ELSEVIER

European Polymer Journal 36 (2000) 1175–1181

EUROPEAN
POLYMER
JOURNAL

Synthesis of block copolymer of ethylene with styrene and isoprene by means of active site transformation from anionic to coordination route

Kiyoshi Endo*, Masatosi Yamamoto

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

Received 21 January 1999; accepted 8 June 1999

Abstract

Synthesis of block copolymer consisting of ethylene with styrene (St) and isoprene (IP) by active site transformation from anion to coordination route was investigated. The active site transformation was achieved by adding VCl_4 to the living polymers initiated with butyllithiums. The block copolymer consisting of IP and ethylene segments was synthesized by means of active site transformation using VCl_4 and the poly(IP) with lithium chain end. When the living poly(St) with lithium chain end was used instead of the poly(IP), the block copolymer of St and ethylene was not obtained. This may be explained by the β-hydride elimination reaction from polystyryl chain. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Active site transformation; Ethylene; Isoprene; Styrene; Block copolymer; VCl_4; Living polymer

1. Introduction

Many approaches have been proposed for synthesizing block copolymers [1]. Among many types of block copolymers, the block copolymers consisting of the conjugated monomers such as styrene (St), isoprene (IP), and butadiene (Bd) with olefins are interesting and potentially important because of quite different polymerization activities between conjugated monomers and olefins. Anionic living polymerization is an excellent process for preparing the well-defined block copolymers. Unfortunately, continuous living anionic polymerizations with alkyllithium (RLi) can not apply for synthesizing block copolymers consisting of the conjugated monomers and olefins.

Previously, we reported that block copolymer consisting of the conjugated monomers and ethylene was synthesized by the active site modification, which achieved by adding adequate *tert*-diamines such as *N,N,N′, N′*,-tetramethylethylenediamine to the living polymers initiated with RLi as shown in Scheme 1 [2,3]. This process is a useful method for synthesizing block copolymers consisting of conjugated monomer and ethylene.

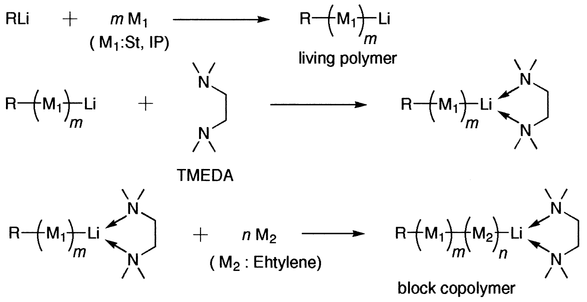
On the other hand, Fontanille et al. [4–7] reported that block copolymer consisting of conjugated monomers and olefins can be synthesized by means of the active site transformation performed by adding $TiCl_4$ to living polymers initiated with RLi. The transformation reaction of active site from an anionic to coordi-

---

* Corresponding author. Tel.: +81-6-6605-2981; fax: +81-6-6605-2698.

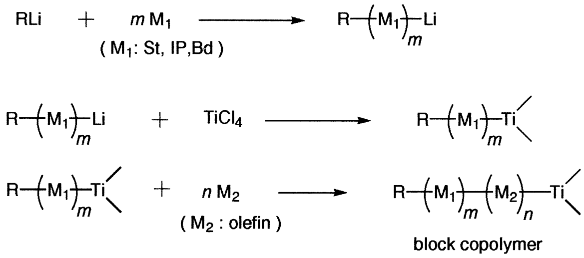
E-mail address: endo@a-chem.eng.osaka-cu.ac.jp (K. Endo).

0014-3057/00/$ - see front matter
PII: S0014-3057(99)00170-6



Scheme 1. Synthesis of block copolymer by means of the active site modification.

nation route was also studied by other workers [8–10]. Scheme 2 shows the synthesis route of the block copolymers using this process.



Scheme 2. Synthesis of block copolymer by means of the active site transformation.

