Polymer Communication

Novel nickel catalyst for the polymerization of phenylacetylenes

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Abstract

Polymerization of substituted acetylenes with the novel nickel catalyst system, Ni(COD)$_2$–CF$_3$COO(allyl), was examined. This catalyst system polymerized phenylacetylene to produce yellowish red polymers in good yield. The molecular weight of the poly(phenylacetylene) was 12,000. Disubstituted and aliphatic acetylenes hardly gave polymers by this catalyst system. The formed polymers had an alternating double bond structure. The UV–visible. spectrum of the poly(phenylacetylene) extended up to 550 nm. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Formerly, it had been difficult to obtain high-molecular-weight substituted polyacetylene. In 1974 Masuda and Higashimura found that phenylacetylene (PA) was polymerized with WCl$_6$ and MoCl$_5$ to give high-molecular-weight polymer in good yield [1]. Since then various types of group V and VI transition-metal catalysts have been reported for the polymerization of mono- and disubstituted acetylenes, and numerous kinds of high-molecular-weight polymers with unique properties have been discovered [2,3]. Living and stereospecific polymerization were also attained by using molybdenum-based catalysts. These polymerizations are considered to proceed by metathesis polymerization mechanism like ring-opening polymerization of cycloolefin [4].

Another type of catalyst for the polymerization of substituted acetylenes is based on rhodium metal. In 1990 it was reported that [Rh(norbornadien)Cl]$_2$ polymerized PA derivatives to form high-molecular-weight polymers quantitatively [5]. Recently, well-defined rhodium catalysts for the living polymerization of PA were also discovered [6,7].

Few catalysts for the polymerization of substituted acetylenes [8] have been reported except the ones described above. The present paper deals with a preliminary report on the novel nickel catalyst for the polymerization of PA. This catalyst was claimed to be effective for the living polymerization of allenes [9] and dienes [10].

2. Experimental

PA, *tert*-butylacetylene and 2-octyne were purchased from Tokyo Kasei Co., dried with CaH$_2$, and distilled under dry nitrogen. *o*-Trimethylsilylphenylacetylene (*o*-TMSPA) [11], *o*-trifluoromethylphenylacetylene [12], and 1-chloro-2-phenylacetylene [11] were synthesized according to the literature. CF$_3$COO(allyl) was purchased from Aldrich and distilled under dry nitrogen. Reagent grade solvents were dried with CaH$_2$ or 4A molecular sieves, and distilled under dry nitrogen. Bis(1,5-cyclooctadiene)-nickel [Ni(COD)$_2$] was purchased from Strem and used without purification.

All polymerization procedures were carried out under dry nitrogen atmosphere using the standard Schlenk tube technique. The standard polymerization condition was as follows: in toluene at room temperature for 24 h, [monomer] = 1.0 M, [Ni(COD)$_2$] = [CF$_3$COO(allyl)] = 20 mM. In 20 ml Schlenk tube nickel complex and cocatalyst were dissolved in toluene followed by aging for 10 min at room temperature. The color of the solution turned yellow to orange. The monomer was then added by syringe to start the polymerization. After polymerization, the solution was poured into dilute HCl solution of methanol to remove the catalyst, filtered, and dried in vacuo. The polymer yield was determined by weighing methanol insoluble product.

The ^{1}H NMR spectrum of the polymer was recorded at room temperature in CDCl$_3$ using a JEOL GX-270 spectrometer. Molecular weight and molecular weight distribution of polymers were determined by size exclusion chromatography (SEC) measured at 40°C. CHCl$_3$ was used as the

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Table 1

Polymerization of phenylacetylene (polymerized in toluene at 25°C for 1 h, [monomer] = 1.0 M, [Ni(COD)$_2$] = [cocatylst] = 20 mM)

| Catalyst	Polymer yield (%)	M_w	M_w/M_n
Ni(COD)$_2$	7	2,100	2.1
Ni(COD)$_2$–CF$_3$COO(allyl)	65	12,000	1.8
Ni(COD)$_2$–CF$_3$COOH	20	3,400	1.7
Ni(COD)$_2$–(allyl)Cl	51	8,100	1.7
Ni(COD)$_2$–(allyl)I	46	7,500	1.9

eluent, and the calibration curve was made by monodisperse polystyrene samples. The UV–visible spectrum was recorded in CHCl$_3$.

