Macromolecules
COMMUNICATION TO THE EDITOR

Macromolecules **2009**, *42*, 5909–5912 **5909**
DOI: 10.1021/ma901069q

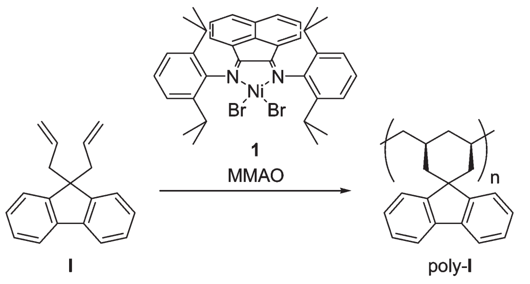
Cyclopolymerization of 9,9-Diallylfluorene Promoted by Ni Complexes. Stereoselective Formation of Six- and Five-Membered Rings during the Polymer Growth

Daisuke Takeuchi, Yusuke Fukuda, Sehoon Park, and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.

Received May 15, 2009
Revised Manuscript Received July 21, 2009

Cyclopolymerization of 1,6-heptadiene catalyzed by early transition metal complexes yields the polymers having five- and/or six-membered rings along the polymer chain.[1] The reaction was studied as a useful probe for regioselectivity in insertion of α-olefins[1i] because intermolecular 1,2- or 2,1-insertion of a C=C bond of the diene monomer would determine size of the ring formed by subsequent intramolecular 1,2-insertion (cyclization) (Scheme 1). Polymerization of 1,5-hexadienes and 1,6-heptadienes by the metallocenes produces the polymers with 1,3-cyclopentanediyl or 1,3-cyclohexanediyl groups in the repeating units, via intermolecular 1,2-insertion rather than 2,1-insertion.[1] The obtained polymers, however, contain trans- and cis-fused rings randomly in most cases due to low stereoselectivity in the cyclization.[1f] In contrast, the cyclopolymerization of 1,6-heptadiene catalyzed by the Fe and Co complexes with a bis(imino)pyridine ligand affords the polymer composed of cis and trans-controlled 1,2-cyclopentanediyl groups.[2] Pd−diimine complexes also bring about cyclopolymerization of substituted 1,6-dienes to yield the polymers having *trans*-1,2-cyclopentane groups in the repeating unit.[3] Formation of the five-membered rings in the reaction catalyzed by late transition metal complexes is consistent with tendency of facile occurrence of 2,1-insertion of α-olefins in their polymerization catalyzed by Pd and Fe complexes.[4] Coates employed a chiral Ni−diimine complex as the catalyst in the polymerization of α-olefins and obtained the polymer having methyl branches.[5] They proposed preferential 1,2-insertion of the monomer into the Ni−polymer bond followed by chain walking reaction to generate primary alkyl−Ni bond. Thus, we conducted the cyclopolymerization using the Ni catalysts with diimine ligands because it would provide new polymers and further information of insertion mode of substituted olefins and because there have been no reports on such reactions. In this paper, we report the cyclopolymerization of 1,6-heptadiene derivatives catalyzed by the Ni− and Pd−diimine complexes and regio- and stereoselectivity of the reaction.



(1)

Scheme 1. Relationship between the Insertion Mode of Vinyl Group and Ring Size of the Formed Polymer in Cyclopolymerization of Non-Conjugated Dienes

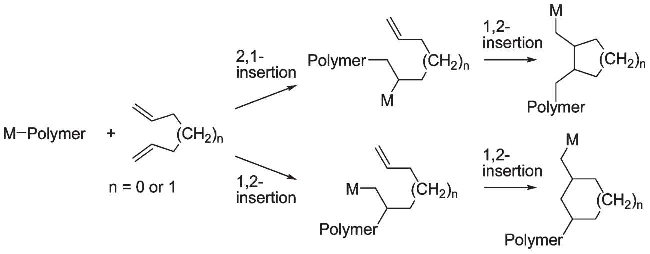
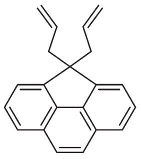