After the active site transformation by $TiCl_4$, the system keeps still homogeneously, and olefins can polymerize without any cocatalyst such as alkylaluminiums. In the case of poly(Bd) with lithium end, the proposed mechanism for this reaction can be expressed as Scheme 3.

In the active site transformation reaction, however, the living polymer with the lithium chain end toward $TiCl_4$ served as not only a alkylation reagent but also a reducing reagent. The reducing reaction causes the decrease of the block conversion as shown in Scheme 3.

Since VCl_4–RLi catalysts as well as the $TiCl_4$–RLi catalysts [11,12] will be able to polymerize olefins under mild conditions, the active site transformation between VCl_4 and living polymers with the lithium chain end is expected to make block copolymers consisting of conjugated monomers and olefins. The active site transformation between VCl_4 and living polymers initiated with RLi was not found in the literature, although many studies of the polymerization of olefins with V-based catalysts were reported [13].

In this paper, we will describe the synthesis of block copolymers of ethylene with St and IP by means of the active site transformation using VCl_4 as a transformation reagent.

2. Experimental

2.1. Materials

Commercial St and IP were purified by distillation over calcium hydride before use. VCl_4 kindly supplied from Sinko Chemicals was used as received. *n*-Butyllithium (*n*-BuLi) and *tert*-butyllithium (*tert*-BuLi) purchased from Kanto Chemicals were used without further purification. Solvents were used after purification by conventional methods.

2.2. Polymerization procedure

Polymerization was carried out using a 300 cm^3 glass reactor equipped with a stirrer and connected to a vacuum line. The required amounts of monomer, a diluted solution of BuLi and *n*-hexane solution of VCl_4 into the reactor were performed by a syringe under the nitrogen atmosphere through a rubber septum. Ethylene was introduced into a reactor through a stainless tube, and kept constant pressure during the polymerization.

Anionic polymerization of St or IP with BuLi was carried out at a constant temperature for a given time. Active site transformation from anionic to coordination route was performed by adding VCl_4 to the polymerization system at −78°C. Block copolymerization of ethylene was carried out at a constant temperature for a given time. After the polymerization, isopropyl alcohol was added to terminate the reactions. The contents of the reactor were, then, poured into a large

$$
\begin{array}{l}
2/3\ \text{PBd -Li} + \text{TiCl}_4 \rightleftharpoons 1/3\ (\text{PBd-TiCl}_3,\ \text{LiCl})_2 + 1/3\ \text{TiCl}_4 \\
1/3\ (\text{PBd-TiCl}_3,\ \text{LiCl})_2 + 1/3\ \text{PBd -Li} \rightleftharpoons 1/3\ (\text{PBd-TiCl}_2,\ \text{TiCl}_3,\ 3\text{LiCl}) + 2/3\ \text{PBd}\bullet \\
\hline
\text{PBd -Li} + \text{TiCl}_4 \rightleftharpoons 1/3\ \text{TiCl}_4 + 1/3\ (\text{PBd-TiCl}_2,\ \text{TiCl}_3,\ 3\text{LiCl}) + 2/3\ \text{PBd}\bullet
\end{array}
$$

Scheme 3. Reaction mechanism for the active site transformation.

amount of methanol containing a small amount of hydrochloric acid to precipitate the polymer formed. The polymer was filtered through a glass filter and washed with methanol and dried under vacuum. Polymer yields were determined by gravimetry.

Polymers were extracted with the Soxhlet extraction apparatus. After the extraction, the soluble fraction was evaporated and precipitated with methanol. The insoluble fraction was dried under vacuum.

2.3. Characterization of polymers

The number- and weight-average molecular weight (M_n and M_w, respectively) and molecular weight distribution (M_w/M_n) of the toluene soluble fraction were determined by gel permeation chromatography (GPC) using Tosoh 8000 series system at 38°C in THF as an eluent, and the molecular weight was calibrated with polystyrene standards. The structure of polymers was determined by ^{1}H-NMR spectra recorded on JEOL A-400 NMR spectrometer in the mixed solvent of d_6-benzene and *o*-dichlorobenzene (3/7 vol%) at 120°C.

