Polymer Bulletin 1, 365–369 (1979)

Polymer Bulletin

The Effect of the Counter-anion on the Steric Structure of Poly(alkenyl Ether)s in Cationic Polymerization*

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ABSTRACT

Ethyl propenyl and butenyl ethers were polymerized in toluene at -78°C by a variety of catalysts, and effect of a counter-anion on steric structure of the polymer was investigated. The trans monomer produced stereoregular polymer with threo-meso structure and its content was independent of kind of the catalysts. In the polymerization of the cis monomer, the contents of the threo-meso and racemic structures of the poly(cis-propenyl ether) depended on the kind of the catalysts whereas those of the poly(cis-butenyl ether) having bulky β-ethyl groups did not. The difference of the counter-anion effect was discussed on the basis of the difference of the β-substituent in bulkiness.

INTRODUCTION

It has been shown that in homogeneous cationic polymerization of vinyl ethers, not only a substituent of monomer but also a counter-anion plays an important role in determining a steric structure of the polymer (OKAMURA et al., 1959 ; KUNITAKE et al., 1976). In cationic polymerization of alkenyl ether having a β-substituent, it is not apparent whether the factors determining the steric structure of the polymer are the same as those in the polymerization of the vinyl ethers. The steric structure of the poly(β-substituted-vinyl ether)s obtained with $BF_3O(C_2H_5)_2$ has been found to depend on a geometrical structure and bulkiness of the substituent of the monomer (HIGASHIMURA et al., 1977 ; HIROKAWA et al., 1979a, 1979b). However, there has been no quantitative report concerning the effect of the counter-anion on the steric structure of poly(α,β-disubstituted olefin).

Therefore, in the present paper, the effect of the counter-anion on the steric structure of the polymer is discussed on the basis of ^{13}C-NMR spectra of poly(ethyl propenyl ether)s and poly(ethyl butenyl ether)s

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*[1] Stereochemistry in Cationic Polymerization of Alkenyl Ethers. Part 4.

0170-0839/79/0001/0365/$01.00

obtained by a variety of catalysts. Since the effect of the counter-anion will clearly appear in a nonpolar solvent, toluene was employed as a solvent.

EXPERIMENTAL

Ethyl propenyl ether and ethyl butenyl ether (EPE and EBE, respectively) were synthesized and purified as described previously (HIGASHIMURA et al., 1977 ; HIROKAWA et al., 1979a, 1979b). $BF_3O(C_2H_5)_2$, $Al(C_2H_5)Cl_2$, and $SnCl_4$ were purified by distillation under reduced pressure. CH_3COClO_4 was prepared by the method reported previously (MASUDA, HIGASHIMURA, 1971). Commercial CCl_3COOH, a cocatalyst for $SnCl_4$, was used without further purification. Toluene was purified by the conventional method.

Polymerization and ^{13}C-NMR measurement were carried out by the methods identical to those described previously (HIGASHIMURA et al., 1977 ; HIROKAWA et al., 1979a, 1979b). The diad tacticities of α- and β-carbons in the polymer coincided with each other within experimental errors.

RESULTS and DISCUSSION

Polymerization of Ethyl Propenyl Ether by Various Catalysts. Trans- and cis-EPE were polymerized by a variety of catalysts in toluene at -78°C and ^{13}C-NMR spectra of the polymers obtained were measured.

The spectra of the poly(trans-EPE)s showed the sharp single peaks assigned to threo-meso structure independent of the kind of the catalysts, as reported on the polymer obtained with $BF_3O(C_2H_5)_2$ (HIROKAWA et al., 1979a). On the other hand, in the spectra of the poly(cis-EPE), the relative intensity of the peaks due to the threo-meso and racemic structures depended on the kind of the catalyst employed and the peak due to the erythro-meso was not observed.

The diad tacticities which were calculated from the peak area in the ^{13}C-NMR spectra of the polymers are shown against a counter-anion size in Figure 1. As the structure of a counter-anion is obscure in cationic polymerization by metal halide, we presumed that the sizes of the counter-anions produced from $BF_3O(C_2H_5)_2$, $Al(C_2H_5)Cl_2$, and $SnCl_4$ are the same as those of BF_4^-, $AlCl_4^-$, and $SnCl_5^-$, respectively, and assumed the values calculated from the length of covalent bond and van der Waals radii (PAULING,1960). As shown in Figure 1, the trans monomer stereospecifically produced the crystalline polymer having the threo-meso structure (about 90%) with all catalysts employed. Thus, in the polymerization of the trans monomer, the counter-anion did not affect the steric structure of the polymer, which agrees with the absence of the solvent effect (HIROKAWA et al., 1979b). The fact indicates that in the polymerization of the trans monomer the substituents of the monomer and of the growing chain end cause a large steric hindrance, promoting one direction of the addition.

On the other hand, in the polymerization of the cis monomer, the racemic fraction increased from 55% to 75% as the size of the counter-anion increased. The dependence of steric structure of the polymer on the size of the counter-anion indicates that, in the polymerization of tne cis monomer, an interaction between the substituents of the monomer and the growing chain end is affected by the counter-anion. This fact is explained by an interpretation that an enhancement of the interaction between the cis monomer and the counter-anion, which was caused by an increase of the size of the latter, restricts the direction of the monomer addition.

