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Nickel(0)-Mediated Coupling Polymerizations via Microwave-Assisted Chemistry

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An important development in the synthesis of electrically conductive and thermally stable polyarylene polymers has been the development of Ni(0)-mediated coupling reactions involving dihalogenated substrates.[1,2] These polymerizations have shown utility in the synthesis of a number of useful conjugated polyarylenes[3−10] and of particular interest to us, electroluminescent polymers.[11−14] Among the many challenges in the development of electroluminescent polymers optimized for display applications is the need to design macromolecules with specific functionality for the optimization of emissive properties.[15] The Edisonian hit-and-miss strategies usually employed often means that the design, synthesis and optimization of macromolecular structures can be labor intensive and time-consuming. These problems are exacerbated by the sensitivity (to oxygen and other impurities) of the Ni(0)-mediated coupling polymerization reactions and low solubility of certain monomers and resulting polymers. These challenges can result in nonideal polymerization conditions and poor control of the molecular weight and structure of the resulting polymers.

Recent reports have shown that microwave heating can be very convenient for use in a large number of organic synthetic methods. Microwave heating is instantaneous and very specific and there is no contact required between the energy source and the reaction vessel. Modern apparatus designed for microwave chemistry have solved most of the earlier problems with this technique such as thermal runaway reactions, explosions, and poor heating. It is now possible to perform microwave-heated reactions with good temperature and pressure control. Perhaps the greatest benefit of microwave-assisted synthesis is that it speeds chemical reactions. Common observations are that reactions that take hours or days under conventional reaction conditions can be performed in seconds to minutes with high yields and lower amounts of side products.[16]

There have been very few reports of the use of microwave heating to carry out polymerizations. Recent examples include the free-radical polymerization of 4-nitrophenyl acrylates,[17] polyimide synthesis,[18] and ring-opening polymerization of lactides.[19] These reports have led us to investigate the usefulness of microwave assisted chemistry to make useful conjugated aromatic polymers.

This communication describes the synthesis (Scheme 1) of poly-2,7-fluorenes from the Ni(0)-mediated condensation polymerization of 2,7-dibromo-9,9-dihexylfluorene (DHF) utilizing microwave heating. Our standard synthetic route (conventional external heating) toward these polymers has been the procedure in which first a solution of bis(1,5-cyclooctadiene)nickel(0), 2,2′-bipyridine and cyclooctadiene in toluene/DMF is activated by heating for 15 min at 80 °C. Then a degassed solution of 2,7-dibromofluorene is carefully added and the mixture is stirred for 4−24 h at 80 °C to effect polymerization. Polymer chain end-capping and control of molecular weight can be achieved by adding different amounts of a monofunctional component, such as 4-(*tert*-butyl)bromobenzene. In addition to the long polymerization time of these reactions, our experience has been that precise batch-to-batch reproducibility is difficult due to the sensitivity of the reaction and high reactivity of the Ni(0) catalyst. Furthermore, obtaining high molecular weight polymer is difficult due to partial precipitation of polymer under these standard reaction conditions.

Table 1. Molecular Weight Data of Polymers Where Molecular Weights Were Determined by GPC Using THF as the Eluent and Calibrated with Polystyrene Standards

	mol % of end cap	M_n/PDI
1		104 600/1.89
2	1.8	39 600/1.78
3	3.8	21 800/1.76
4	6.5	8400/2.22
5	11.5	5100/1.65

By utilizing microwave-assisted chemistry, we have the ability to reach high internal reaction temperatures operating at elevated pressures, accordingly the polymerization can be driven to completion in 10 min.[20] The microwave synthesizer used was specially designed to operate at elevated temperatures and pressures.[21] Another advantage is that we have been able to perform these polymerizations in a one-step, one-pot fashion and have found there is no need to perform the separate catalyst activation step. The reactions are so fast that there is little time for side pathways to undesired products, oxidation of catalyst or reactions with glassware, etc. We observed conversion rates of >99.5% facilitated, in part, by the increased temperature and pressure of the reactions. No precipitation of the polymers from reaction solution was observed, even when molecular weights higher than 100K were reached (Table 1).

We also observed that polymer molecular weight could be controlled by adding varying quantities of a monobromo end-capping unit, 4-bromobiphenyl, to the reaction mixture. The molecular weights of the isolated polymers were determined by GPC. While a small degree of fractionation during the isolation procedure cannot be strictly ruled out, the low solubility of these polymers and the high isolated yields makes the likelihood of significant fractionation unlikely. Polymers of molecular weight from 5K to 40K were synthesized, and all samples were monomodal with polydispersity indices between 1.65 and 2.22.[22] Figure 1 shows the molecular weight of the polymers obtained compared to the theoretical values predicted by Carother's equation at 99.7% conversion.