3. Results and discussion

3.1. Block copolymerization of IP and ethylene

Table 1 shows the results for polymerizations of IP and ethylene. The anionic polymerization of IP with *tert*-BuLi catalyst gave the living polymer, i.e., the molecular weight distribution (M_w/M_n) was 1.08, and the observed molecular weight of the poly(IP) ($M_n = 4.1 \times 10^3$) was in a good agreement with the calculated value. The microstructure of IP was 69.9% *cis*-1,4, 23.1% *trans*-1,4, and 7.0% 3,4-units, which was consistent with the reported values [14]. The polymerization of ethylene also proceeded with the VCl_4–*tert*-BuLi catalyst.

Taking these polymerization behaviors of isoprene and ethylene into consideration, the synthesis of the block copolymer of IP and ethylene seems to be possible by means of active site transformation by adding VCl_4 to the living polymer, because the living poly(IP) with the lithium chain end can be regarded as a kind of the alkyllithium. So, the block copolymerization of ethylene and IP by means of the active site transformation was examined. When VCl_4 was added to the living poly(IP) with the lithium chain end, the color of the polymerization system turned from pale yellow to dark red, but the polymerization system kept homogeneously. This suggests that the reaction between VCl_4 and the living poly(IP) with the lithium end took place.

GPC elution curves of the poly(IP) before and after addition of VCl_4 are depicted in Fig. 1. The elution curve of the poly(IP) before addition of VCl_4 was a unimodal and the M_w/M_n was narrow ($M_w/M_n = 1.08$). After addition of VCl_4, the molecular weight of the poly(IP) increased and the M_w/M_n became somewhat broad. Thus, we presumed that the reactions of the VCl_4 and the living poly(IP) occurred to result active sites for olefin polymerizations. The reactions may be similar to those of $TiCl_4$ and living polymers initiated with alkyllithiums as reported previously by Fontanille et al. [4–7].

After the active site transformation was performed, the polymerization of ethylene took place without any cocatalysts, and the product that is insoluble in the

Table 1
Polymerization of IP and ethylene with VCl_4 and *tert*-BuLi catalyst in toluene[a]

Monomer[b]		$BuLi/VCl_4$ mole ratio[c]	Polymer yield		Insoluble part (wt.%)
1st polymerization	2nd polymerization		Whole (g)	Polyethylene (g)	
IP	–	–	8.2[e]	–	–
Ethylene	–	1.0	0.8	0.8	~100
Ethylene	–	3.0	2.0	2.0	~100
IP	Ethylene[d]	1.0[f]	8.7[g]	0.6	13.1
IP	Ethylene[d]	3.0[f]	9.8[g]	1.6	19.6

[a] [*tert*-BuLi] = 1.8×10^{-2} mol/l, [IP] = 1.1 mol/l, ethylene pressure = 1.0 kg/cm^2, toluene = 100 ml.

[b] Polymerized at 40°C for 3 h for IP, and at −78°C for 30 min for ethylene.

[c] Catalyst was aged at −78°C for 45 min after addition of VCl_4.

[d] Extracted with toluene.

[e] Molecular weight of poly(IP) was $M_n = 4.0 \times 10^3$ ($M_w/M_n = 1.08$). By addition of VCl_4, molecular weight changed to $M_n = 8.9 \times 10^3$ ($M_w/M_n = 1.5$).

[f] VCl_4 was added after 1st polymerization.

[g] Polymer yield of IP was 100%.

polymerization solvent was obtained. Whereas, the polymerization of ethylene did not initiate without the VCl_4.

