Macromolecules **1994,** *27,* 4413-4414 **4413**

A Novel Living Coordination Polymerization of Methoxyallene by π-Allylnickel Catalyst

Ikuyoshi Tomita, Yukiko Kondo, Koji Takagi, and Takeshi Endo*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama, 227 Japan

Received April 14, 1994

Revised Manuscript Received May 23, 1994

Allene derivatives are attractive monomers to produce reactive polymers bearing *exo*-methylene moieties in the side chain by the vinyl polymerization of either part of the cumulated double bonds. Previously, we have reported radical and cationic polymerizations of substituted allenes to obtain soluble polymers containing *exo*-methylene moieties.[1,2] These polymerization techniques, however, have low abilities to control the molecular weight and the structure (such as the double-bond content in the polymer chain).

Although several works on the coordination polymerization of allene derivatives using nickel and other transition-metal catalysts to produce poly(allene)s[3] have been reported, no further polymerization behaviors have been clarified. Recently, living polymerization systems of butadiene[4] and isocyanides[5] using η^3-allyl $NiOCOCF_3$ (1)[6] have been established where the molecular weight of the polymer can be controlled by the ratio of monomer to initiator.

In the coordination polymerization of allene derivatives, (η^3-allyl)metal intermediates might be continuously formed by the insertion of the monomer toward the initiator and the propagating species at the center carbon of the allene moieties. Additionally, the fact that propagating (η^3-allyl)-metals from allene derivatives do not have β-hydrogen may enhance the living polymerization. Thus, coordination polymerizations of methoxyallene (2) by 1 are examined here (Scheme 1).

Polymerization reactions were carried out by adding the monomer to a toluene solution of $1/PPh_3$ at 0 °C under nitrogen.[7] For example, in the polymerization of methoxyallene (2) at the feed ratio of [2]/[1] = 239, polymer 3 was obtained in 88% yield after precipitation with *n*-hexane.[8] The obtained 3 was soluble in organic solvents such as chloroform, dichloromethane, benzene, and tetrahydrofuran. The number-average molecular weight ($\bar{M}_n$) of 3 was estimated as 18 700 (GPC, on the basis of polystyrene calibration curves). As shown in Table 1 and Figure 1, $\bar{M}_n$ of 3 varied linearly by changing the [2]/[1] ratio. The molecular weight distributions ($\bar{M}_w/\bar{M}_n$) of the polymers obtained here were always less than 1.1.

The structure of 3 was determined by ^{1}H-NMR, ^{13}C-NMR, and IR spectra.[9] As shown in Figure 2, the ^{1}H-NMR spectrum gave the information of the unit ratio (*x*:*y* in Scheme 1) and the content of double bonds. The unit ratio was calculated as 32:68 from protons of double bonds. The integral ratio between these two peaks and the other peaks (1:3.54) was in good agreement with the expected value (1:3.52). Therefore, the obtained polymer contained only the expected two units in the structure (double-bond content, >99%). That is, either part of the double bond in the cumulated double bonds may selectively participate in polymerization.

Scheme 1

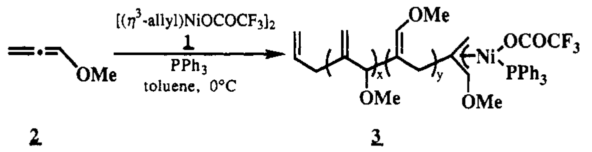

Table 1. Effect of the [2]/[1] Ratio on the Molecular Weight of the Resulting Polymer[a]

run	[2]/[1]	yield (%)[b]	$\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
1	39	82	2750	1.09
2	91	78	7620	1.07
3	103	76	8740	1.09
4	205	90	18100	1.08
5	239	88	18700	1.10

[a] Polymerizations were carried out for 6 h at 0 °C (ambient temperature) under nitrogen ([2] = 1.0 M). [b] *n*-Hexane-insoluble part. [c] GPC (THF, polystyrene standard).

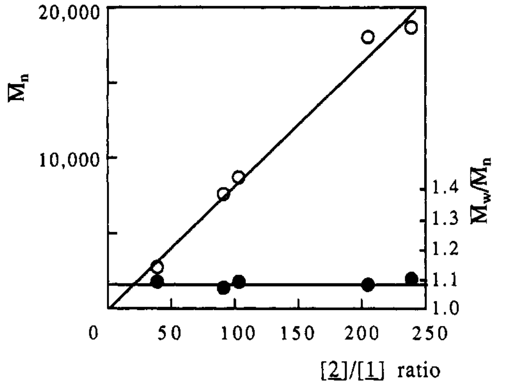

Figure 1. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ vs feed ratio of monomer to initiator ([2]/[1]).