3. Results and discussion

Table 1 summarizes the polymerization of PA by nickel catalysts. When only Ni(COD)$_2$ was used as catalyst, polymerization took place, though polymer yield and molecular weight remained very low even after 24 h polymerization. Addition of equimolar amount of allyl compounds dramatically increased polymer yields and molecular weight of the produced polymer. The poly(PA) was yellowish red solid, and was soluble in various organic solvents such as toluene and CHCl$_3$. Among these allyl compounds, CF$_3$COO(allyl) was most effective. When this cocatalyst was used, the polymer yield and the weight average molecular weight (M_w) reached 65% and 12,000, respectively. The molecular weight distribution of the poly(PA) was around two, and the SEC curve was monomodal. These facts indicate that

the active species of the polymerization should be homogeneous. The corresponding acid, CF$_3$COOH, showed only a small cocatalyst effect for the polymerization. (Allyl)X is known to produce π-allyl nickel dimeric complex as described in Eq. (1) which is effective for the polymerization of dienes or allenes. Polymerization activity of PA by Ni(COD)$_2$–CF$_3$COO(allyl) increased with increasing [CF$_3$COO(allyl)]/[Ni(COD)$_2$], and was saturated at around [CF$_3$COO(allyl)]/[Ni(COD)$_2$] = 1. Thus, CF$_3$COO(allyl) should be used only for the produce of [CF$_3$COONi(π-allyl)]$_2$.

$$Ni(COD)_2 + (allyl)X \rightarrow [Ni(\pi\text{-allyl})X]_2$$

$$(X = CF_3COO, Cl, I)$$

(1)
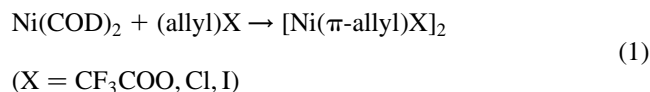
The polymerization results of various substituted acetylenes with the Ni(COD)$_2$–CF$_3$COO(allyl) catalyst system are detailed in Table 2. Monosubstituted aromatic acetylenes gave polymers in good yield. In the metathesis polymerization of monosubstituted acetylenes using the group VI transition metal catalyst, polymerization activity increases with increasing bulkiness of the substituent. For example, polymerization activity of *o*-TMSPA, which has bulkier substituent than PA, is much higher than that of PA. As shown in Table 2, though Ni(COD)$_2$–CF$_3$COO(allyl) catalyst system formed purple poly(*o*-TMSPA), the polymerization activity of *o*-TMSPA was lower than that of PA. This fact indicates that the polymerization may not proceed with metathesis polymerization, but with insertion polymerization like rhodium-based catalysts. The polymer yield of *o*-trifluoromethylphenylacetylene was similar to that of PA. Disubstituted and aliphatic acetylenes hardly gave polymers by this catalyst system.

The elemental analysis values for the poly(PA) agreed well with the ones calculated for the polymerization products:

Anal. calcd. for (C$_8$H$_6$)$_n$: C, 94.1%; H, 5.9%.
Found for poly(PA) obtained by Ni(COD)$_2$–CF$_3$COO (allyl): C, 94.2%; H, 5.8%.

Fig. 1 describes the IR spectrum of poly(PA) produced with Ni(COD)$_2$–CF$_3$COO(allyl). While strong ≡C–H (3300 cm^{-1}) and weak C≡C (2100 cm^{-1}) absorptions were observed in the IR spectrum of the monomer, these bands disappeared in the polymer. Strong absorptions characteristic of the phenyl group were seen around 3100 cm^{-1}. Four peaks due to monosubstituted phenyl group were also observed at 1700–2000 cm^{-1}.

