Living Coordination Polymerization of Alkylallenes by π-Allylnickel Catalyst: Observation of an Extremely High Polymerizability of 1,2-Cyclononadiene

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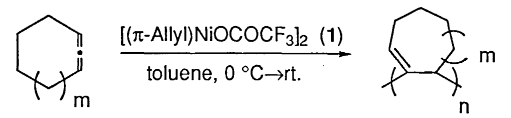
(Received August 4, 1997; CL-970606)

The coordination polymerization of cyclic allenes by $[(\pi\text{-allyl})NiOCOCF_3]_2$ was investigated to produce polymers with narrow molecular weight distributions in high yields. The polymerization proceeded in a living mechanism, and the molecular weight of the resulting polymer had a linear relationship with the monomer feed ratio. Especially, the polymerization of 1,2-cyclononadiene (i.e., a monomer with substantial ring strain) proceeded dramatically fast compared with acyclic monomers.

The living polymerization technique is of importance to obtain well-defined polymers (i.e., those with predictable molecular weights, narrow molecular weight distributions, and functionalized ends).[1] It is also quite important to construct a living polymerization system yielding a precision reactive polymers, because they are regarded as key synthetic intermediates of numerous functional polymers and their characters (i.e., molecular weights, molecular weight distributions, stereoregularities etc.) directly reflect on the functional polymers derived from the subsequent polymer reactions. Allene derivatives are one of a candidate to produce polymers bearing reactive double bonds through 1,2- or 2,3-polymerization. In order to obtain precision polymers from allene derivatives, we have recently reported the living coordination polymerization of alkoxyallenes,[2] arylallenes,[3] and alkylallenes,[4] in which the relationship between the monomer structures and their polymerizability has been examined. In the case of alkylallenes, the number and the position of the substituents effect largely on the polymerizability (i.e., the polymerization rate is in the order of monoalkyl- > α,α-dialkyl- > α,γ-dialkylallenes). Here, we found an extremely high polymerizability of 1,2-cyclononadiene (**2a**), which has substantial ring strain energy, in the coordination polymerization of cyclic alkylallenes (**2a** and 1,2-cyclotridecadiene (**2b**)) (Scheme 1).



2a (m=3), 2b (m=7)

Scheme 1.

The coordination polymerization of 1,2-cyclononadiene (**2a**) (40 equiv. relative to **1**) by **1**[5] was carried out at 0 °C to ambient temperature in toluene. The reaction completed smoothly within 30 min to give a polymer (M_n=6,390, M_w/M_n=1.09) in 96% yield.[6] The poly(**2a**) was confirmed to have an objective head to tail structure having one double bond in each repeating unit.[6] By the polymerization of **2a** under the various feed ratio of [**2a**]/[**1**], the polymers were obtained almost quantitatively, whose number average molecular weights (M_n) had a good linear relationship with the monomer feed ratio and the molecular weight distribution was always narrow (Figure 1). Accordingly, it was supported that the present polymerization proceeds through a living mechanism.

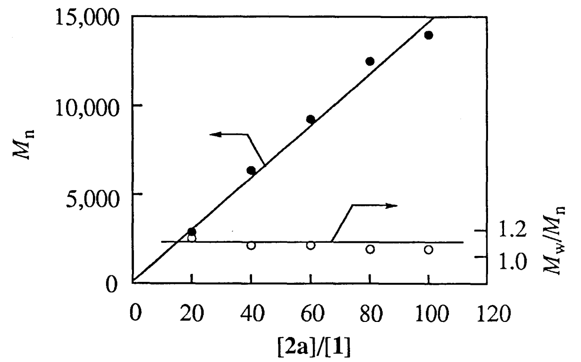


Figure 1. M_n and M_w/M_n vs. the feed ratio ([**2a**]/[**1**]).

Likewise, the polymerization of 1,2-cyclotridecadiene (**2b**) (40 equiv. relative to **1**) by **1** also produced the corresponding polymer (M_n=8,930, M_w/M_n=1.10) in 96% yield,[7] though the polymerization took a longer reaction period (ca. 3 days).

To estimate the polymerization rates of **2a** and **2b** and to compare them with those of acyclic monomers (1,2-nonadiene (**2c**) and 2,3-nonadiene (**2d**)), the monomer conversions of **2a** and **2b** were monitored by GC after designated reaction times (Figure 2).[8]

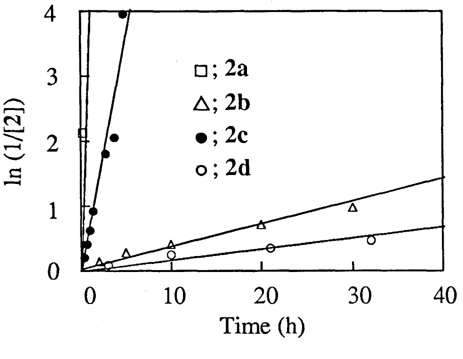


Figure 2. Time - ln(1/[2]) curves for **2a**, **2b**, **2c**, and **2d** ($[2]_0$=1.0 M, $[2]_0/[1]$=40).