The resulting product was extracted with a toluene to confirm the formation of block copolymers consisting of IP and ethylene segment. Fig. 2 shows the ^{13}C-NMR spectra of the soluble and the insoluble fractions, and main characteristic peaks were assigned as shown in the chart according to the literature [3]. In the ^{13}C-NMR spectrum of the soluble fraction, the peaks based on the poly(IP) segment were observed besides signals based on the *tert*-butyl group derived from the initiator, but the peaks based on the polyethylene segment were not detected. Whereas, in the insoluble fraction, the characteristic peak of polyethylene segment appeared at 29.6 ppm besides the peaks based on poly(IP) segment that is soluble in the extraction solvent. Moreover, methylene carbon at the junction part of two segments was observed at about 38.3 ppm [3]. Thus, it will be concluded that the poly(IP)-block-poly(ethylene) was synthesized by means of the active site transformation from anionic to coordination using VCl_4 as a transforming agent. In the insoluble fraction, polyethylene may be contaminated as a result of the chain transfer reaction during the polymerization of the ethylene. Judging from the ^{13}C-NMR spectra of the insoluble part, the formation of homopolymer of the ethylene seems to be negligible from comparison with the reported chart [3].

The block conversion estimated from the weight of insoluble and soluble fraction was not high. This may be explained by the following reasons: the living poly(IP) with lithium chain end served as a reduction reagent to VCl_4, and all V-poly(IP) complex formed by the active site transformation did not initiate the polymerization of ethylene.

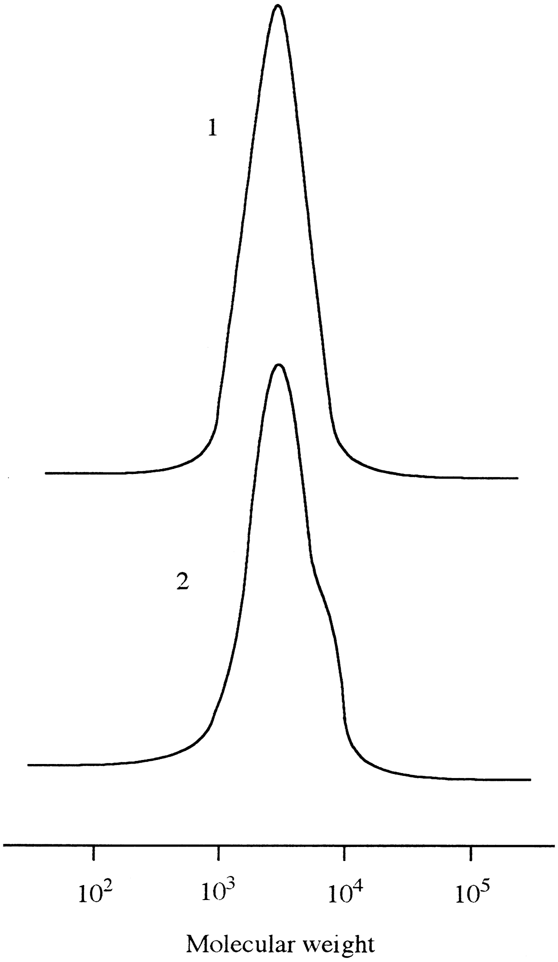


Fig. 1. GPC elution curves of poly(IP) (1) before and (2) after addition of VCl_4.

3.2. Polymerization of St and ethylene

Synthesis of the block copolymerization of ethylene and the living poly(St) obtained from the polymerization of St with *n*-BuLi was examined by means of active site transformation by adding VCl_4 to the living polymer. Table 2 shows the results for the polymerization of St and ethylene. When the VCl_4 was added to the living poly(St), the cherry red solution turned to dark red, indicating that the VCl_4 reacted with the living poly(St) having the lithium chain end.

The polymerization of ethylene with the VCl_4 in combination with the living poly(St) with lithium chain end proceeded to give a product that is insoluble in toluene. The product was extracted with cyclohexane to check the formation of the block copolymer. Fig. 3 shows the ^{13}C-NMR spectra of the product. In the soluble fraction, the peaks based on poly(St) segment were observed, but peaks of polyethylene segment based on the formation of the block copolymer were not observed clearly. While, the insoluble fraction was found to be only polyethylene. Consequently, the block copolymer consisting of St and ethylene segments could not be synthesized by this route.