These observations indicate that the polymer has the alternating double bond structure; (–CH=CPh–).

The main-chain microstructure of substituted polyacetylenes depends on the kind of catalyst and the polymerization conditions. Cis poly(PA) is reddish yellow solid, and the reddish color increases with increasing trans content. Fig. 2 illustrates the UV–visible spectrum of poly(PA) obtained by Ni(COD)$_2$–CF$_3$COO(allyl) in toluene. The spectrum of
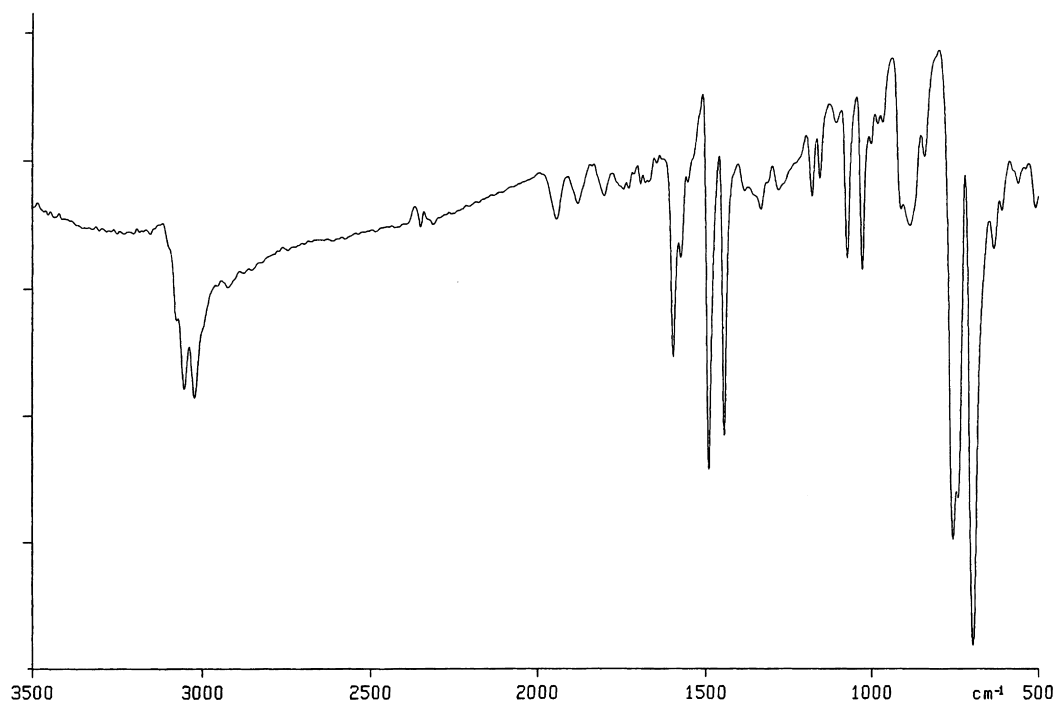
Table 2

Polymerization of alkynes with Ni(COD)$_2$–CF$_3$COO(allyl) (Polymerized in toluene at 25°C for 1 h, [monomer] = 1.0 M, [Ni(COD)$_2$] = [CF$_3$COO(allyl)] = 20 mM)

Monomer	Polymer yield (%)	M_w	M_w/M_n
HC≡C–C$_6$H$_5$	65	12,000	1.8
HC≡C–C$_6$H$_4$(CF$_3$)	61	10,000	2.0
HC≡C–C$_6$H$_4$(SiMe$_3$)	41	9500	1.7
ClC≡C–C$_6$H$_5$	0	–	–
HC≡C-*t*-Bu	Trace	–	–
MeC≡C-*n*-C$_5$H$_{11}$	0	–	–