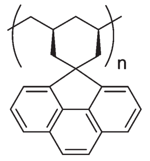
Table 1. Cyclopolymerization of 1,6-Heptadienes by Ni Complexes[a]

run	monomer	Ni complex	time/h	yield (%)	M_n[b]	M_w/M_n[b]
1	**I**	**1**	3	51	6100	1.36
2	**II**	**1**	24	15	2700	1.53
3	**III**	**1**	72	trace		
4	**I**	**2**	6	86	18200	2.05
5	**I**	**3**	18	53	23900	1.77

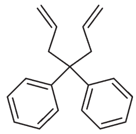
[a] Reaction conditions: Ni complex = 10 μmol, [Al]/[Ni] = 300, [monomer]/[Ni] = 100, and solvent = toluene (2 mL), at 0 °C. [b] Determined by GPC based on a polystyrene standard.

Stirring a toluene solution of 9,9-diallylfluorene (**I**, 0.246 g, 1.00 mmol), Ni-diimine complex with 2,6-diisopropylphenyl groups at the coordinating nitrogen (**1**, 0.010 mmol), and modified methylaluminoxane (MMAO) ([Al]/[Ni] = 300) at 0 °C for 3 h affords poly-**I** in 51% yield (eq 1). The obtained polymer is soluble in common organic solvents, and GPC analysis of the polymer shows molecular weight, M_n = 6100 and M_w/M_n = 1.36 (Table 1, run 1). ^{1}H NMR spectrum of poly-**I** in $C_2D_2Cl_4$ at 130 °C contains no signals in the range, δ 3 − 6, indicating almost complete cyclization during the polymer growth. Figure 1(A) shows ^{13}C{^{1}H} NMR spectrum of the polymer. Four signals at δ 139.4, 140.3, 152.3, and 154.0 are assigned to the aromatic carbons of the five-membered ring (f, f′, g, and g′), while the remaining quaternary carbon (e) exhibits a single signal at δ 51.0. Positions of the signals attributed to the CH and CH_2 carbons (δ 29.1, 35.8, 39.0, and 42.1) differ distinctly from those of polymers of **I** with cis- or trans-1,2-cyclopentane groups[2] but are almost similar to those of a model compound (*cis*- and *trans*-3,5-diethylspiro-[cyclohexane-1,9′-fluorene]). These results and appearance of two pairs of the signals due to the carbons f, f′, g, and g′ indicate that the obtained polymer has *cis*-1,3-cyclohexanediyl groups along the polymer.


II



poly-II


III

Nickel complex **1** promotes cyclopolymerization of 4,4-diallyl-4*H*-cyclopenta[def]phenanthrene (**II**) to produce the corresponding polymer, poly-**II**, in 15% yield (Table 1, run 2). ^{13}C{^{1}H} NMR spectrum of the polymer, thus obtained, shows the signals

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*Corresponding author. E-mail: kosakada@res.titech.ac.jp.

