Stereo- and regiospecific polymerization of cyclic conjugated dienes using highly active nickel catalysts†

Mitsuru Nakano,* Qing Yao, Arimitsu Usuki, Shinobu Tanimura and Takaaki Matsuoka

Functional Polymer Synthesis Laboratory and Computational Materials Engineering Laboratory, Toyota Central R&D Labs., Inc., Yokomichi 41-1, Nagakute, Aichi 480-1192, Japan. E-mail: mnakano@mosk.tytlabs.co.jp; Fax: +81-561-63-6137; Phone: +81-561-63-5251

Received (in Cambridge, UK) 15th August 2000, Accepted 2nd October 2000
First published as an Advance Article on the web 31st October 2000

A markedly active and selective nickel catalyst, bis(allylnickel bromide)–methylaluminoxane, has been developed for cyclohexa-1,3-diene polymerization; the obtained crystalline polymer is a 1,4-linked *cis*-syndiotactic structure as determined by NMR and molecular dynamics using the COMPASS force field.

Interest in cyclic olefin polymers has been growing dramatically over the past decade due to their thermal and chemical stabilities and high mechanical strength and modulus that originates from the restricted molecular motion of a cyclic group. In addition, cyclic olefin polymers are recognized as promising optical materials because of their low birefringence. Among the various cyclic unsaturated compounds, we have focused on cyclohexa-1,3-diene (CHD) because it can be converted from cyclohexene, a known inexpensive by-product from ε-caprolactam synthesis. However, the monomer is so bulky that most catalysts are not effective for CHD polymerization.[1] Grubbs and coworkers reported that bis[(η^3-allyl)(trifluoroacetato)nickel(II)] catalyzed the polymerization of CHD derivatives, though the catalytic activity was not high enough for rapid CHD homopolymer production.[2] Recently, *n*-BuLi–TMEDA was developed for living anionic polymerization of CHD by Natori *et al.*[3] In this anionic polymerization system, however, the regio- and stereostructure of poly(CHD) were poorly controlled. To our knowledge, there are very few reports of initiators having high regio- and stereoselectivity *and* high catalytic activity. We herein report a markedly active bis(allylnickel bromide) (ANiBr)–methylaluminoxane (MAO) catalyst for CHD polymerization. Furthermore, the polymer obtained from the catalyst system exhibited a very high regio- and stereoregular structure, which was fully characterized by NMR and molecular dynamics using the COMPASS force field.

CHD polymerization catalyzed by ANiBr–MAO was rapidly completed at rt.[4] As shown in Table 1, the polymer yields are quite high, especially in halogenated aromatics or in cyclohexane. On the other hand, both the zirconium- and titanium-based catalysts had low activities for CHD polymerization, resulting in low yields of polymer. Late transition metal catalysts such as neutral allylnickel and cationic allylpalladium complexes were also ineffective for CHD polymerization. The ANiBr–MAO catalyst exhibited extremely high activity for the following reasons: (1) allylnickel should have an identical structure with the propagating species, allowing immediate initiation. (2) MAO activates ANiBr to form a highly electron-deficient species. (3) ANiBr has very high solubility in various organic solvents. (4) Allylnickel species should have enough space for the sterically demanding monomer.

In order to explore the polymerization mechanism, we synthesized the well-structured single component Ni complex[5] $[(\eta^3\text{-allyl})\text{Ni(cycloocta-1,5-diene)}]^+\text{B}(\text{C}_6\text{F}_5)_4^-$ for CHD polymerization. Although the complex exhibited slightly lower catalytic activity than ANiBr–MAO, the obtained polymer showed the same regio- and stereostructure as the one produced using ANiBr–MAO (*vide infra*), which means that the cationic allylnickel is presumably the true propagating species in the CHD polymerization.

