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A. Mizote[a]; T. Higashimura[a]; S. Okamura[a]
[a] Department of Polymer Chemistry, Kyoto University, Kyoto, Japan

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Cationic Polymerization of β-Phenylvinyl Alkyl Ethers*

A. MIZOTE, T. HIGASHIMURA, and S. OKAMURA

Department of Polymer Chemistry
Kyoto University
Kyoto, Japan

SUMMARY

The cationic polymerization of β-phenylvinyl alkyl ethers (alkyl: methyl, ethyl, n-propyl, and n-butyl) was examined in toluene and in methylene chloride with boron fluoride etherate and with stannic chloride at −78°C. Despite the fact that these monomers have bulky substituents on the α- and β-carbons, they could be homopolymerized easily even in nonpolar solvent at −78°C. The general features of β-phenylvinyl alkyl ethers in homopolymerization and copolymerization with n-butyl vinyl ether suggested that β-phenylvinyl alkyl ethers behaved as derivatives of vinyl ethers, not as derivatives of styrenes. The polymerization products were white powders having a high softening point.

INTRODUCTION

The cationic polymerization of β-phenylvinyl alkyl ethers have not been reported as far as is known. β-Phenylvinyl alkyl ethers can be regarded as derivatives of β-substituted styrenes and can also be regarded as derivatives of β-substituted vinyl ethers. Also, bulky substituents exist on both α- and β-carbons. Thus it is interesting to study β-phenylvinyl alkyl ethers from the viewpoint of their general features in polymerization.

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*This is the seventh in a series of papers concerned with cationic polymerization of α, β-disubstituted olefins. For the sixth paper, see Y. Ohsumi et al., *J. Polymer Sci.*, **A-1**, to be published.

In this paper the polymerization of four monomers of β-phenylvinyl alkyl (alkyl: methyl, ethyl, n-propyl, and n-butyl) ethers will be reported. It was found that these β-phenylvinyl alkyl ethers could be easily homopolymerized even in toluene with boron fluoride etherate at a dry ice-methanol temperature, in spite of the existence of bulky substituents on the α and β positions in a monomer which retards the polymerization sterically. The polymerization products were white powders having a high softening point, and some of them were found by X-ray diffraction analysis to be slightly crystalline.

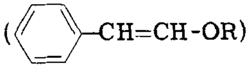
The general feature of β-phenylvinyl alkyl ethers in homopolymerization and in copolymerization with n-butyl vinyl ether indicated that these α, β-disubstituted olefins behave as derivatives of vinyl ethers in cationic polymerization.

EXPERIMENTAL

Materials

β-Phenylvinyl Alkyl Ethers. According to Miller [1], these monomers were prepared from phenyl acetylene and alcohols with the corresponding sodium alkoxide. The physical properties of β-phenylvinyl alkyl ethers are shown in Table 1. As far as is known, β-phenylvinyl ethyl ether and β-phenylvinyl n-propyl ether have not been synthesized. The main components (not less than 98%) of the geometric isomers in these monomers were cis isomers. As β-phenylvinyl alkyl ethers were oxidized in air, the monomers were

Table 1. Physical Properties of β-Phenylvinyl Alkyl Ethers


(C_6H_5-CH=CH-OR)

R	b. p., °C	n_D	d	Ref.
CH_3	77-78 (6 mm Hg)	1.5667 (23°C)	0.990 (20°C)	a
	210 (760 mm Hg)	1.5683 (20°C)	—	1
C_2H_5	88-90 (6.5 mm Hg)	1.5485 (20°C)	0.981 (20°C)	a
n-C_3H_7	96-97 (7 mm Hg)	1.5442 (18°C)	0.973 (15°C)	a
n-C_4H_9	108 (5 mm Hg)	1.5330 (20°C)	0.957 (15°C)	a
	139 (19 mm Hg)	1.5381 (20°C)	0.940 (20°C)	2

[a] Present data.

used immediately after purification by distillation at reduced pressure under a nitrogen atmosphere.

Other Materials. The n-butyl vinyl ether, solvents, and catalysts used were all commercial products and the materials were purified by conventional methods.

Procedure

Polymerization. Polymerizations were carried out in a way similar to that described in Part I of this series [3]. To a reaction vessel containing monomer and solvent under slight pressure of dry nitrogen, a small amount of catalyst solution was added through the rubber cap. The reaction was killed by adding cold methanol. Copolymerization products were taken out under less than 10% conversion.

Molecular Weight. The molecular weight of poly-β-phenylvinyl methyl ether was measured by an ebuliometer (Takara twin type). Polymerization products other than β-phenylvinyl methyl ether contained a small amount of insoluble material in benzene, toluene, and chlorinated hydrocarbons such as methylene chloride at room temperature. Therefore, the molecular weights of those products were not measured.

