1988 *Macromolecules* **2002,** *35,* 1988−1990

The First High Molecular Weight Poly(*N*-alkyl-3,6-carbazole)s

Zhong-Biao Zhang,[†,‡,§] **Michiya Fujiki,***[†,‡]
Hong-Zhi Tang,[‡] **Masao Motonaga,**[‡] **and**
Keiichi Torimitsu[†]

NTT Basic Research Laboratories, NTT Corporation, and
CREST-JST, 3-1 Wakamiya, Morinosato, Atsugi,
Kanagawa 243-0198, Japan

Received November 2, 2001
Revised Manuscript Received January 29, 2002

Introduction. π-Conjugated polymers have been promising advanced material candidates for more than 2 decades.[1] Well-defined molecular structures have been realized using efficient organic synthesis tools, aiming at generating various polymer-based electrical or optical properties.[2] Carbazole-containing polymers, especially those with carbazole as the pendant unit or copolymers, have been extensively investigated due to their hole transport ability, photorefractive, and high-temperature dielectric properties.[3] However, the research on the carbazole main-chain homopolymers still remains limited because both the chemical and electrochemical syntheses resulted in products with low molecular weight or poor solubility.[4] In this communication, we report the successful synthesis of carbazole main-chain homopolymers with high molecular weights by applying the reverse addition order of a nickel catalyst based on the well-established Yamamoto coupling method[2a] and some preliminary studies of their thermal and optical properties. This result may provide a novel kind of material candidate for the future evaluation of luminescent, electrochromic, photorefractive, or chemical sensing materials. The simple alteration of the Yamamoto method may lead to a general and more efficient means of preparing other types of π-conjugated polymers, especially when the molecular weight of the polymer plays an important role in the properties and performance of some devices based on that polymer.

Results and Discussion. As shown in Scheme 1, *N*-alkyl-3,6-dibromocarbazoles were synthesized from 3,6-dibromocarbazole (Aldrich) upon reaction with potassium carbonate and bromoalkanes in anhydrous *N*,*N*-dimethylformaldehyde (DMF) at 50 °C in 80−90% yields. Polymerization was carried out by the Yamamoto coupling reaction[2a] using the zerovalent nickel reagent, bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) (Kanto), in the presence of 1,5-cyclooctadiene (COD) and molar equivalent of 2,2′-bipyridyl (Bpy) at 60 °C. The synthetic data and molecular weights of the polymers are summarized in Table 1. All the monomers and polymers were confirmed by NMR spectroscopies and elemental analyses (see Supporting Information).

Table 1. Synthesis and Characterization of Polycarbazoles[a]

polymer	order	yield (%)	M_w[b] ($\times 10^3$)	M_n[b] ($\times 10^3$)	PDI[b]
PDC-1	A	85	2.6	1.7	1.5
PDC-2	B	61	91.0	53.4	1.7
PDOC	B	67	120.0	84.2	1.4

[a] The ratio between the monomer and $Ni(COD)_2$ is 1:1.2. [b] Molecular weights and polydispersity index (PDI) were estimated by size exclusion chromatography against polystyrene standards.

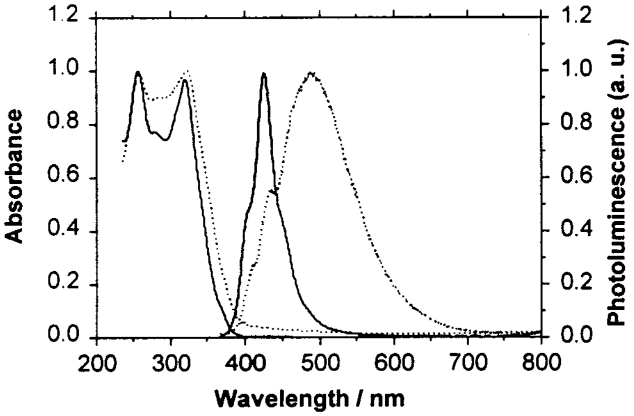


Figure 1. Optical properties of **PDC**. Solid lines: in THF, 1.7×10^{-6} M. Dotted lines: thin solid film cast on quartz substrate from chloroform solution. Excited at 320 nm; the quantum yield in dilute solution was calculated in an integrating sphere with quinine sulfate as the standard.

