

HI/I₂ 촉매로 중합되는 Alkyl Vinyl Ether의 양이온 리빙 중합에 있어서 Tacticity 분석으로 본 중합활성점의 구조적 특성

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Tacticity Analysis and the Nature of Active Propagating Species in the Living Cationic Polymerization of Alkyl Vinyl Ethers Initiated by HI/I₂ Catalyst

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요 약 : 리빙 중합조건하에서 HI/I₂ 촉매에 의하여 합성된 poly(ethyl vinyl ether)와 poly(n-butyl vinyl ether)의 tacticity를 탄소 핵자기 공명을 이용하여 분석하였으며, 그 분석결과를 BF₃OEt₂나 SbCl₅가 사용된 리빙 중합이 아닌 중합계에서 얻어진 고분자의 분석결과와 비교하였다. HI/I₂ 촉매에 의하여 얻어진 polymer의 sequence distribution은 Bernoullian 통계를 따르지 않았고 반면에 BF₃OEt₂를 사용하여 얻어진 것은 random statistics를 따르고 있었다. 중합온도가 감소할 때, 얻어진 고분자의 isotacticity는 증가하였고 random statistics로부터의 deviation은 증가하였다.

Abstract : Ethyl vinyl ether(EVE) and n-butyl vinyl ether(nBVE) were polymerized by HI/I₂ catalyst under living polymerization conditions, and the tacticities of the obtained polymers were determined by carbon-13 NMR spectroscopy. The tacticity result was analyzed and compared with reported data which were obtained from nonliving polymerization systems catalyzed by BF₃OEt₂ or SbCl₅. Sequence distribution of a polymer obtained with HI/I₂ catalyst did not follow Bernoullian statistics, whereas that of the polymer obtained from BF₃OEt₂ catalyst system followed the random statistics. As the polymerization temperature decreased, the isotacticity of the polymer obtained increased, and the deviation from random statistics became larger.

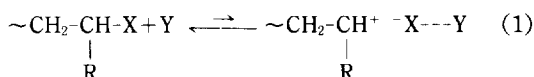
INTRODUCTION

In recent years many new polymerization methods, which could control molecular weights and

polydispersities of polymers, have been developed in ionic polymerization area. Especially in cationic polymerization area, the discovery of living polymerizations of vinyl monomers has been received

quite attention because it had been almost impossible to obtain near-monodispersed polyvinyls.¹ Monomers used in cationic polymerizations are electron-rich monomers such as alkyl vinyl ethers,¹ p-methoxystyrene,¹ p-methylstyrene,² isobutylene,³ etc. Applied initiation systems are A) HI/I₂,⁴ HI/ZnI₂,⁵ Acetates/Lewis Acids,^{3,6} B) Acids/Lewis Bases such as dioxane,⁷ THF,⁷ dialkyl sulfide,⁸ dimethyl sulfoxide,⁹ dimethyl acetamide,¹⁰ and C) HI/Bu₄NClO₄.¹¹

In group A, Lewis acid activates a small portion of inactive carbon-iodine or carbon-acetate bond to active carbocation as in equation 1, and this makes possible the molecular weight build up. Previous investigation of alkyl vinyl ethers/HI-I₂ system revealed that the total concentration of activated carbocation is very small portion compared to that of the carbon-iodine bond, and the two species are in a dynamic equilibrium.¹²

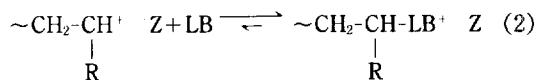


X = I, OAc

Y = Lewis Acid

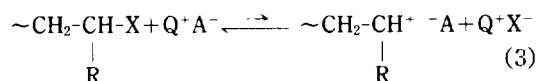
R = Substituent (e.g. alkoxy or p-methoxyphenyl group)

In group B, Lewis bases stabilize a carbocation by the formation of a covalent carbon-Lewis base bond⁸ as in equation 2. In group C, small portion of anions exchanges each other in an equilibrium reaction to make an active species as in equation 3.



LB = Dialkyl sulfide, THF, Dioxane, etc.

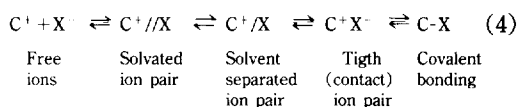
Z = Counter ion



X = I, Q⁺A⁻ = Bu₄N⁺ClO₄⁻

In all cases, polymerization proceeds via ionic intermediates, and the concentration is quite re-

duced compared to a conventional non-living cationic polymerization. The equilibrium (equation 4) in the Winstein spectrum¹³ (continuous equilibrium of ionic species with solvation) shifts to the right hand side during the polymerization. The covalent species stays as a dormant species and the ionic species are responsible for the polymerization. These species coexist with equilibrium reactions which are fast compared to the polymer growth reaction. Thus the living polymerization methods regulate the rate of polymerization. On the other hand, the rate of polymerization in a conventional carbocationic polymerization is usually explosively fast.