When active site transformation took place between the living poly(St) with Li chain end and the VCl_4, the polystyryl–vanadium bond formed as the reaction product easily underwent β-hydride elimination, leading to the formation of the poly(St) and a vanadium hydride that can initiate the polymerization of ethylene. Similar observation was reported in the active site transformation of $TiCl_4$ with the living polymer with lithium chain end [5]. Thus, the homopolymers of St and ethylene were recovered without the formation of the poly(St)-block-poly(ethylene).

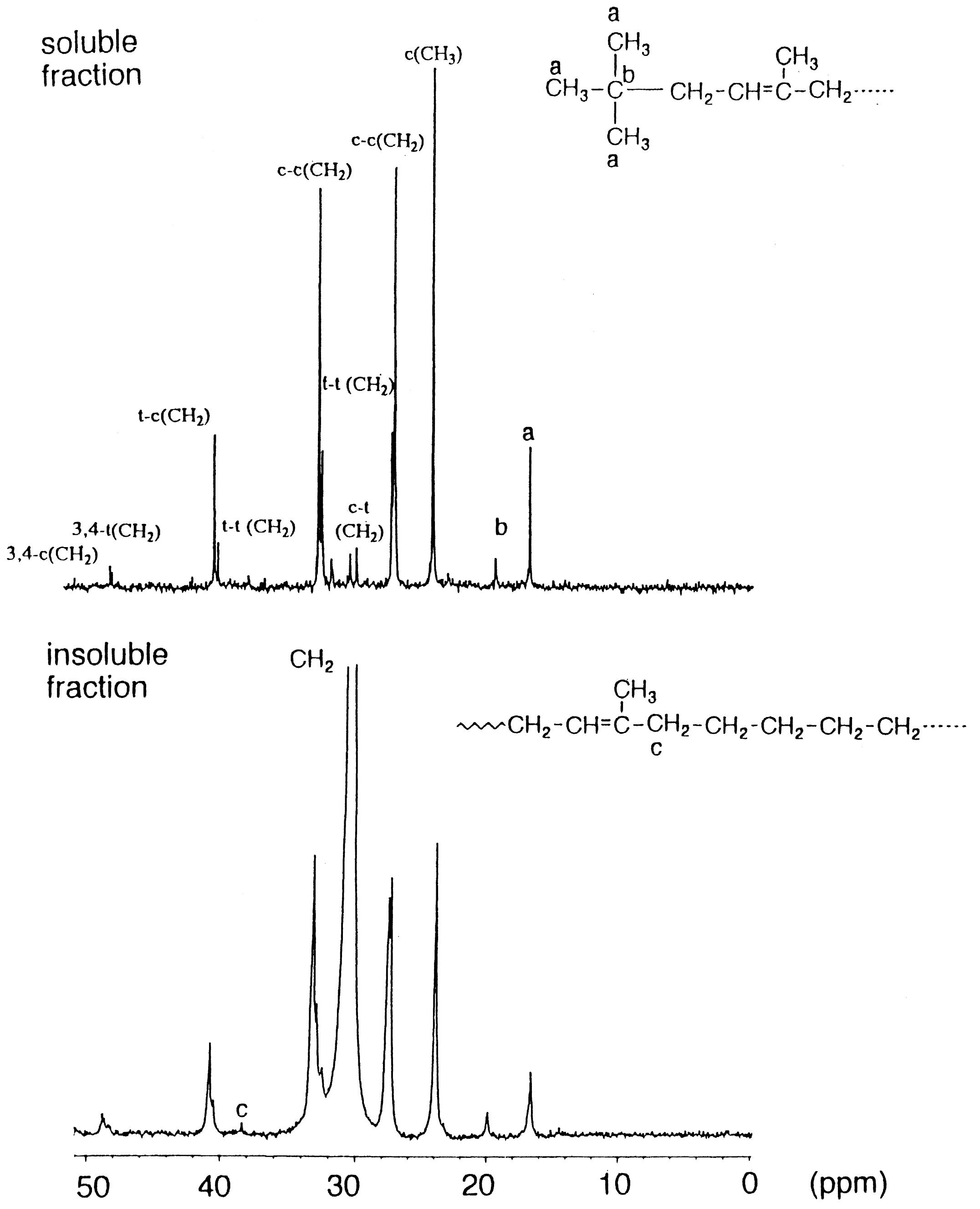


Fig. 2. ^{13}C-NMR spectra of the product obtained from the polymerization of ethylene and living poly(IP) with lithium chain end by active site transformation by VCl_4.

4. Conclusion

The block copolymer consisting of poly(IP) and polyethylene segments was synthesized by means of the active site transformation by adding VCl_4 to the living poly(IP) bearing the lithium chain end. The living polymer served as not only a alkylation reagent but also a reducing agent toward the VCl_4, the efficiency of the transformation reaction from the anionic to the coordination was not high. On the other hand, when the living poly(St) was used, block copolymer of St and ethylene was not synthesized, and homopolymers