The difference in the addition order of the monomer and the nickel reagent was found to be the key in determining the molecular weight of the resulting polymers. The normal addition order, order A, i.e., adding monomer to the nickel reagent solution, resulted in a low molecular weight (M_w) of several thousand. However, the reverse order, order B, i.e., slowly adding the hot nickel reagent into the monomer solution, gave a high M_w of around 100 000 (Table 1). It is known that the oxidative addition (insertion of Ni(0) into the C−X bond), the disproportionation between the formed adducts, and the reductive elimination of the Ni(II) compound are the successive fundamental reactions during the polymerization using the Ni(0) reagent.[5] The complexes such as X−Ar−Ni(X)L_m,[6] X−Ar−NiL_m−Ar−X,[7] and even L_m(X)Ni−Ar−Ni(X)L_m[8] when the C−X bond has high stability (X = halogen; Ar = arylene; L = coordination ligand; m = the number of ligands) can be isolated. It was postulated that the common addition order A resulted in the preferential formation of the L_m(Br)Ni−Ar−Ni(Br)L_m complex compared to the reverse order B due to the high ratio between the Ni(0) reagent and the monomer during the initial state (Scheme 2). This dinickel-substituted complex has less stability than the other two species,[8] resulting in the easy decomposition or hydrolization on one or both sides. Consequently, the termination of the propagation of the polymer chain would occur. The concept of avoiding the formation of the dinickel-substituted complex could be applied to the preparation of other π-conjugated polymers with high molecular weights.

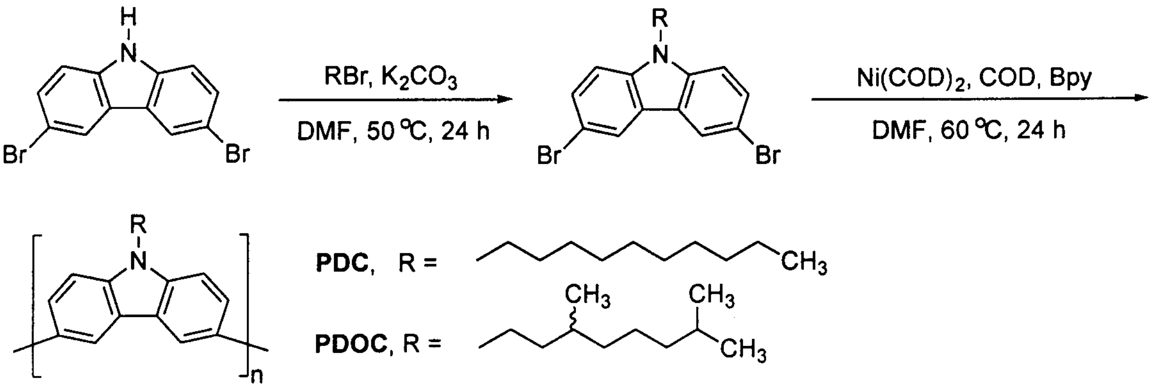
The high molecular weight polycarbazoles, **PDC-2** and **PDOC**, have good solubilities in common organic solvents such as chloroform, tetrahydrofuran (THF), toluene, dichloromethane, and 1,2-dichloroethane. These polymers also show good film-forming abilities, which make them easily fabricated into thin films using either spin-coating or simple solvent-casting techniques. Figure 1 shows the UV−vis and photoluminescence spectra of **PDC-2** in THF solution and in a solid film prepared