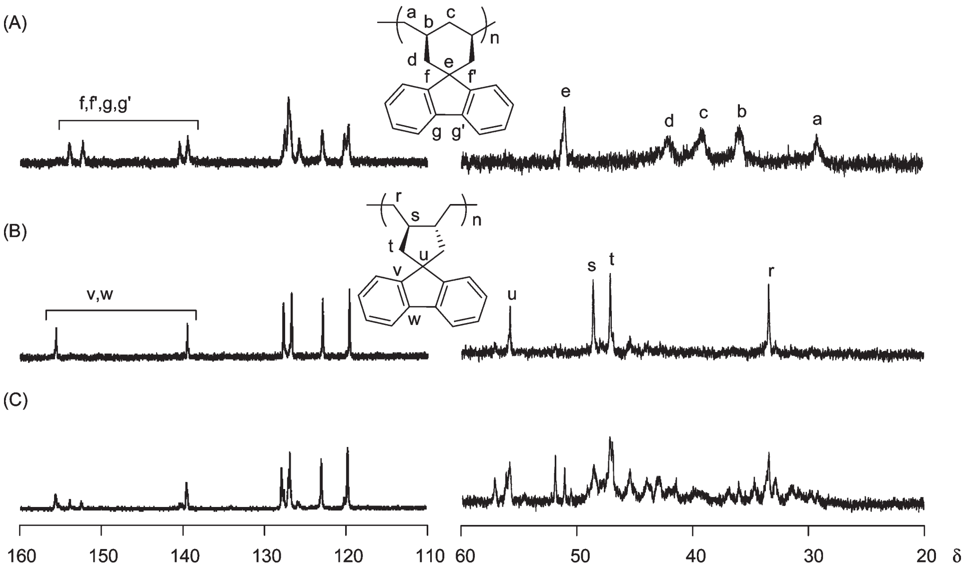
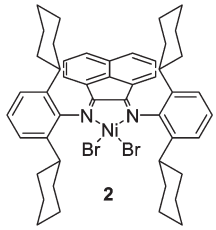
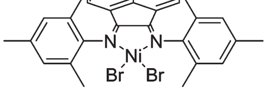


Figure 1. $^{13}C\{^1H\}$ NMR spectra in $C_2D_2Cl_4$ at 130 °C of polymers of **I** obtained by (A) **1**, (B) **2**, and (C) **3**.

at similar positions to those of poly-**I**, and indicates the structure with *cis*-1,3-cyclohexanediyl groups. 4,4-Diphenyl-1,6-heptadiene (**III**), however, does not polymerize under similar conditions (Table 1, run 3).



2



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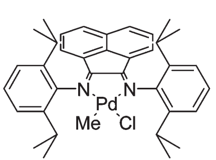
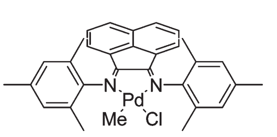
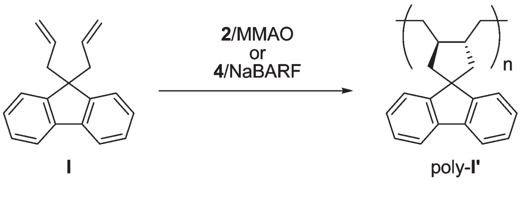


4



5

Ni complex **2** with 2,6-dicyclohexylphenyl group at the imine nitrogen of the ligand also promotes the cyclopolymerization of **I** in the presence of MMAO to produce poly-**I'** having a different structure from poly-**I** (eq 2).



(2)

Diimine Pd complexes **4** and **5** are also effective for the polymerization of **I** in the presence of NaBARF (BARF = $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4^-]$) to afford poly-**I′**. $^{13}C\{^1H\}$ NMR spectrum of poly-**I′** obtained by using the catalysts **2**/MMAO, **4**/NaBARF, and **5**/NaBARF revealed the presence of the repeating units containing *trans*-1,2-cyclopentane ring, exclusively. Each carbon signal of the cyclopentane ring of the polymer obtained by **2**/MMAO appears as almost single peak, which may indicate high degree of controlled tacticity of the obtained polymer. It is not clear, however, whether the obtained polymer is of threo-diisotactic or threo-disyndiotactic structure. Catalyst **3**/MMAO polymerizes **I**, and the $^{13}C\{^1H\}$ NMR spectrum suggests that the polymer contains both *cis*-1,3-cyclohexanediyl and *trans*-1,2-cyclopentanediyl groups (Figure 1 (C)).