As pointed out in the literature,⁸ however, it is still unknown which ionic species contributes most to the polymerization reaction, and why chain transfer reactions are suppressed to give living polymers with those above-mentioned catalysts. One speculation is that drastically reduced relative concentration of active propagating species and monomer in this system gives living behavior due to a kinetic effect, regardless of ionic dissociation state. The other is that the monomer and the propagating species make charge transfer complex which is stable to chain transfer reactions. In both cases, the situation becomes really controversial if polymerization proceeds via fully dissociated carbocation. At present, however, there is no definite explanation or supporting data for these ideas. The study of other possible reasons is needed.

It is well known that the local environment of the growing active species affects microstructure of a polymer during polymerization reaction. In coordination or anionic polymerization the microstructure is controlled by the reaction condition and catalyst. And often, the information of microstructure is used in the study of the polymerization mechanism as seen in group transfer polymerization¹⁴ and others.¹⁵ In cationic polymerization area,

likewise, many workers¹⁶ tried to relate the microstructure of a polymer and the nature of active propagating species during the polymerization, even though the research efforts are quite less.

In the polymerization of alkyl vinyl ethers, it has been suggested that the extent of association between the growing cation and the counter ion is a significant factor in the steric control of the resultant polymers.¹⁷⁻²¹ Ledwith et al.¹⁹ reported that nonpolar solvents favor tight association between the propagating cation and its counter ion, leading to a more isotactic polymer, whereas polar solvents favor a more syndiotactic or random polymer.

In this research EVE and nBVE were polymerized by HI/I₂ catalyst and the resultant polymers were analyzed by carbon-13 NMR. Obtained tacticity information was related with the degree of association between the growing cation and the counter ion in this living cationic polymerization, in order to identify the true nature of the active propagating species.

EXPERIMENTAL

Polymer samples were obtained by the polymerization of EVE or nBVE with HI/I₂ catalyst under a living polymerization condition. Obtained polymers were characterized by gel permeation chromatography (GPC) with polystyrene standards. THF was used as the GPC solvent with flow rate

of 1 ml/min. The preparation of materials and the polymerization procedure were reported in detail in literature.¹²

Carbon-13 NMR spectra (50.3 MHz) were recorded on a Bruker WP-200SY spectrometer in CDCl₃ at room temperature. Proton decoupled carbon-13 NMR spectra were obtained with or without nuclear overhauser enhancement (NOE). Relaxation delay between each pulse was 5 sec. Areas of resonance peaks were determined by integration or by the weights of paper cuts.

RESULT AND DISCUSSION

Tacticity Analysis

Number average molecular weights of the obtained polymers ranged from 2,000 to 15,000. All samples showed very narrow polydispersities ($M_w/M_n < 1.1$). Fig. 1 shows the GPC chromatograms of poly(nBVE)s. Proton decoupled carbon-13 NMR spectra of poly(EVE) were obtained without NOE as shown in Fig. 2. The side group methyl carbon (-CH₃) and the main chain methine carbon (-CH-) were insensitive to the stereochemical configuration. The microstructures of the main chain methylene carbon (-CH₂-) and the side group methylene carbon (-CH₂-) were assigned according to Hatada's paper.²² The assignment was based on the microstructure of poly(methyl vinyl ether), in the order of rrr, mrr, mrm, rmr, mmm,

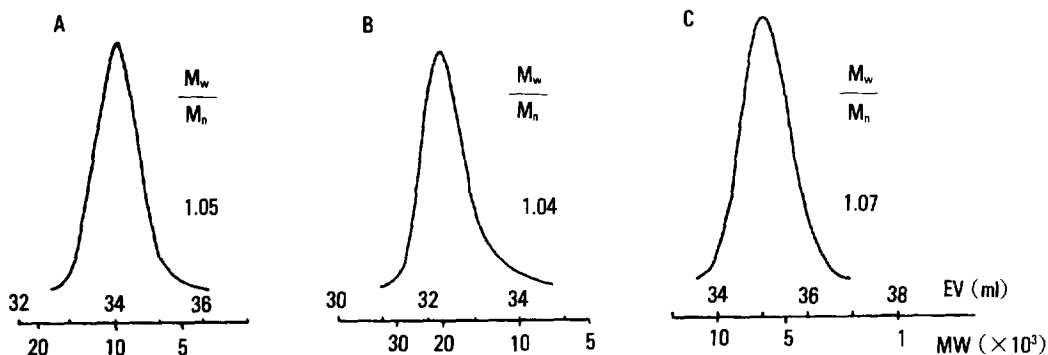


Fig. 1. GPC chromatograms of poly(nBVE)s obtained at different temperatures in n-hexane : A) -5°C , B) -15°C , C) -45°C .