---

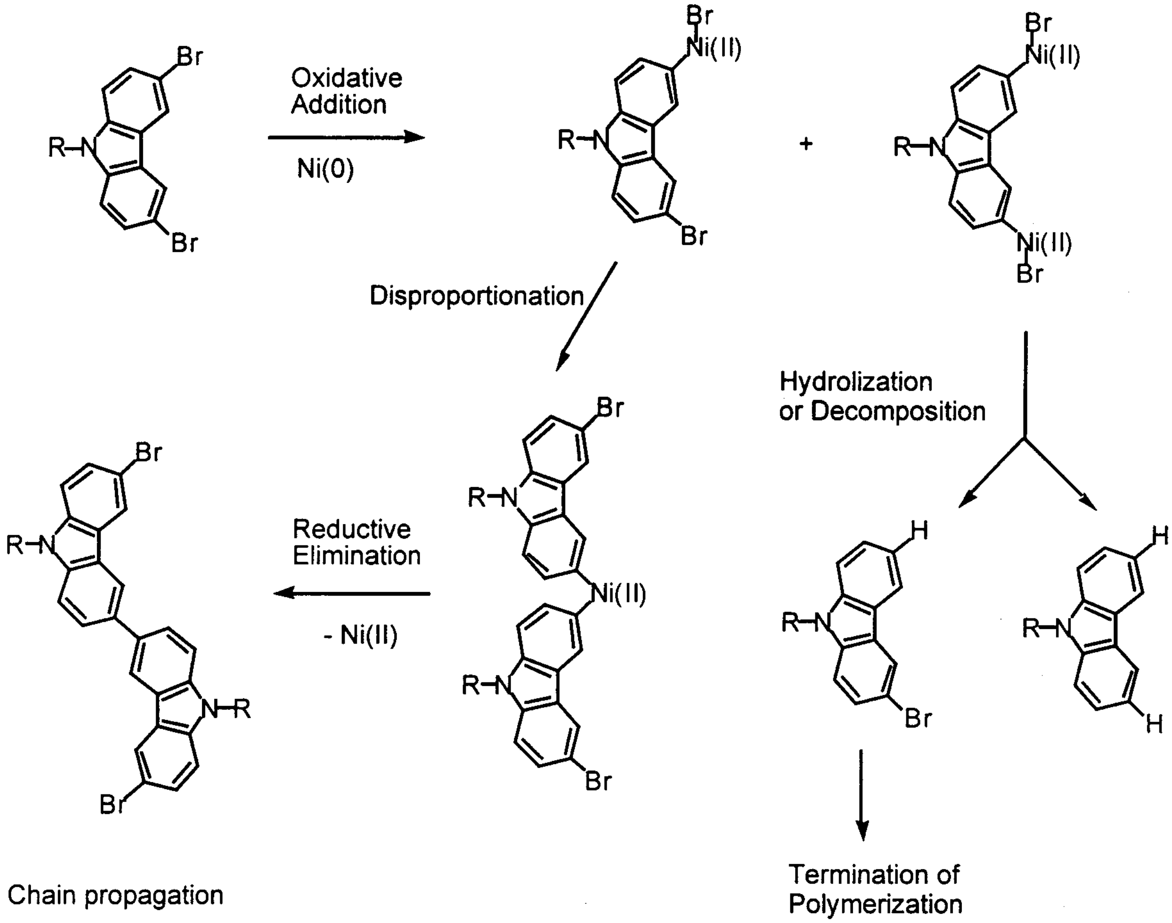
[†] NTT Basic Research Laboratories.
[‡] CREST-JST.
[§] Present address: Department of Chemistry, University of Southern California, Los Angeles, CA 90089.

10.1021/ma011911b CCC: $22.00

Scheme 1. Synthesis of Polycarbazoles



Scheme 2. Proposed Mechanism for the Chain Propagation and Termination of Polycarbazole



by the solvent-casting method. In dilute solution or in the thin solid film, **PDC-2** exhibits an absorption maximum at 320 nm. **PDC-2** shows a fairly intense blue photoluminescence at 420 nm in THF with about a 15% quantum yield. A large Stokes shift of about 100 nm indicates a large difference in the structures between the ground and excited states. In the solid film, **PDC** exhibits a broad emission band with an extreme value at 490 nm. The existence of a sideband at around 420 nm indicates a different origin of the broad band, which was supposed to have originated from the interchain excimer emission, probably due to the proximity of the polymer chains and the high crystallinity in the solid sate.[9]

Differential scanning calorimetric (DSC) and thermogravimetric analyses (TGA) were carried out to determine the thermal transition and degradation behavior of the polymers. The DSC measurements showed a glass transition temperature of 142 °C for **PDC-2** and 151 °C for **PDOC**. Both **PDC-2** and **PDOC** showed a high thermal stability based on the TGA measurements. The 5% weight loss temperatures of the polymers during heating runs were 430 °C for **PDC-2** and 400 °C for **PDOC**.