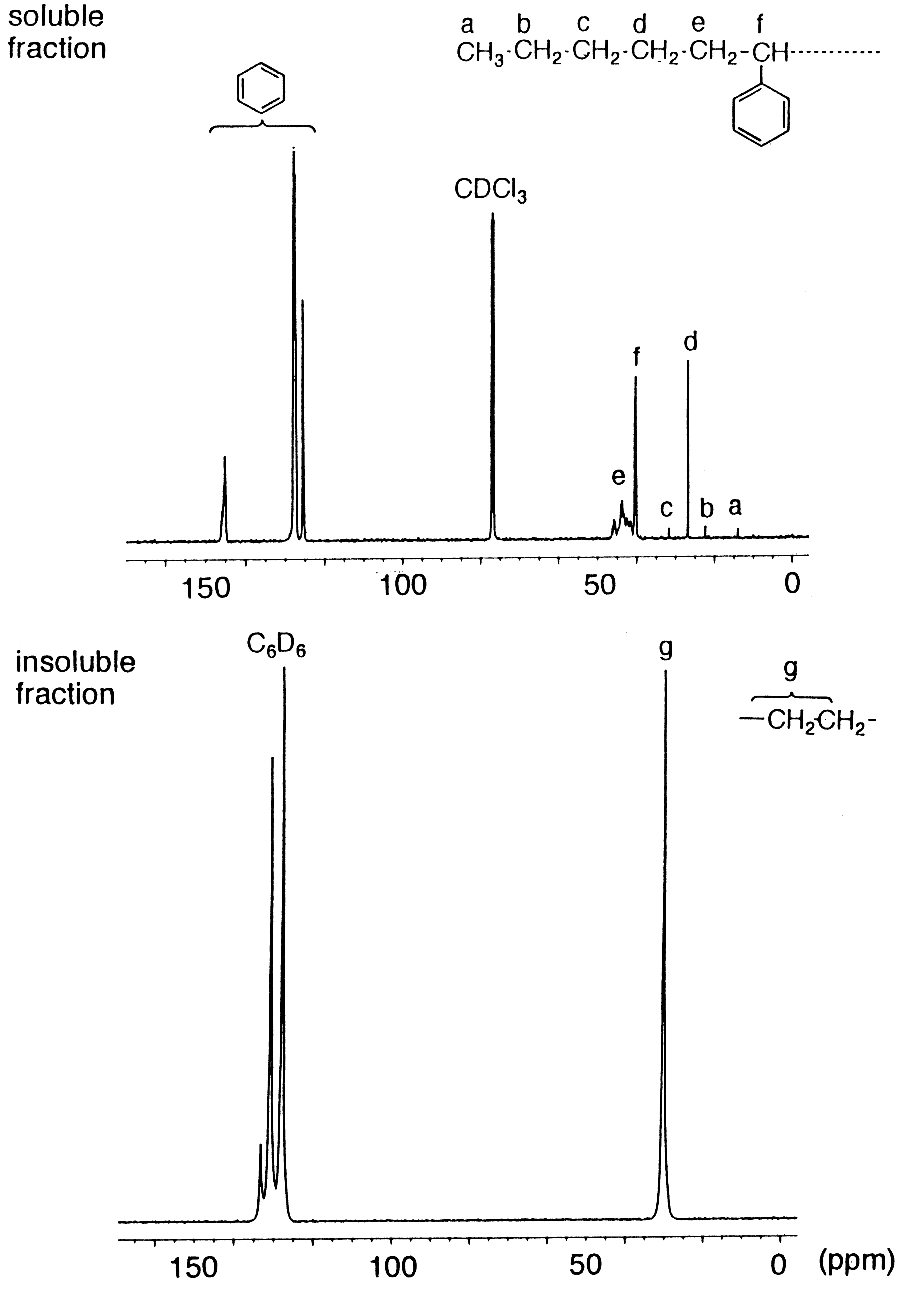


Fig. 3. ^{13}C-NMR spectra of the product obtained from the polymerization of ethylene and living poly(St) with lithium chain end by active site transformation by VCl_4.

Table 2
Polymerization of St and ethylene with VCl_4 and *n*-BuLi catalysts in toluene[a]

Monomer[b]		$BuLi/VCl_4$ mole ratio[c]	Yield (g)	Poly(St) yield (%)	Polyethylene yield (g)
1st polymerization	2nd polymerization				
St	–	–	12.3	100[d]	–
Ethylene	–	3.0	1.7	–	2.7
St	Ethylene[d]	3.0	14.5	100	2.2

[a] $[n\text{-BuLi}] = 2.3 \times 10^{-2}$ mol/l, $[\text{St}] = 0.9$ mol/l, ethylene pressure $= 1.0$ kg/cm^2, toluene $=$ 100 ml.

[b] St polymerized at 50°C for 3 h. Ethylene polymerized at −78°C for 30 min.

[c] Catalyst was aged at −78°C for 45 min after addition of VCl_4.

[d] Molecular weight of poly(St) was $M_n = 4.1 \times 10^3$ ($M_w/M_n = 1.06$). By addition of VCl_4, molecular weight changed to $M_n = 8.5 \times 10^3$ ($M_w/M_n = 1.30$).

of St and ethylene were recovered. In this case, we supposed that a β-hydrogen transfer of alkyl–vanadium bond formed by the active site transformation took place to break the polymer chain.

