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SHORT COMMUNICATIONS

Living Polymerization of 1,2-Diisocyanoarenes Promoted by (Quinoxalinyl)nickel Complexes

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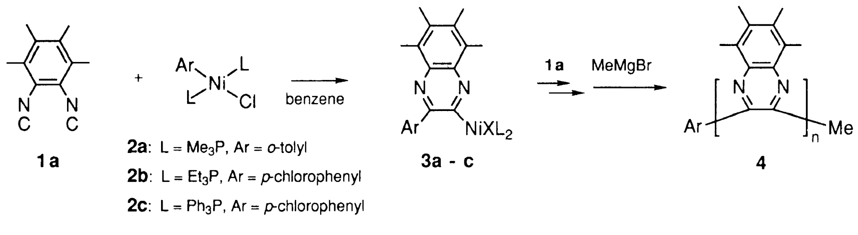
Poly(quinoxaline) has acquired significant interests in view of heat-resistant polymer and is generally prepared by the reaction of bis(*o*-diamines) with bis(glyoxals).[1] Recently, we reported a new living polymerization of 1,2-diisocyanoarenes catalyzed by *trans*-$(Me_2PhP)_2Br(Me)Pd(II)$ giving a new type of conjugated polymer, poly(2,3-quinoxaline), in which oligomeric (2,3-quinoxalinyl)palladium(II) complexes are involved as the propagating species.[2] On the other hand, successful polymerization of isocyanides forming poly(*N*-substituted iminomethylene) so far reported has mostly been achieved by nickel(II) catalyst.[3] However, use of organonickel(II) complexes $[(Me_2PhP)_2X(R)Ni$, R-: Me_3SiCH_2-, *o*-tolyl-] in the polymerization of 1,2-diisocyanoarenes resulted in a formation of only a trace amount of poly(2,3-quinoxaline) with unidentified tarry materials. Now we found that (quinoxalinyl)nickel(II) complexes having suitable phosphine ligands successfully promote the living polymerization of 3,6-bis[(trimethylsilyl)methyl]-1,2-diisocyanobenzene to afford poly(2,3-quinoxaline) of an extremely sharp distribution of molecular weight.

When an excess of *trans*-$(Me_3P)_2Cl$(*o*-tolyl)Ni(II) (**2a**), generated *in situ* from *trans*-$(Me_3P)_2Cl_2Ni(II)$ and (*o*-tolyl)MgCl, was reacted with 1,2-diisocyano-3,4,5,6-tetramethylbenzene (**1a**) at 0°C in benzene, the desired (quinoxalinyl)nickel complex (**3a**)[4] was produced in 36% yield by successive insertion of the ortho isocyano groups into Ni–C bond. Then, the isolated nickel complex **3a** having Me_3P as ligands was treated with 3-fold excess of **1a** to give a mixture of oligo(2,3-quinoxaline) (**4**) of up to the hexamer in 50% total yield after a termination with MeMgBr. The similar result was also obtained with arylnickel complex (**2b**) having Et_3P as ligands. In contrast, the reaction of *trans*-$(Ph_3P)_2Cl$(*p*-chlorophenyl)Ni(II) (**2c**) with **1a** did not give the corresponding **3c**, but a trace amount of



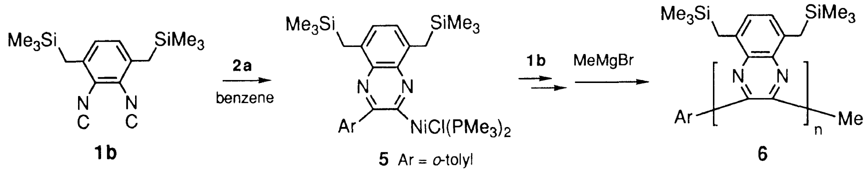


Table I. Living polymerization of **1b** catalyzed by **5**

Entry	**1b**/**5**	Yield/%	$\bar{M}_n$ (calcd)[a]	$\bar{M}_n$ (obsd)[b]	$\bar{M}_w/\bar{M}_n$[c]
1	2	76 [**6** ($n=3$) 70%, **6** ($n=4$) 6%][d]	—	—	—
2	7	82	2630	3010	1.05
3	15	94	4880	4890	1.10

[a] Calculated from monomer to initiator ratio. [b] Determined by VPO. [c] Determined by GPC. [d] Yield of isolation by HPLC.

oligomeric **4** together with unidentified tarry products. Remarked here is an observation that Ph_3P ligand of **2c** was liberated up to 54% from the nickel(II) complex during the reaction. It is likely that the ligand substitution of Ph_3P on nickel by isocyano groups of **1a** may cause the intractable polymerization. Indeed, $Ni(acac)_2$ catalyzed polymerization of 1,2-diisocyanoarenes in the absence of phosphine ligand, in which two or more isocyano groups of **1a** should be involved on coordination sphere of the nickel, produced the similar intractable tarry materials.