Analysis of Copolymer Composition. The copolymerization products of n-butyl vinyl ether and β-phenylvinyl alkyl ethers were analyzed by elementary analysis. Monomer reactivity ratios were determined by the intersection method.

RESULTS

Homopolymerization of β-Phenylvinyl Methyl Ether and β-Phenylvinyl Ethyl Ether

Although the homopolymerization of β-phenylvinyl alkyl ethers is hard by the radical mechanisms [4], these monomers could be homopolymerized by a Friedel-Craft catalyst such as boron fluoride etherate or stannic chloride even at a dry ice-methanol temperature, in spite of the fact that the existence of a β substituent in the monomer generally decreases the polymerizability.

The results of the homopolymerization of β-phenylvinyl methyl ether and β-phenylvinyl ethyl ether catalyzed by boron fluoride etherate and stannic chloride are summarized in Table 2.

Table 2. Cationic Polymerization of β-Phenylvinyl Methyl Ether and β-Phenylvinyl Ethyl Ether at —78°C

Expt. No.	Monomer, moles/liter	Catalyst, moles/liter	Solvent	Reaction time, hr.	Conversion, %	M_n
	β-phenylvinyl methyl ether	$BF_3 \cdot OEt_2$				
1	0.18	0.12	Toluene	20	97	15×10^3
2	0.37	0.06	Toluene	20	94	14×10^3
3	0.74	0.12	Toluene	20	94	10×10^3
4	0.74	0.08	Toluene	3	1	10×10^3
5	0.74	0.08	CH_2Cl_2	3	29	7.5×10^3
		$SnCl_4$				
6	0.74	0.01	Toluene	35	8.7	—
7	1.47	0.01	Toluene	35	2.1	—
8	0.74	0.01	CH_2Cl_2	33	41.2	—
9	1.47	0.01	CH_2Cl_2	33	26.7	—
	β-phenylvinyl ethyl ether	$BF_3 \cdot OEt_2$				
10	0.66	0.08	Toluene	3	95	—
11	0.66	0.08	CH_2Cl_2	3	93	—

The solution of the polymerization systems went from yellow to orange during polymerization, and the color deepened with increasing conversion and monomer concentration.

It is seen in Table 2 that the polymer yield was higher in methylene chloride than in toluene (Expts. 5 and 4, 8 and 6, 9 and 7) and at a lower monomer concentration (Expts. 6 and 7 or 8 and 9). On the other hand, higher molecular weight polymers were obtained in toluene than in methylene chloride (Expts. 3, 4, and 5) and at a lower monomer concentration (Expts. 1, 2, and 3). β-Phenylvinyl ethyl ether polymerized much faster than β-phenylvinyl methyl ether (Expts. 10 and 11).

Quantitative experiments on the homopolymerization of β-phenylvinyl n-propyl ether and β-phenylvinyl n-butyl ether were not carried out, but the appearance of the polymerization systems were similar to those of β-phenylvinyl methyl ether. The solution of the polymerization systems became yellow and turbid during the polymerization.

Polymerization Products of β-Phenylvinyl Alkyl Ethers

The poly(β-phenylvinyl alkyl ethers) (alkyl: methyl, ethyl, n-propyl, and n-butyl) were white powdery materials. The polymers had considerably high softening points as shown in Table 3. Poly(β-phenylvinyl methyl ether) was soluble in aromatic solvents and chlorinated hydrocarbons, but polymers other than poly(β-phenylvinyl methyl ether) contained a small insoluble part. The molecular weight of poly(β-phenylvinyl methyl ether) in these experiments was about 7.5-15 × 10^3 as shown in Table 2. The IR spectrum of poly(β-phenyl vinyl methyl ether) is shown in Fig. 1. The other poly(β-phenylvinyl alkyl ethers) gave similar IR spectra. The absorption peak at 1650 cm^{-1} ($\gamma_{C=C}$ stretching) in the monomer disappeared completely in the spectra of the polymer, while the characteristic absorption peaks of monosubstituted phenyl and etheric linkage remained. This means that the polymerization product was

Table 3. Softening Points of Poly(β-phenylvinyl Alkyl Ethers), $-\!\left(\mathrm{CH}\cdot\mathrm{C_6H_5}-\mathrm{CHOR}\right)\!-_n{}^{a}$

R	CH_3	C_2H_5	n-C_3H_7	n-C_4H_9
Softening point, °C	200-215	275-285, decomp.	280, decomp.	255-265

[a](Solvent, toluene; catalyst, $BF_3 \cdot OEt_2$, temperature, -78°C.)