Conclusion. The high molecular weight poly(*N*-alkyl-3,6-carbazole)s were successfully synthesized for the first time using a reverse addition order for the zerovalent nickel reagent based on the Yamamoto coupling reaction. This method could be applied to the preparation of other polymers when using similar organometallic polycondensation reactions. The obtained polycarbazoles possess good solubility, film-forming ability, thermal stability, and moderately high photoluminescence efficiency. These advantages together with the presence of nitrogen atoms in the backbone, which may possess activity for interaction or derivation, make this class of conjugated polymers promising candidates for advanced material research.

Acknowledgment. The authors thank Dr. Hiroshi Nakashima and Prof. Julian R. Koe for their valuable discussion. The authors also gratefully thank Drs. Masao Morita and Hideaki Takayanagi for their generous support.

Supporting Information Available: Synthetic and purification details, ^{1}H and ^{13}C NMR spectroscopic data, and elemental analysis of all the monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) *Handbook of Organic Conductive Molecules and Polymers;* Nalwa, H. S., Ed.; John Wiley & Sons: Chichester, 1997; Vols. 1−4. For recent reviews, see: (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Markes, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121−128. (c) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737−1750. (d) Mitschke, U.; Bauerle, P. *J. Mater. Chem.* **2000**, *10*, 1471−1507. (e) Mcquade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537−2574. (f) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595−2574. (g) Goldenberg, L. M.; Bryce, M. R.; Petty, M. C. *J. Mater. Chem.* **1999**, *9*, 1957−1974. (h) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817−1845. (i) Samyn, C. Verbiest, T.; Persoons, A. *Macromol. Rapid Commun.* **2000**, *21*, 1−15. (j) McGehee, M. D.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 1655−1668. (k) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1−25. (l) Bao, Z.; Rogers, J. A.; Katz, H. E. *J. Mater. Chem.* **1999**, *9*, 1895−1904.

(2) (a) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621−638. (b) McCullough, R. D.; Lowe, R. *J. Chem. Soc., Chem. Commun.* **1992**, 70−72. (c) Chen, T. A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087−10088. (d) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686−7691. (e) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359−369.

(3) (a) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature (London)* **1997**, *388*, 845−851. (b) Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O. *Chem. Rev.* **1997**, *97*, 207−281. (c) Zhang, Y.; Wada, T.; Sasabe, H. *J. Mater. Chem.* **1998**, *8*, 809−828.

(4) (a) Sarac, A. S.; Sezer, E.; Ustamehmetoglu, B. *Polym. Adv. Technol.* **1997**, *8*, 556−562. (b) Sadki, S.; Kham, K.; Chevrot, C. *J. Chim. Phys.* **1995**, *92*, 819−822. (c) Jenekhe, S. A.; Wellinghoff, S. T.; Reed, J. F. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 175−189. (d) Siove, A.; Ades, D.; Chevrot, C.; Feyer, G. *Makromol. Chem.* **1989**, *190*, 1361−1368. (e) Ngbilo, E.; Chevrot, C. *Synth. Met.* **1993**, *55−57*, 861−866. (f) Faïd, K.; Siove, A.; Adès, D.; Chevrot, C. *Polymer* **1993**, *34*, 3911−3916. (g) Ngbilo, E. Adès, D.; Chevrot, C. Siove, A. *Polym. Bull. (Berlin)* **1990**, *24*, 17−22. (h) Iraqi, A.; Wataru, I. *Synth. Met.* **2001**, *119*, 159−160.

(5) (a) Yamamoto, T.; Wakabayashi, S.; Osakada, K. *J. Organomet. Chem.* **1992**, *428*, 223−237. (b) Yamamoto, T.; Muruyama, T.; Zhou, Z.-H.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832−4845.

(6) Zhou, Z.-H.; Yamamoto, T. *J. Organomet. Chem.* **1991**, *414*, 119−127.

(7) (a) Yamamoto, T.; Abla, M. *J. Organomet. Chem.* **1997**, *535*, 209−211. (b) Murakami, Y.; Yamamoto, T. *Inorg. Chem.* **1997**, *36*, 5682−5683.

(8) Kim, Y.-J.; Sato, R.; Maruyama, T.; Osakada, K.; Yamamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 943−948.

(9) (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416−7417. (b) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765−768.

MA011911B