The ease of the microwave-assisted technique coupled with its high speed and high conversions makes it a valuable tool for the synthesis of macromolecules. Studies on small molecular substrates shows that microwave

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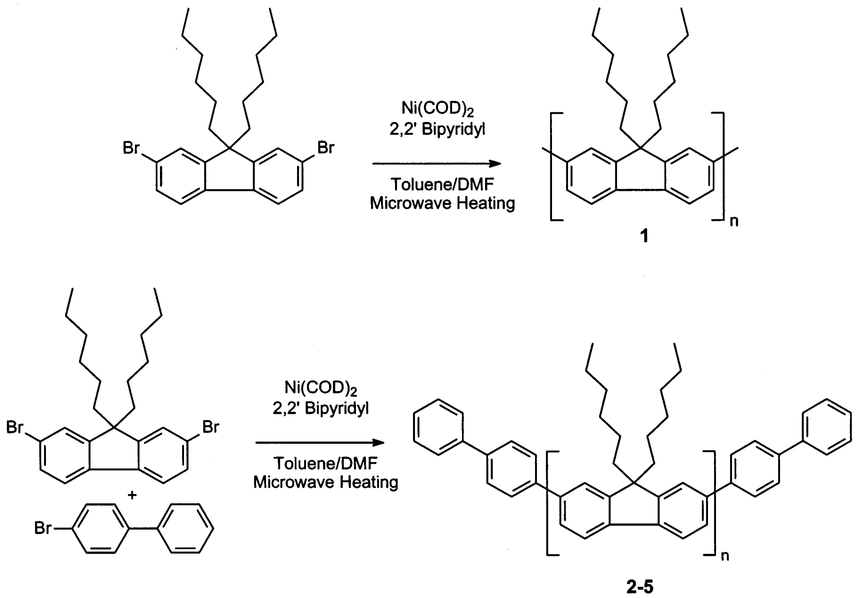
Scheme 1. Synthesis of Poly-2,7-fluorenes



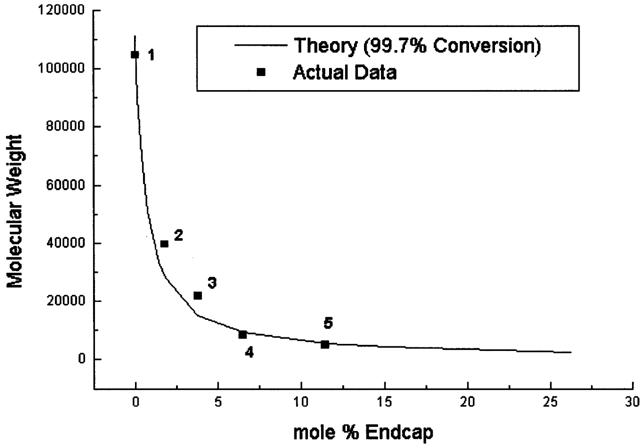


Figure 1. Graph of molecular weights observed vs calculated values based on Carother's equation (calculated at 99.7% conversion).

assisted heating can also be used under Suzuki conditions to give high yield reactions.[23,24] We are in the process of studying the utility of microwave-assisted heating to make conjugated polymers by the Pd-catalyzed Suzuki coupling route. There is no reason to suspect that this technique is limited to poly-2,7-fluorenes, and the synthesis of other polyarylenes of interest is underway.

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Supporting Information Available: (1) A gel permeation chromatograph of poly-2,7-fluorene, **5**, and (2) a plot generated by the microwave synthesizer of power/heating/pressure profile of polymerization reaction used to make poly-2,7-fluorene, **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) A typical experimental procedure is as follows. All chemicals were handled under air-free conditions. A catalyst stock solution was prepared consisting of 704 mg of bis(1,5-cyclooctadiene)nickel(0), 410 mg of 2,2′-bipyridine and 281 mg of cyclooctadiene in 17.5 g of toluene/DMF (1.15:1). In a separate vial, a monomer solution containing 600 mg of 2,7-dibromo-9,9-dihexylfluorene in 17.3 g of toluene was prepared. Polymerization was accomplished by charging a 10 mL reaction vial with 2.2 g of the catalyst solution and 1.77 g of the monomer solution. The reaction vial was sealed and

placed in a microwave reactor (SmithCreator, Personal Chemistry, Inc.) and heated to 250 °C for 10 min. After cooling, the reaction solution was filtered (0.45 um) and precipitated into 15 mL of methanol. The polymer was isolated by centrifugation and washed several times successively with methanol, water, and acetone to effect removal of dissolved salts. Final yield after drying was 40 mg, essentially quantitative.

(21) The SmithCreator reactor functions by allowing the user to specify reaction times and temperatures. Sample temperature is constantly monitored by IR and microwave power is automatically adjusted to maintain programmed temperature profiles. The instrument limits are 250 °C and 25 bar pressure. Supporting Information is available.

(22) Molecular weights were determined by gel permeation chromatography (GPC) using THF as the eluent. Molecular weights are vs polystyrene standards.

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