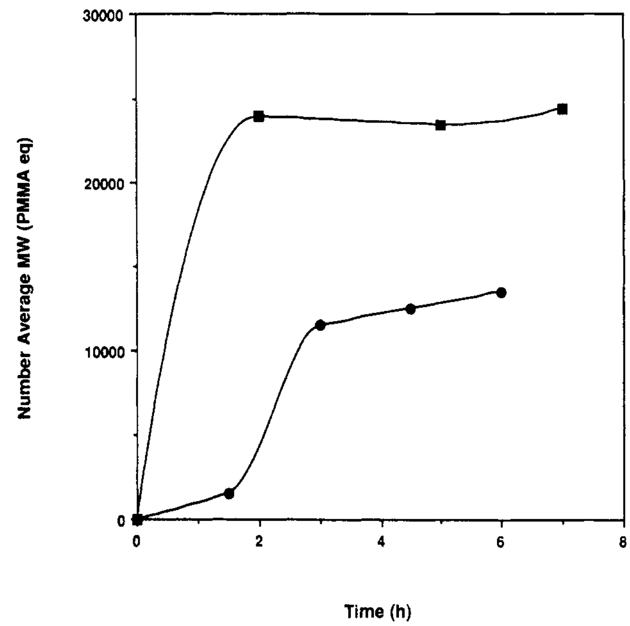
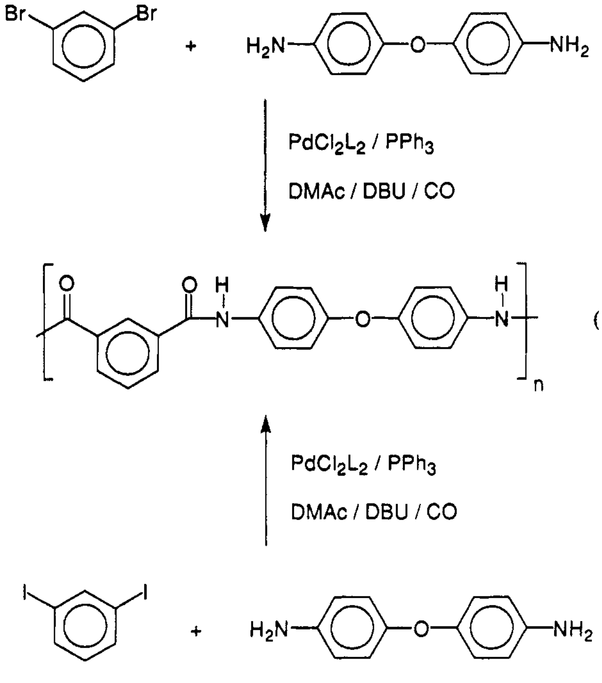


Figure 1. Comparison of the increase in number-average molecular weight (PMMA equivalents) with time for *m*-dibromobenzene and *m*-diiodobenzene with time at 1 atm of CO and 90 °C: (■) iodo; (●) bromo.



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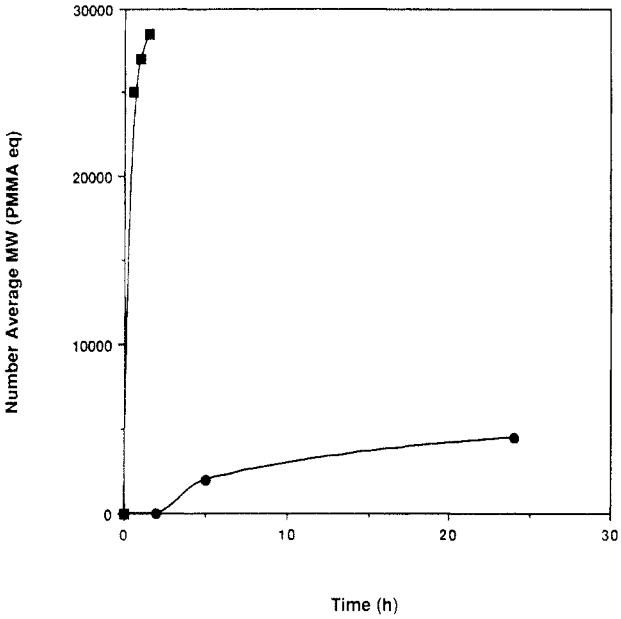

Figure 2. Comparison of the increase in number-average molecular weight (PMMA equivalents) with time for *m*-dibromobenzene and *m*-diiodobenzene with time at 90 psig CO and 90 °C: (■) iodo; (●) bromo.

At 90 psig CO (Figure 2) the difference between *m*-diiodobenzene and *m*-dibromobenzene is dramatic. At this CO pressure there was little increase in the molecular weight of the aromatic polyamide from the dibromo polymerization after 24 h (about 5000 M_n with η_{inh} = 0.15 dL/g) while the diiodo polymerization goes to a M_n of around 30 000 (η_{inh} = 0.95 dL/g) in 90 min.

We believe that the difference in the rate of the molecular weight increase and the sensitivity differences to CO pressure between the diiodoaromatic and dibromoaromatic is due to a change in the rate-determining step for the two halogenated monomers. It is well documented that zero-valent Pd compounds undergo oxidative addition to aryl iodides (the first step in the coupling reaction) faster than aryl bromides[3] and that the rate-limiting step for α-ketoamide formation in aryl iodides is CO insertion.[4] On the other hand, it is known that, for the esterification of aryl bromides with Pd, CO, and an alcohol, the rate-limiting step is oxidative addition of the Pd.[5,6] Higher CO pressures have been shown to promote a greater degree of CO coordination to Pd[7], rendering the Pd less nucleophilic and thus slowing the oxidative addition reaction.[8] Therefore, in the dibromoaromatic polymerization, the rate-determining step is the oxidative addition of the catalyst and increasing CO pressures slows this reaction. In the diiodo case, the rate-determining step is the CO insertion reaction. Increasing the CO pressure (concentration of CO) increases the rate of reaction and the rate of molecular weight gain.

The reason for the difference in the final molecular weight of the polymers obtained for these reactions is less clear. The rate of formation of polymer should not effect the final molecular weight of the polymer formed if the reaction can be carried to sufficient conversion. It is possible that the catalyst becomes inactive during the polymerization and thus limits the molecular weight. It is also possible that side reactions of the amine and/or of the dibromoaromatic compound occur during the slow reaction to disturb the stoichiometry necessary for high molecular weight.

We are continuing to study this reaction with model compounds to elucidate these possible side reactions. We are applying this efficient reaction to other diiodoaromatic compounds and are finding it to be broad in scope. A future report will describe the results of these studies.

References and Notes

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Registry No. ($H_2NC_6H_4$-*p*-O-*p*-$C_6H_4NH_2$)(BrC_6H_4-*m*-Br)(CO) (copolymer), 114492-47-6; ($H_2NC_6H_4$-*p*-O-*p*-$C_6H_4NH_2$)(IC_6H_4-*m*-I)(CO) (copolymer), 139162-25-7.