Since the CHD homopolymer[6] is insoluble in any organic solvents, buta-1,3-diene (BD) was copolymerized with CHD to determine the regiostructure of the polymer obtained.[7] Since no signals of the 1,2-poly(BD) units were observed around 114 and 143 ppm in the ^{13}C NMR spectrum of the copolymer, only the 1,4-poly(BD) units were taken into account to assign the ^{1}H NMR signals of poly(BD). Based on ^{1}H COSY spectra,† all signals were assigned as follows (Fig. 1). For the poly(CHD) unit, protons of H_o, H_a and H_b are identified with peak A at 5.73 ppm, peak D at 2.01 ppm and peak E at 1.56 ppm, respectively. On the other hand, peaks B and C are due to protons of H_o' and H_a' in the 1,4-poly(BD) unit, respectively. Assuming that the integral value of peak B is 2.0, peak A can be estimated to be 5.27. Concerning the number of protons in poly(CHD), H_o is equal to H_a in the 1,4-unit while H_o is 3/2 of H_a in the 1,2-unit. Therefore, the calculated value of the integral area of peaks C

Table 1 Polymerization of cyclohexa-1,3-diene using various transition metal catalysts[a]

Entry	Catalyst	Cocatalyst	[Al]/[Cat]	Solvent	Time	Polymer yield (%)
1	ANiBr	MAO	100	Toluene	5 min	78
2	ANiBr	MAO	100	Chlorobenzene	< 1 min	88
3	ANiBr	MAO	100	*o*-Dichlorobenzene	< 1 min	96
4	ANiBr	MAO	100	Cyclohexane	< 1 min	92
5	$(\text{EBTHI})\text{ZrCl}_2$[b]	MAO	1000	Toluene	5 days	10
6	CpTiCl_3	MAO	1000	Toluene	4 days	30
7	$[(\eta^3\text{-C}_3\text{H}_5)\text{Ni(OC(O)CF}_3)]_2$	None		Toluene	34 hours[c]	40
8	$[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}]^+\ \text{SbF}^-$	None		Dichloromethane	7 days	10
9	$[(\eta^3\text{-C}_3\text{H}_5)\text{Ni(cod)}]^+\ [\text{B}(\text{C}_6\text{F}_5)_4]^-$	None		*o*-Dichlorobenzene	20 min	72

[a] Polymerization conditions: $[\text{CHD}]_o = 1.5$ mol l^{-1}, $[\text{CHD}]_o/[\text{Cat}] = 500$, at rt. [b] $(\text{EBTHI})\text{ZrCl}_2$: *rac*-Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride. [c] Polymerization was carried out at rt for 24 h followed by 50 °C for 10 h.

---

† Electronic supplementary information (ESI) available: ^{1}H COSY spectra of the CHD–BD copolymer. See http://www.org/suppdata/cc/b0/b006676l/

DOI: 10.1039/b006676l

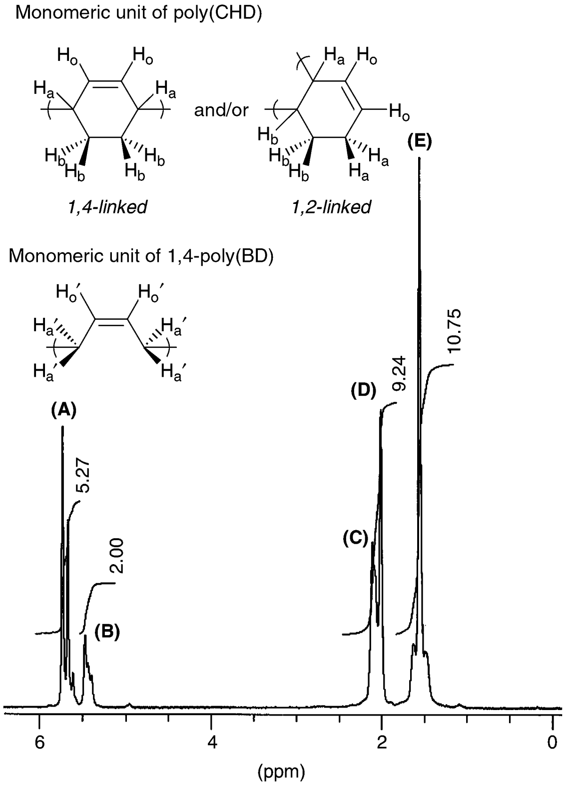

Fig. 1 ^{1}H NMR spectrum of CHD–BD copolymer catalyzed by ANiBr–MAO (polymer composition of [CHD]/[BD] = 72/28).