Fig. 1. IR spectrum of poly(PA) obtained with Ni(COD)$_2$–CF$_3$COO(allyl) (KBr pellet).
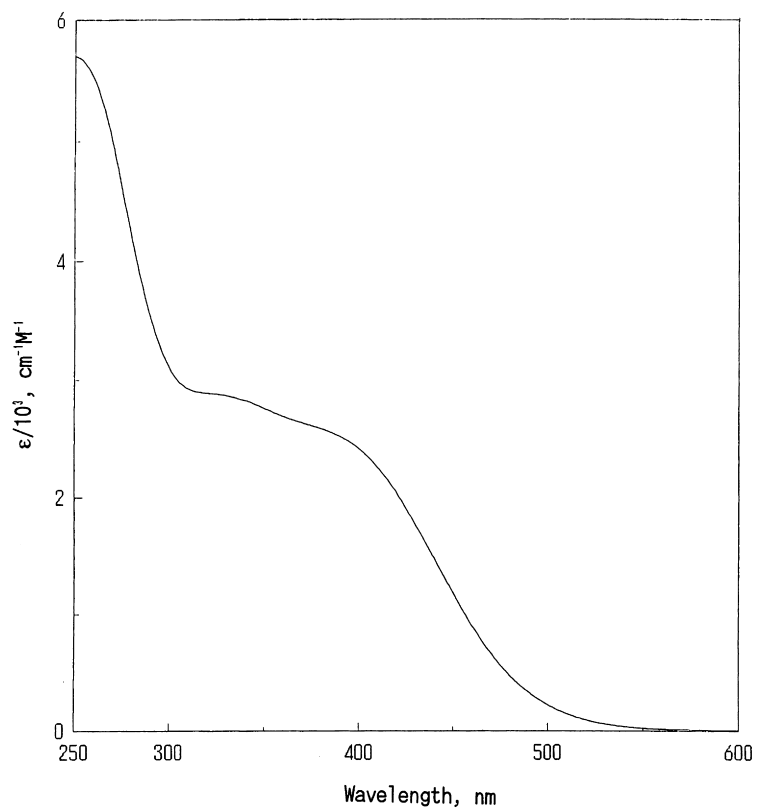
Fig. 2. UV–visible spectrum of poly(PA) obtained with Ni(COD)$_2$–CF$_3$COO(allyl) (measured in CHCl$_3$).

the poly(PA) extended up to 550 nm. This spectrum corresponded to the color of the polymer and was similar to that obtained with the MoCl$_5$ catalyst. Further, in the ^{1}H NMR spectrum of the poly(PA) measured in CHCl$_3$, each peak was broad. From these results, the microstructure of this polymer may be a mixture of cis and trans structures. This is different from the poly(PA) obtained with rhodium-based catalysts which produce highly cis poly(PA).

References

[1] Masuda T, Hasegawa K, Higashimura T. Macromolecules 1974;7:728.
[2] Masuda T, Higashimura T. Adv Polym Sci 1987;81:121.
[3] Shirakawa H, Masuda T, Takeda K. The chemistry of triple-bonded functional groups, Chichester: Wiley, 1994 (suppl. C2).
[4] Ivin KJ, Mol JC. Olefin metathesis and metathesis polymerization. London: Academic Press, 199.
[5] Tabata M, Yang W, Yokota K. Polym J 1990;22:1105.
[6] Kishimoto Y, Eckerle P, Miyatake T, Ikariya T, Noyori R. J Am Chem Soc 1994;116:12 131.
[7] Misumi Y, Masuda T. Macromolecules 1998;31:7572.
[8] Douglas WE, Overend AS. J Mater Chem 1994;4:1167.
[9] Tomita I, Kondo Y, Takagi K, Endo T. Macromolecules 1994;27:4413.
[10] Hadjiandreou P, Julémont M, Teyssié P. Macromolecules 1984;17:2455.
[11] Brandsma L. Preparative acetylenic chemistry, 2. Amsterdam: Elsevier, 1988.
[12] Carpita A, Lessi A, Rossi R. Synthesis 1984;571.