References

[1] Rless G, Hurtrez G. In: Encyclopedia of polymer science and engineering, vol. 2, 2nd ed. New York: Wiley, 1985. p. 324.

[2] Endo K, Otsu T. J Chem Soc Chem Commun 1990;(19):1372.

[3] Endo K, Otsu T. Macromol Rapid Commun 1992;13:135.

[4] Siove A, Fontanille M. Makromol Chem 1980;181:1815.

[5] Siove A, Fontanille M. Eur Polym J 1981;17:1175.

[6] Soum A, Siove A, Fontanille M. J Appl Polym Sci 1983;28:961.

[7] Siove A, Fontanille M. J Polym Sci, Polym Chem Ed 1984;22:3877.

[8] Richards DR. Br Polym J 1980;12:89.

[9] Drezewinski MA, Cohen RH. J Polym Sci, Polym Chem Ed 1982;23:1523.

[10] Endo K, McGrath JE. Polym Prepr Jpn 1986;36:211.

[11] Friedlander HN, Oita K. Ind Eng Chem 1957;49:1885.

[12] Frankel M, Rabanim J, Zilkha A. J Polym Sci 1958;28:387.

[13] Boor Jr. J. In: Ziegler-Natta catalysts and polymerizations. New York: Academic Press, 1979. p. 117.

[14] Tanaka Y, Tabuchi T, Kobayashi M, Tadokoro H. J Polym Sci, Part A 1971;9:43.