and D should be in the region from 9.27 (= 2.00 × 2 + 5.27) to 11.91 (= 2.00 × 2 + 5.27 × 3/2). The observed value of 9.24 is practically the same as 9.27, which means the CHD segment is perfectly 1,4-linked as well as the poly(BD) segment. In addition, the observed integral value of peak E is also very close to the calculated one, leading us to postulate that 1,4-linkage is dominant in the poly(CHD) main chain. Another experiment confirming the regiostructure was the synthesis of CHD oligomer anchored by a soluble poly(norbornene) with high molecular weight. The propagating species of norbornene polymerization initiated with ANiBr–MAO was long-lived enough to produce a soluble norbornene–CHD diblock copolymer. The ^{1}H NMR spectrum showed a sharp single peak of olefinic protons at 5.75 ppm, which is totally different from the doublet signal of anionically polymerized CHD.[3]

As shown in Fig. 2(a), the poly(CHD) catalyzed by *n*-BuLi-based initiator revealed the typical amorphous XRD pattern even when the polymer main chain consisted of >90% 1,4-units.[3] On the other hand, the poly(CHD) obtained with the ANiBr–MAO catalyst was found to be highly crystalline with three major peaks based on a X-ray powder diffraction (XRD) spectrum (Fig. 2(b)). Additionally, the crystalline XRD pattern did not change when the poly(BD) unit was introduced into the main chain though the peak intensity decreased. The crystallinity of poly(CHD) initiated with ANiBr–MAO catalyst should originate from the stereoregular structure. In general, there are four stereoisomers, *i.e. cis*-isotactic, *cis*-syndiotactic, *trans*-isotactic and *trans*-syndiotactic in 1,4-linked poly(CHD).[8] We performed constant-temperature and constant-pressure molecular dynamics simulations of the crystalline poly(CHD) at 300 K and under zero pressure using the COMPASS force field. By use of the simulated atomic coordinates of the crystalline poly(CHD), time-averaged X-ray powder diffraction spectra were calculated. Interestingly, it was confirmed that only the simulated crystalline structure of the *cis*-syndiotactic 1,4-linked poly(CHD) could reproduce the experimental XRD pattern shown in Fig. 2(c). Although Ni-catalyzed poly(CHD) is believed to be a *cis*-rich structure from a *syn*-coordinative mechanism,[9] this simulation is the first evidence of the stereoregular structure of poly(CHD).

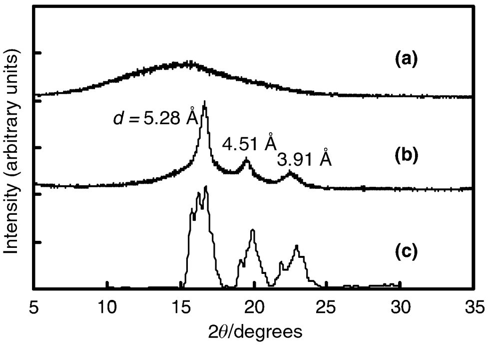

Fig. 2 X-ray diffraction patterns of (a) poly(CHD) obtained from *n*-BuLi–TMEDA, (b) poly(CHD) obtained from ANiBr–MAO, (c) *cis*-syndiotactic 1,4-poly(CHD) simulated using the COMPASS force field.