As revealed in the previous paper (HIROKAWA et al., 1979b), however, the threo-meso fraction increased and the racemic fraction decreased as the solvent polarity increased in the polymerization of cis monomer. In a

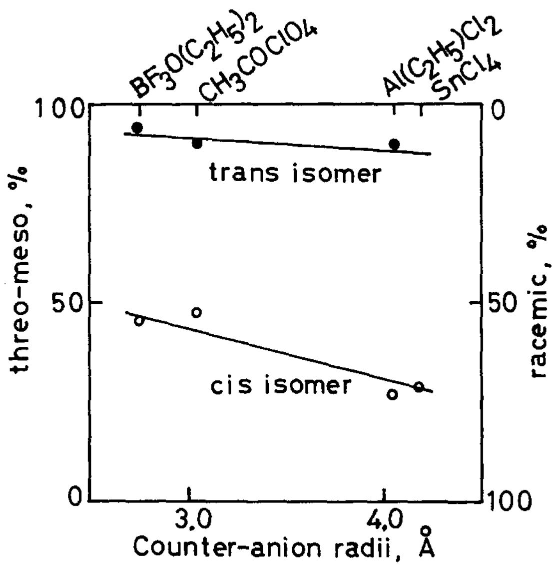

Figure 1. Effect of the counter-anion on the steric structure of poly(ethyl propenyl ether)s obtained in toluene at -78°C. Polymerization conditions; $[Monomer]_o$: 10 vol%, $[Catalyst]_o$: 0.3-5.0 mmoles/l, ^{o}time 18-22 hr, conv.: ^{o}>85%, [η] of the polymers: 0.1~0.8 dl/g.

polar solvent, the counter-anion is located in a place apart from the propagating species. Therefore, the steric structure of the polymer is determined only by the interaction of the propagating chain end with the incoming monomer, resulting in the easy formation of the threo-meso structure as with the polymerization of the trans monomer.

Thus, it was revealed that the steric structure of the polymer depended on the counter-anion for the polymerization of the cis monomer whereas that did not for the polymerization of the trans monomer.

Polymerization of Ethyl Butenyl Ether by Various Catalysts. Trans- and cis-EBE were polymerized in toluene at -78°C by various catalysts and the steric structure of the polymers obtained were measured by means of ^{13}C-NMR spectroscopy. In the polymerization of cis monomer, both resonances due to the α-carbon in the main chain and the β-methyl carbon in the β-ethyl group split into three, indicating the presence of the three steric structures (threo- and erythro-meso and racemic) concerning both α- and β-carbons (HIROKAWA et al., 1979a). On the other hand, the spectra of the

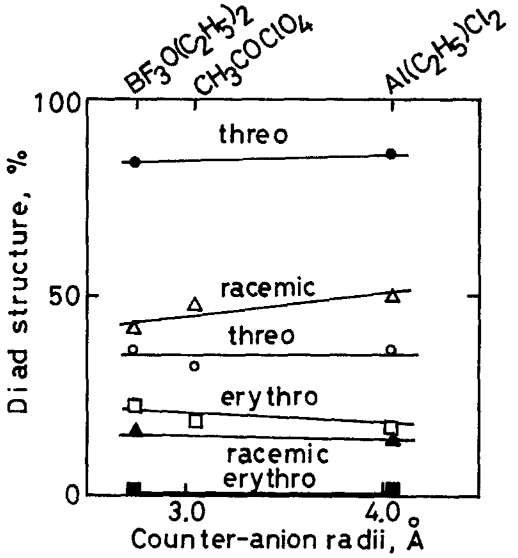

Figure 2. Effect of the counter-anion on the steric structure of poly(ethyl butenyl ether)s obtained in toluene at -78°C. Polymerization conditions; $[\text{Monomer}]_0$: 10 vol%, $[\text{Catalyst}]_0$: 0.3-20 mmoles/l, time: 20-22 hr, conv.: >85%, [η] of the polymers: 0.1-0.2 dl/g. (Filled marks: trans monomer, open marks: cis monomer)

polymers obtained from the trans monomer were the same as that of the polymer with $BF_3O(C_2H_5)_2$, indicating the stereospecific formation of the threo-meso structure.

Figure 2 shows the effect of the size of the counter-anion on the diad structures which were calculated from the peak area in the ^{13}C-NMR spectra of the polymers. The evaluation of the size of the counter-anion was mentioned above, and the assignment of the peak to the steric structure was reported previously (HIROKAWA et al., 1979a). As shown in Figure 2, the steric structure of the polymer did not depend on the size of the counter-anion in the polymerization of the cis monomer as well as the trans monomer.

In the polymerization of vinyl ethers, there has been reported that the steric structure of the polymer remarkably depended on the catalyst (OKAMURA et al., 1959 ; KUNITAKE et al., 1976). On the other hand, the steric structure of the poly(β-substituted-vinyl ether) scarcely depended on the kind of the catalyst as described above. These facts indicate that in the polymerization of α,β-disubstituted monomers such as β-substituted-vinyl ether the steric hindrance between the substituents of the monomer and of the growing chain end plays an more important role in determining the steric structure of the polymer than the steric interaction between the growing chain end and the counter-anion.

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Received February 13, 1979