Scheme 2 (i) shows the plausible mechanism for ring formation in the cyclopolymerization of **I** catalyzed by **1**/MMAO (R = ^{i}Pr). The Ni complex prefers coordination of **I** with orientation of the C═C bond shown in **A** so as to avoid steric repulsion between the monomer and of an N-aryl group of the ligand. Smooth migratory insertion of the C═C bond of **A** into the Ni-polymer bond leads to intermediate **B** having primary alkyl group bonded to Ni, and subsequent cyclization affords the six-membered ring at the growing end of the polymer. Ni complex **3** with less bulky diimine ligand than **1** allows not only 1,2-insertion but also 2,1-insertion of a C═C bond of the monomer. The Pd-complex-catalyzed reaction produces the polymer with five-membered rings via intermolecular 2,1-insertion of a C═C bond. Larger covalent bond radius of Pd (1.28 Å) than of Ni (1.15 Å) may release steric repulsion between the ligand and the π-coordinated monomer prior to insertion, which may be one of the reason for the 2,1-insertion. Scheme 2(ii) shows a possible explanation for formation of the five-membered ring in the polymerization of **I** cataylzed by **2**/MMAO. Recently, Rieger studied structures of the Ni-diimine complex having two substituted aryl groups at 2,6-positions of the N−Ar groups in the ligand, and confirmed possible rotation of the N−Ar bond due to repulsion between these substituents.[6] An aryl group with two bulky cyclohexyl groups of **2** may also twist to some degree, which lowers symmetry of the C_{2v}-symmetric catalyst. This change in structure of the complex facilitates coordination of the monomer with opposite direction to that of the intermediate of polymerization catalyzed by **1**/MMAO (**A′**) and promotes 2,1-insertion (**B′**) and formation of the five-membered ring (**C′**). The above mechanisms are based on our results as well as those for previous ones of the late transition metal catalysts in polymerization. The generality of them will be established after further mechanistic studies based on experiments and calculation.

Table 2 summarizes thermal properties of polymers of **I** obtained by Ni and Pd complexes. TG analysis of poly-**I** obtained by **1**/MMAO (M_n = 10300, M_w/M_n = 1.66) shows T_d^5 at 383 °C, which is higher than poly-**I′** obtained by **4**/NaBARF (M_n = 15000, M_w/M_n = 1.70, T_d^5 = 274 °C). The former polymer does not show glass transition in the region of −50 to +300 °C, whereas poly-**I′** shows T_g at 154 °C. The polymer of **I** obtained by

Table 2. Thermal Properties of the Polymer of I Obtained by Ni and Pd Complexes

		six-membered ring		five-membered ring					
run	complex	cis	trans	cis	trans	M_n[a]	M_w/M_n[a]	T_d^5[b]	T_g[c]
1	**1**	yes	no	no	no	10300	1.66	383	
2	**4**	no	no	no	yes	15000	1.70	274	154
3	**3**	yes	*d*	*d*	yes	13000	1.61	338	209

[a] Determined by GPC based on a polystyrene standard. [b] Determined by TG. [c] Determined by DSC. [d] Not confirmed.

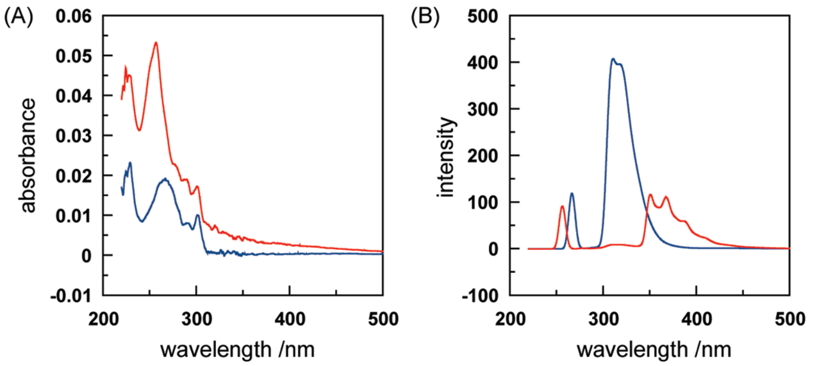
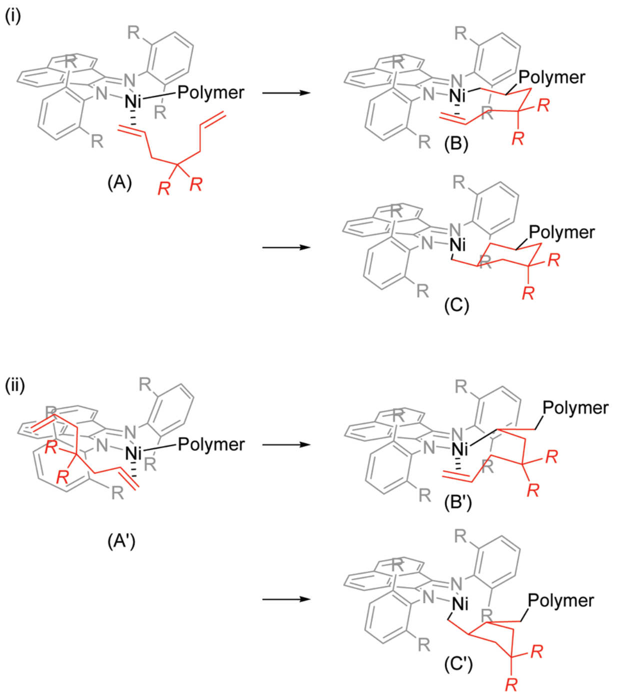