In summary, it was found that the ANiBr–MAO catalyst showed remarkably high activity for the CHD polymerization. The obtained polymer was a *cis*-syndiotactic 1,4-linked structure, which induced crystallization. In order to precisely control the poly(CHD) structure, further intensive studies using other nickel catalysts with dimine or phenanthroline ligands are in progress.

The authors are grateful to Ms K. Fukumoto for the NMR analyses.

Notes and references

1 G. Lefebvre and F. Dawans, *J. Polym. Sci., Part A*, 1964, **2**, 3277; P. E. Cassidy, C. S. Marvel and S. Ray, *J. Polym. Sci., Part A*, 1965, **3**, 1553; Y. Imanishi, T. Yamane, S. Kohjiya and S. Okamura, *J. Macromol. Sci.-Chem.*, 1969, **A3**, (**2**), 243; Y. Imanishi, K. Matsuzaki, T. Yamane, S. Kohjiya and S. Okamura, *J. Macromol. Sci.-Chem.*, 1969, **A3**, (**2**), 249; B. A. Dolgoplosk, S. I. Beilin, Yu. V. Korshak, G. M. Chernenko, L. M. Vardanyan and M. P. Teterina, *Eur. Polym. J.*, 1973, **9**, 895; A. Sen and T. Lai, *Organometallics*, 1982, **1**, 415; H. R. Allcock, G. K. Dudley and E. N. Silverberg, *Macromolecules*, 1994, **27**, 1039.

2 D. L. Gin, V. P. Conticello and R. H. Grubbs, *J. Am. Chem. Soc.*, 1994, **116**, 10507.

3 I. Natori, *Macromolecules*, 1997, **30**, 3696; I. Natori and S. Inoue, *Macromolecules*, 1998, **31**, 4687.

4 A typical polymerization was performed with stirring at rt in a 20 ml glass bottle which was successively charged with 4.5 ml of toluene, 1 g (12.5 mmol) of CHD, 4.4 mg (24 μmol) of ANiBr, and 0.95 g of MAO (toluene solution, 2.6 mmol of Al). The polymerization solution immediately became heterogeneous at rt as a white precipitate formed. The reaction was quenched in a solution containing 500 ml MeOH and 10 ml 1 M HCl with a small amount of 2,6-di-*tert*-butyl-4-methylphenol as the antioxidant reagent. After drying under vacuum, an off-white powdery polymer was obtained.

5 J. Ascenso, A. R. Dias, P. T. Gomes, C. C. Romao, D. Neibecker, I. Tkatchenko and A. Revillon, *Makromol. Chem.*, 1989, **190**, 2773.

6 CP–MAS ^{13}C NMR (300 MHz): δ 130 (–CH_2=), 40 (–H*C*<), 25(–CH_2–). Elemental analysis. Calcd for $(C_6H_8)_n$: C, 90.0; H,10.0. Found : C, 87.4; H, 9.8. The obtained polymer was stable up to 320–330 °C under N_2 and the melting point was not observed below 320 °C by DSC or a polarized microscopy.

7 The copolymerization of CHD with BD was accomplished by ANiBr–MAO catalyst to produce a copolymer almost quantitatively (yield 95%). While the monomer feed ratio was [CHD]/[BD] = 70/30, the polymer composition was determined to be [CHD]/[BD] = 72/28 by ^{1}H NMR. Based on GPC in *o*-dichlorobenzene at 135 °C, M_n, M_w and PDI were estimated to be 29.3×10^3, 63.0×10^3 and 2.15 (*vs.* polystyrene standards), respectively. Although the relative reactivity of CHD was somewhat higher than that of BD in the copolymerization, the regiostructure of the CHD segment did not change throughout the polymerization.

8 In this context, *cis–trans* means that bridging C–C bonds between monomer units are in a *cis–trans* relationships on the face of the cyclohexenyl ring.

9 L. Porri and M. Aglietto, *Makromol. Chem.*, 1976, **177**, 1465.