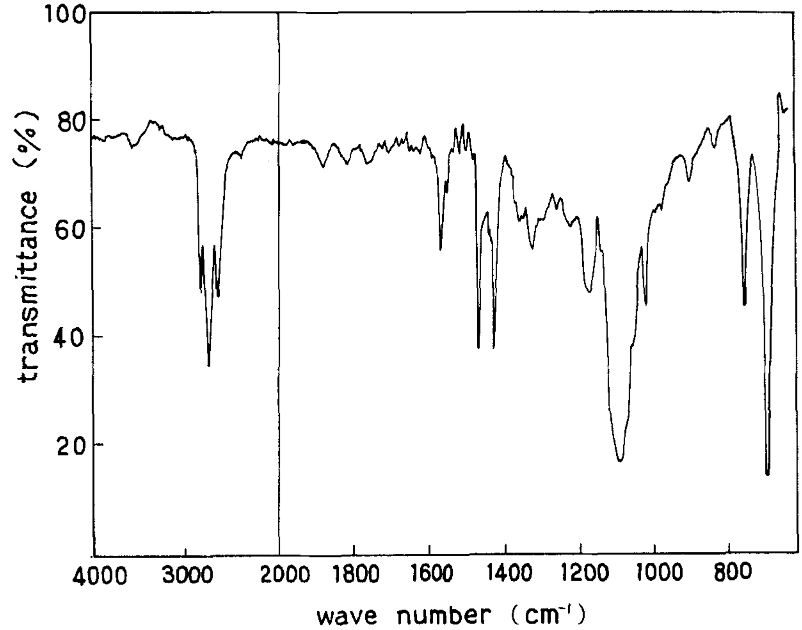


Fig. 1. Infrared spectrum of poly(β-phenylvinyl methyl ether) (KBr disk).

yielded by the vinyl polymerization. X-ray diffraction patterns of poly(β-phenylvinyl methyl ether) showed it to be amorphous, while those of other poly(β-phenylvinyl alkyl ethers) were not completely amorphous but could be regarded as being crystalline to some extent.

Copolymerization of β-Phenylvinyl Alkyl Ether with n-Butyl Vinyl Ether

The copolymerization product from n-butyl vinyl ether and β-phenylvinyl n-butyl ether in which the mole fraction of β-phenylvinyl ether in the polymer was 0.8 was powdery and soluble in n-hexane at a room temperature, while poly(β-phenylvinyl ether) was insoluble and poly(n-butyl vinyl ether) was soluble in n-hexane. This fact shows that β-phenylvinyl n-butyl ether was copolymerized with n-butyl vinyl ether.

Figure 2 shows the copolymer composition curves of the copolymerization of β-phenylvinyl alkyl ethers with n-butyl vinyl ether catalyzed by boron fluoride etherate in toluene at −78°C. The monomer reactivity ratios were determined by the intersection method and those values are listed in Table 4.

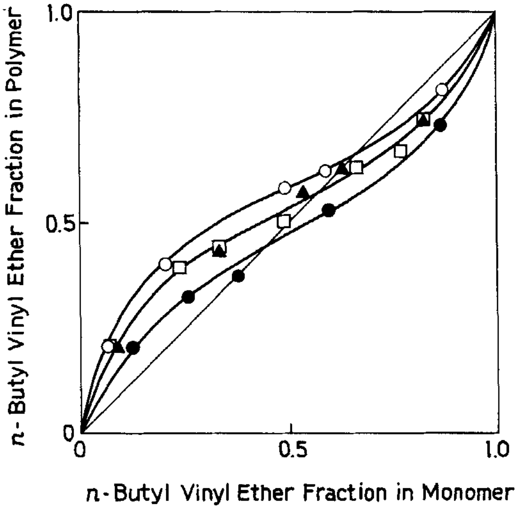


Fig. 2. Copolymer composition curves of n-butyl vinyl ether and β-phenylvinyl alkyl ethers ($C_6H_5 \cdot CH{=}CHOR$) Monomer, 10 vol.%; solvent, toluene; catalyst, $BF_3 \cdot OEt_2$; temperature, −78°C. R: ○, CH_3; ▲, C_2H_5; □, n-C_3H_7; ●, n-C_4H_9.

Table 4. Monomer Reactivity Ratios of the Copolymerization of n-Butyl vinyl ether (M_1) and β-Phenylvinyl alkyl ethers (M_2) ($Ph \cdot CH{=}CHOR$)[a]

M_2	r_1	r_2
Methyl	0.55 ± 0.1	0.15 ± 0.05
Ethyl	0.45 ± 0.1	0.25 ± 0.1
n-Propyl	0.45 ± 0.1	0.25 ± 0.1
n-Butyl	0.25 ± 0.1	0.45 ± 0.1

[a] Calculated from Fig. 2.