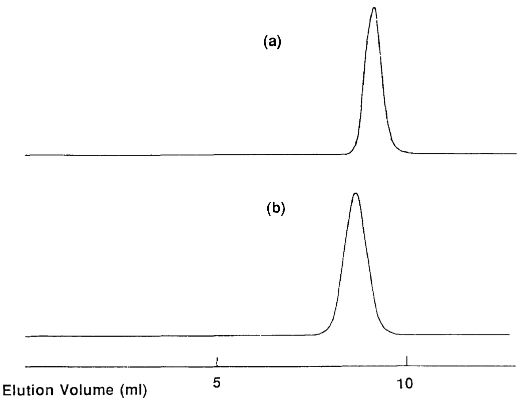


Figure 1. GPC curves of polyquinoxaline (**6**): (a) feeding ratio = 7 (entry 2); (b) feeding ratio = 15 (entry 3).

Finally, a controlled living polymerization was achieved by use of 3,6-bis[(trimethylsilyl)methyl]-1,2-diisocyanobenzene (**1b**) and (quinoxalinyl)nickel complex having Me_3P ligands (**5**). An initiating nickel(II) catalyst (**5**) was produced by the reaction of **1b** with **2a** and was so stable to allow isolation by TLC (39%) and full characterization (IR, ^1H and ^{13}C NMR, combustion analysis).[5] Oligomerization of **1b** induced by **5** with varying feeding ratio (**1b**/**5**) was carried out in THF at room temperature, and poly(2,3-quinoxaline) (**6**) was obtained in good yield after the quenching with MeMgBr (Table I). The higher poly(2,3-quinoxaline) was produced with the higher feeding ratio (**1b**/**5**). In addition, the molecular weight distribution (polydispersity) of the resultant polymer which was determined by using polystyrene as internal standard in measuring GPC profile was quite narrow and close to a monodisperse distribution ($\bar{M}_w/\bar{M}_n = 1.05$–$1.10$) (Figure 1). The sterically bulky (trimethylsilyl)methyl substituents on the neighboring quinoxaline ring may stabilize the propagating $(Me_3P)_2Cl$(quinoxalinyl)Ni(II) complex, which can be assumed to be of a square pyramidal structure based on the X-ray crystal study of analogous palladium(II) complex,[2] and make the living polymerization of **1b** feasible.[6]

The achievement of the living polymerization of 1,2-diisocyanoarene by nickel(II) catalyst provides a synthetic route to new poly(2,3-quinoxaline) with a controlled molecular-weight and a narrow molecular weight distribution.

REFERENCES AND NOTES

1. J. K. Stille, "Encyclopedia of Polymer Science and Technology," Vol. 11, Interscience: New York, 1969, p 389.
2. Y. Ito, E. Ihara, M. Murakami, and M. Shiro, *J. Am. Chem. Soc.*, **112**, 6446 (1990).
3. W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.* **12**, 30 (1979) and references cited therein.
4. Though **3a** was not so stable as **5**, **3a** was identified by isolation and its ^{1}H NMR spectrum; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, $J_{\text{P-H}}=3.9$ Hz, 18 H), 2.40 (s, 3 H), 2.44 (s, 3H), 2.54 (s, 3H), 2.70 (s, 3H), 2.85 (s, 3H), 7.3—7.7 (m, 4H).
5. **5**: mp 178°C (dec). IR (KBr) 2964, 2900, 1508, 1248, 1158, 952, 848, 734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.19 (s, 9H), 0.04 (s, 9H), 0.89 (t, $J_{\text{P-H}}=3.9$ Hz, 18H), 2.60 (s, 3H), 2.67 (s, 2H), 2.75 (s, 2H), 7.05 (d, $J=7.4$ Hz, 1H), 7.17 (d, $J=7.4$ Hz, 1H), 7.3—7.7 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −1.43, −0.80, 12.41 (t, $J_{\text{P-C}}=13.9$ Hz), 20.55, 20.68, 22.11, 124.75, 125.88, 127.00, 128.09 (t, $J_{\text{P-C}}=3.4$ Hz), 128.80, 131.96, 133.59, 135.04, 136.45, 137.85, 139.58, 139.76, 153.04. *Anal.* Calcd for $C_{29}H_{49}ClN_2NiP_2Si_2$: C, 54.60%; H, 7.74%; N, 4.39%. Found: C, 54.61%; H, 7.90%; N, 4.44%.
6. The ortho substituents of aryl group were found to have an effect to stabilize [1-(arylimino)alkyl]metal; M. Murakami, H. Ito, and Y. Ito, *J. Org. Chem.*, **53**, 4158 (1988); M. Murakami, H. Ito, W. A. W. A. Bakar, A. B. Baba, and Y. Ito, *Chem. Lett.*, 1603 (1989).