Figure 2. (A) UV−vis and (B) PL spectra in CH_2Cl_2 at room temperature of poly-**I** (red line) and poly-**II** (blue line) obtained by **1**-MMAO.

Scheme 2. Mechanism of Cyclopolymerization of I Catalyzed by (i) 1 and (ii) 2



3/MMAO which contains both five- and six-membered rings, shows T_d^5 and T_g between those of the two polymers (338 and 209 °C, respectively). Thus, the polymer containing cis-fused six membered rings in this study is thermally more stable compared to those containing trans-fused five membered rings obtained by the cyclopolymerization catalyzed by the Pd complex.

Poly-**I** and poly-**II** (CH_2Cl_2 solution, 1 μmol (repeating unit) L^{-1}) absorbed at λ_{max} = 267 nm (ε = 2090 L mol^{-1} cm^{-1}) and at λ_{max} = 257 (ε = 5270 L mol^{-1} cm^{-1}), respectively (Figure 2). Poly-**I**, upon excitation at λ_{ex} = 267 nm, shows fluorescence at λ_{em} = 311 nm. The quantum yield (Φ) was calculated to be 20%, which is lower than that of the corresponding monomer **I** (Φ = 27%, λ_{ex} = 266 nm (ε = 2280 L mol^{-1} cm^{-1}), λ_{em} = 311 nm). Poly-**II** also shows weak fluorescence at λ_{em} = 367 nm upon irradiation on λ_{ex} = 257 nm. In this case, the quantum yield (Φ = 3.3%) is almost similar to that of **II** (Φ = 3.5%, λ_{ex} = 257 nm (ε = 5640 L mol^{-1} cm^{-1}), λ_{em} = 351 nm).

In summary, the Ni complexes with diimine ligands promote cyclopolymerization of 9,9-diallylfluorene to give the polymer with five- and/or six-membered rings depending on the catalyst. This result is in contrast to the cyclopolymerization of the same monomer by Fe, Co, and Pd complexes, where only the polymer containing five-membered ring is obtained. The complexes with 2,6-diisopropylphenyl group and 2,6-dicyclohexylphenyl group show high selectivity in the ring formation, but the structure of the obtained polymer are different.[7]

Acknowledgment. This work was supported by a Grant-in-Aid for Young Scientist (No. 18750094) for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Text giving experimental procedures for preparation of monomer and model compound (including a reaction scheme) and polymerization, a table of polymerization data, and figures showing NMR spectra of the model compound and produced polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Note added in proof: Hf-catalyzed cyclopolymerization of 1,6-heptadiene to produce the polymer with *cis*-1,3-cyclohexane rings and isotactic structure was reported almost at the same time as this paper. Edson, J. B.; Coates, G. W. *Macromol. Rapid Commun.*, in press.