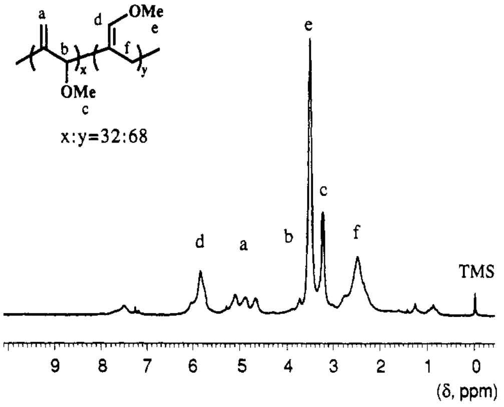

Figure 2. ^{1}H-NMR spectrum of 3.

From the time vs conversion curves of 2, the present polymerization was found to proceed following the first-order kinetics of the monomer concentration. After complete consumption of 2 (it took 5 h), the same amount of 2 was added, which again was consumed within an additional 5 h (Figure 3a). The relationship between the conversion of 2 and the molecular weight of the resulting polymer (3) was almost linear, and $\bar{M}_w/\bar{M}_n$ were always around 1.1 (Figure 3b). These results support that the present polymerization proceeds by a living mechanism.

As both the initiator and the propagating end have similar (η^3-allyl)nickel structures, the initiation efficiency may be supposed to be 100%, and the rate of initiation and that of propagation may be almost equal which is suitable for the living system.

0024-9297/94/2227-4413$04.50/0

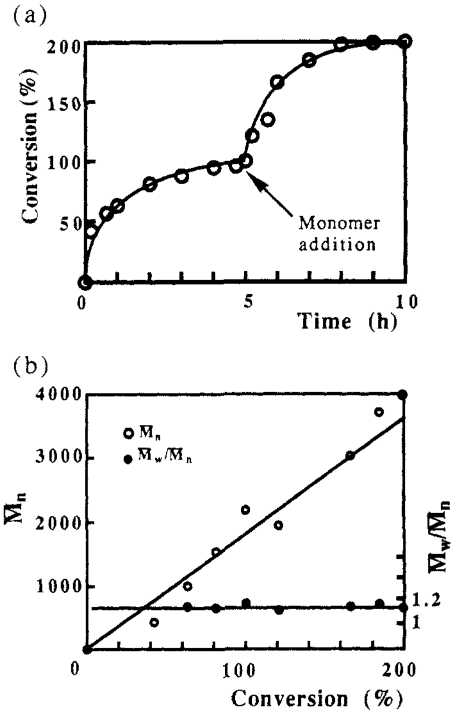

Figure 3. (a) Time vs conversion of 2. (b) $\bar{M}_n$ vs conversion of 2.

As the living polymerization system is suitable for the designed synthesis of macromolecules, end functionalization and block copolymerization are now in progress.

References and Notes

(1) Yokozawa, T.; Tanaka, M.; Endo, T. *Chem. Lett.* **1987**, 1831.
(2) Takahashi, T.; Yokozawa, T.; Endo, T. *Makromol. Chem.* **1991**, *192*, 1207.
(3) (a) Otsuka, S.; Mori, K.; Imaizumi, F. *J. Am. Chem. Soc.* **1965**, *87*, 3017. (b) Otsuka, S.; Mori, K.; Imaizumi, F. *Eur. Polym. J.* **1967**, *3*, 73. Ghalamkar-Moazzam, M.; Jacobs, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 615.
(4) Hadjiandreou, P.; Julémont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455.
(5) Deming, T. J.; Novak, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 4400.
(6) Dawans, F.; Marechal, J. C.; Teyssie, P. *J. Organomet. Chem.* **1970**, *21*, 259.
(7) By the polymerization of **2** using **1** without any additives, white powdery polymer was precipitated during the polymerization which was hardly soluble in organic solvents. However, by the addition of more than 1 equiv of PPh_3 to **1** in the polymerization system, only a soluble elastic polymer was produced. Thus, polymerizations were carried out by adding 2 equiv of PPh_3 to **1**.
(8) A typical experimental procedure is as follows: To a nitrogen-substituted flask equipped with a three-way stopcock were added a toluene solution of $Ni(COD)_2$ (0.106 M, 0.19 mL, 0.020 mmol) and a toluene solution of allyl trifluoroacetate (1.0 M, 0.020 mL), and the reaction mixture was stirred for 20 min at ambient temperature. To the resulting orange solution were added a toluene solution of PPh_3 (1.0 M, 0.040 mL) and 4.7 mL of toluene, and the resulting solution was cooled to 0 °C. **2** (0.335 g, 4.78 mmol) was added to this solution and was allowed to react for 6 h. By precipitation with *n*-hexane, an elastic polymer (**3**) was obtained in 88% (0.294 g).
(9) **3**: ^{13}C-NMR (δ, $CDCl_3$) 29.2 ($-CH_2-$, br), 55.4 ($>CHOCH_3$), 58.8 ($C{=}COCH_3$), 83.9 ($>CHO$), 113.1 ($>C{=}CH_2$), 144.8 ($<C{=}CHO$); IR (neat) 2930, 2836, 1668, 1460, 1223, 1128, 1001, 909 cm^{-1}.