In the homopolymerization of α,β-disubstituted olefins, the steric hindrance of the β substituent [5] is observed. However, when the propagating species from the vinyl monomer without β-substituent attacks the α,β-disubstituted olefins, the steric hindrance due to the β substitutent in the monomer is very much decreased. Thus the net monomer reactivity of α,β-disubstituted olefins could be estimated by the copolymerization.

The relative monomer reactivities of these β-phenylvinyl alkyl ethers against the propagating species of n-butyl vinyl ether were larger than n-butyl vinyl ether. The order of the reactivity of the β-phenylvinyl alkyl ethers against n-butyl vinyl ether were alkyl: n-butyl > n-propyl ≈ ethyl > methyl. The difference in the monomer reactivity between each monomers was small.

DISCUSSION

β-Substituted vinyl monomers were considered to have a lowered homopolymerizability due to the steric hindrance between the β substitutent of an incoming monomer and that of a growing chain end at the transition state. However, it was found that β-phenylvinyl alkyl ethers could be homopolymerized to yield white powdery products having higher melting points by the cationic mechanism.

β-Phenylvinyl alkyl ethers can be regarded as derivatives of vinyl ethers and also can be regarded as derivatives of styrenes. Styrenes and vinyl ethers are well-known monomers which can be polymerized cationically, but their behavior in cationic polymerization is somewhat different. For example, in the cationic polymerization of vinyl ethers, the molecular weight of the polymer decreases with increasing polarity of the solvent used in the polymerization [6]. On the other hand, the molecular weight of polystyrene increases with increasing polarity of the solvent [7]. The cationic polymerization of β-phenylvinyl alkyl ethers is not known to be present. Table 2 shows that the molecular weight of poly(β-phenylvinyl methyl ether) decreased with increasing polarity of solvent and with increasing monomer concentration in toluene. Moreover, β-phenylvinyl ethyl ether was much more reactive than β-phenylvinyl methyl ether in the rate of homopolymerization. This fact is also comparable to the fact that the monomer reactivity of ethyl vinyl ether is larger than methyl vinyl ether. While the introduction of β substituent on styrene decreases the polymerizability markedly, β-substituted vinyl ethers have still higher polymerizability, even when the β substituent was a large and rigid group such as a phenyl group.

β-Phenylvinyl alkyl ethers can be copolymerized with n-butyl vinyl ether and the relative monomer reactivitites of β-phenylvinyl alkyl ethers against n-butyl vinyl ether's chain end were larger than n-butyl vinyl ether. This means that β-phenyl substitution on the vinyl ethers enhances the monomer reactivities of vinyl ethers. The same effects of β substitution were recognized on the monomer reactivities of vinyl ethers when methyl and ethyl groups were introduced to the cis position against alkoxy groups [8, 9].

The monomer reactivity ratios of the four pairs of copolymerizations in Table 4 were all less than unity. When n-butyl vinyl ether's chain end attacks β-phenylvinyl alkyl ethers, steric hindrance by the β substituent would be much smaller. The relative monomer reactivities (r_1) of β-phenylvinyl alkyl ethers against n-butyl vinyl ether's chain end would be reflected in the net monomer reactivities with less influence by steric hindrance.

On the other hand, the relative monomer reactivity ratios (r_2) were also all less than unity. This could be explained by steric hindrance in the self-addition process of β-phenylvinyl alkyl ethers. In fact, although the relative monomer reactivities (r_1) of β-phenylvinyl ethers were larger than n-butyl vinyl ether in copolymerization, the rate of homopolymerization of the β-phenylvinyl ethers was observed to be much smaller than that of n-butyl vinyl ether. There were a few cases [3, 5] in which both monomer reactivity ratios were less than unity in copolymerization, when one comonomer was β-substituted monomer, and steric hindrance should be considered.

The monomer reactivities of β-phenylvinyl alkyl ethers increased in the order of the size of the alkyl group: methyl $<$ ethyl $\approx$ n-propyl $<$ n-butyl. Taking into consideration that vinyl ethers can hardly copolymerize with styrene and that β-ethyl styrene could not be homopolymerized [5], these results show that β-phenylvinyl alkyl ethers behave as β-substituted derivatives of vinyl ether, not as β-substituted derivatives of styrene.

The poly(β-phenylvinyl alkyl ethers) were white powders and looked like polystyrene. However, their softening points were higher than that of polystyrene and were over 200°C. X-ray diffraction analysis of poly(β-phenylvinyl alkyl ethers) showed a pattern that could be considered evidence of partially crystalline polymer. Crystalline polymers could not be obtained from the cis isomer of propenyl alkyl ethers with a homogeneous catalyst. The β-phenylvinyl alkyl ethers studied were cis isomers. Therefore, it would be an interesting problem to see whether or not these cis monomers could give crystalline polymers with a homogeneous catalyst, and further studies on this point should be carried out.

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