Table 1. Tacticities of Poly(EVE) and Poly(nBVE)

Polymer	Polymerization System	Triads Observed ^a (%)			Diads Calculated ^b (%)		Diads Observed ^c (%)		Persistence Ratio (ρ)
		rr	rm	mm	r	m	r	m	
Poly(EVE)	HI-I ₂ /CCl ₄ /-16°C	7.8	63	29.2	39	61	38 ^d	62 ^d	0.757
Poly(EVE) ^e	BF ₃ OEt ₂ /toluene/-78°C	8	37	55	26	74	—	—	1.07
Poly(EVE) ^f	BF ₃ OEt ₂ /toluene/-78°C	8	36	56	26	74	25	75	1.07
Poly(EVE) ^f	BF ₃ OEt ₂ /CH ₂ Cl ₂ /0°C	12	50	38	37	63	35	65	0.93
Poly(EVE) ^f	PF ₅ /CH ₂ Cl ₂ /0°C	12	54	34	39	61	36	64	0.88
Poly(nBVE)	HI-I ₂ /n-hexane/-5°C	16.2	38.8	45	35.6	64.4	—	—	1.185
Poly(nBVE)	HI-I ₂ /n-hexane/-15.5°C	13.9	33.9	52.1	30.9	69.1	—	—	1.260
Poly(nBVE)	HI-I ₂ /n-hexane/-45°C	12	30	58	27	73	—	—	1.314

^a Determined from the resonance peaks of the side group -OCH₂-.

^b Calculated from the triads, $m = mm + (1/2)mr$, $r = rr + (1/2)mr$.

^c Determined from the resonance peaks of the main chain -CH₂-.

^d Determined by the weight of paper cut.

^e Data from ref) 22.

^f Data from ref) 23.

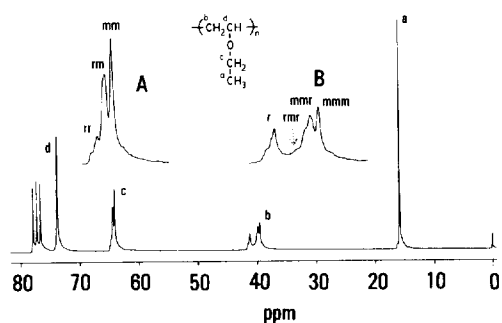


Fig. 2. 50.3 MHz carbon-13 NMR spectra of poly(EVE) in CDCl₃ at room temperature: Mn, 14,000; Polymerization temperature, -16°C, A) expanded plot of side chain methylene, B) expanded plot of main chain methylene.

mmm, from low to high field. The individual integrations of tetrads of the main chain methylene carbon were not carried out because of the poor resolution, whereas they were summed up and integrated as r and m. The integration result of the main chain carbon and the result of the side chain methylene carbon showed very similar tacticity result as shown in Table 1; i.e., the assignments

were internally consistent.²³

The reported spin-lattice relaxation time T_1 values of the side chain -OCH₂- are 0.29 sec at 22°C (68 MHz) for poly(allyl vinyl ether), and 1.19 sec (mm diad) for poly(EVE) at 110°C.²⁴ At room temperature the relaxation delay 5 sec between each pulse was assumed to be enough from a corresponding T_1 versus temperature relationship.²⁵ No difference was observed in the tacticity results of either the spectra with or without NOE.

Proton decoupled carbon-13 NMR spectra of poly(nBVE) were obtained with and without NOE. For a specific carbon in poly(nBVE), the spectra did not show any difference. For the tacticity measurement, decoupled spectra with NOE were used. As shown in Figure 3, only the main chain methylene carbon and the side chain methylene carbon were sensitive to the stereoconfiguration. These two resonance peaks were very similar to that of poly(EVE). Although the side chain methylene peak revealed fine microstructure, assignment was carried out only for triads, rr, mr, mm, due to the difficulty of the assignment of the peaks more than triads.

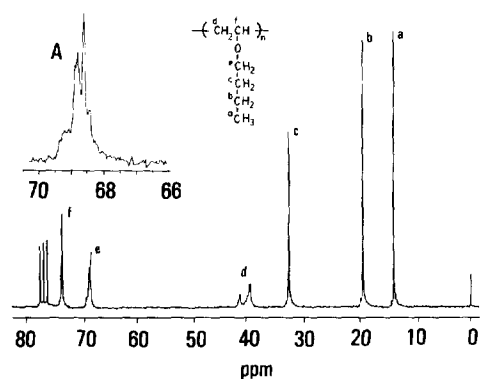


Fig. 3. 50.3 MHz carbon-13 NMR spectra of poly (nBVE) in CDCl_3 at room temperature: M_n , 15, 000; Polymerization temperature, -15.5°C , A) expanded plot of side chain methylene.