From the results, both **2a** and **2b** were found to have higher polymerizabilities in comparison with the acyclic α,γ-dialkylallene (**2d**),[9] although they have α,γ-disubstituted structure. Especially, the polymerization of **2a** was much faster than that of the monoalkylallene (**2c**). Since **2a** has been reported to be the smallest cyclic allene system,[10] the remarkably high polymerizability of **2a** may be arisen from its large ring strain energy.[11] The release of the ring strain energy in **2a** by means of the monomer insertion toward the π-allylnickel species may be most probably the driving force for the observed high polymerizability.

References and Notes

1 For the recent review, see, for example: (a) M. Sawamoto *Petrotech (Tokyo)*, **19**, 814 (1996). (b) T. Aida *Petrotech (Tokyo)*, **19**, 811 (1996). (c) T. Endo and I. Tomita *Macromol. Symp.*, **84**, 73 (1994). (d) M. M. Green *Chemtracts: Macromol. Chem.*, **3**, 326 (1992). (e) R. H. Grubbs and W. Tumas *Science*, **243**, 907 (1989).

2 (a) I. Tomita, Y. Kondo, K. Takagi, and T. Endo *Macromolecules*, **27**, 4413 (1994). (b) I. Tomita, Y. Kondo, K. Takagi, and T. Endo *Acta Polymerica*, **46**, 432 (1995).

3 (a) K. Takagi, I. Tomita, and T. Endo *Macromolecules*, submitted. (b) I. Tomita, Y. Kondo, K. Takagi, and T. Endo *Polym. Prepr. Jpn.*, **44**, 1296 (1995).

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5 To a flask containing a magnetic stir bar, were added a toluene solution of **1** (2.0×10^{-2} mmol) and then **2a** (0.098 g, 0.80 mmol, 40 equiv. relative to **1**) at 0 °C and the polymerization was conducted at ambient temperature. After confirming the complete conversion of **2a** by gas chromatography (it required ca. 30 min), the solvent was removed under reduced pressure and the viscous product was dissolved into $CHCl_3$ (3 ml). By the precipitation in MeOH (100 ml), poly(**2a**) was obtained in 96% yield (0.094 g).

6 Poly(**2a**): ^{1}H NMR ($CDCl_3$, δ, ppm) 0.20-4.30 (-$(CH_2)_6$-, >CH-, 13H), 5.57 (=CH-, br, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 26.7, 27.6, 28.3, 52.9, 127.7, 139.5; IR (neat, cm^{-1}) 2922, 2851, 1655, 1478, 1443, 1263. From the ^{1}H NMR spectrum, the double bond on the polymer backbone was observed quantitatively by comparing the integral ratio of the double bond peak with aliphatic ones.

7 Though the polymerization medium became slightly turbid at the last stage of the polymerization, a polymer with narrow molecular weight distribution was obtained in high yields which is soluble in $CHCl_3$ and THF. From the ^{1}H NMR spectrum of poly(**2b**), the double bond in the polymer could be also detected quantitatively, similar to the case of poly(**2a**). Additionaly, the living character of the polymerization of **2b** was supported by the experiments varying the feed ratio of **2b**/**1**, where a linear relationship was observed between the monomer feed ratio and M_n of the polymer. Poly(**2b**): ^{1}H NMR ($CDCl_3$, δ, ppm) 0.20-4.30 (-$(CH_2)_6$-, >CH-, 21H), 5.24 (=CH-, br, 1H); ^{13}C NMR ($CDCl_3$, δ, ppm) 24.4, 27.5, 31.6, 49.7, 129.0, 142.3; IR (neat, cm^{-1}) 2930, 2857, 1638, 1462, 1446, 1265.

8 The polymerization of **2** ($[\mathbf{2}]_0/[\mathbf{1}]=40$, $[\mathbf{2}]_0=1.0$ M,) was performed in toluene containing *n*-tetradecane (0.038 M) as an internal standard at 0 °C similarly to the above mentioned procedure. After the designated reaction period at 0 °C, a small portion of the reaction mixture was sampled by the syringe (ca. 10 μl) and the conversion of the monomer was estimated by the GC analyses.

9 Although the polymerization of **2a** was too fast to follow the conversion continuously under the present experimantal conditions, the time-conversion curves of **2b** and **2c** were in good agreement with the first order kinetic equation (i.e., $-d[\mathbf{2}]/dt=k_{obs}[\mathbf{1}][\mathbf{2}]$). The first order kinetic coefficients for **2a**, **2b**, and **2c** were estimated to be 340, 1.19, and 0.80 l•mol^{-1}•h^{-1}, respectively, although the value for **2a** may include a substantial error.

10 W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962).

11 According to the calculation of the strain energies of **2a**, see, A. L. A. Frank and Y. Issa *J. Am. Chem. Soc.*, **99**, 7640 (1977). In the addition reaction of hydrogen bromide to cyclic allenes, more strained cyclic allene has been reported to afford a HBr adduct in higher yield (86 % from **2a**, 75 % from 1,2-cyclodecadiene, and 70 % from **2b**). See, S. N. Moorthy, A. Singh, D. Devaprabhakara *J. Org. Chem.*, **40**, 3452 (1975).