The persistence ratio, ρ , which is a criterion for Bernoullian random statistics,²⁶ was calculated by equation 5, and the calculated results are shown in the Table 1.

$$\rho = \frac{2(m)(r)}{(mr)} \quad (5)$$

The data deviate noticeably from the Bernoullian statistics, $\rho=1$. On the other hand, the reported values for the polymers prepared with BF_3OEt_2 ,^{22,23} showed close resemblance to the Bernoullian statistics. Also it is very interesting to note that higher isotacticity was observed for the polymerization catalyzed by BF_3OEt_2 , compared to the living EVE polymerization system.

On the Polymerization Intermediate

As shown in the Table 1, BF_3OEt_2 system undergoes polymerization with Bernoullian statistics. A similar phenomenon was reported in the polymerization system of SbCl_5 /pentane/ -72°C .^{17,24} In these polymerization systems the propagating species are believed to be free carbenium ions which are not strongly associated with counter ions and have planar sp^2 hybrid orbitals. An attack upon this ion by incoming monomer should be of the same probability irrespective of which side the monomer approaches from.²¹ Consequently, propa-

gation of such a free carbenium ion should lead to the formation of an atactic polymer unless there is a strong steric interaction of alkoxide groups between the growing chain end and the incoming monomer.

The polymerization system with HI/I_2 , however, did not follow Bernoullian statistics. This indicates that there is a steric interaction between the growing chain end and the incoming monomer by some ways. The reason may be due to the counter ion effect as described by Higashimura^{21,27} and Kunitake.²⁸ When a carbenium ion is closely associated with its counter ion the propagating chain end is considered to have a partial sp^3 character. Presumably this changes the stereoregularity of the resultant polymer.

As the polymerization temperature decreased, isotacticity of poly(nBVE) increased as shown in the Table 1. This isotacticity promotion may due to the tighter association of carbocation with its counter ion as the temperature decreases. Similar behavior is observed even in non-living systems such as (-)-menthyl vinyl ether or (S)-1-methyl propyl vinyl ether polymerization.¹⁹ Isotacticity increase was also reported either by the use of bigger counter ion or by the use of less polar reaction medium, in α -substituted vinyl ethers²⁹ and α -methylstyrene.¹⁸

If it is possible to make living polymerization system with a fully dissociated carbocation, then the reduced concentration or complexation may be the reason of the livingness, and the tacticity-temperature relationship may occur due to the change in complexation behavior which is unknown so far. But if one assumes that a chain transfer reaction cannot be prevented with a fully dissociated carbocation such as free ion or solvated ion pair, then possible species will be solvent separated ion pair and contact ion pair in the Winstein spectrum. The relative contribution to the reaction of the two species will be different, depending on the exact definitions of the species and their reactivities.

There has been no quantitative comparison on the reactivities of different ionic species, though a

recent report³⁰ claims that the reactivities of a free ion and an ion pair are almost same in a carbocationic polymerization. In general, the relative reactivity order of the species in the Winstein spectrum is known¹³ that : free ions > solvated ion pair > solvent separated ion pair > tight ion pair > covalent bond.

In this research, the reactivity of contact ion pair is considered to be quite less than that of solvent separated ion pair, and less reactivity is expected as the species becomes tighter. Therefore the relative concentration has to be, solvent separated ion pair << contact ion pair, in order to prevent the formation of a fully dissociated carbocation because all these species are in a series of continuous equilibria during the polymerization reaction. Even a small concentration of the solvent separated ion pair contributes much to the overall propagating reaction, but contributes less to the isotacticity of the polymer due to the less steric interaction between the growing species and incoming monomer.

In order to observe isotacticity, therefore, it is essential to have a considerable concentration of contact ion pair. It is easier to understand why isotacticity increases as the temperature decreases ; Lower temperature makes the contact ion pair more populated than the other to increase the isotacticity of the resultant polymer. And the contact ion pair itself becomes tighter. Thus the active propagating species will be more likely contact ion pair and solvent separated ion pair, where the concentration of the former is predominant.

Though this research was limited to the living polymerization system of alkyl vinyl ethers initiated with HI/I₂, other living cationic polymerization systems initiated with other catalysts are expected to yield a similar behavior. The study on other systems will be reported elsewhere.

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