Copolymerization of Optically Active Ethyl 2-Methyl-2-ethyl-2-butenoate with Vinyl Acetate

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In order to investigate the steric effect on the radical polymerization of vinyl compounds, we have prepared ethyl 2-methyl-2-ethyl-2-butenoate (Et-MEB)* which has an optical center nearest to the vinyl group, and studied the polymerization of the ester at 60°C. in the presence of benzoyl peroxide. The ester polymerized only slightly by itself, while it polymerized to a certain extent with vinyl acetate (VAc) under the experimental conditions. A sample of (+)-Et-MEB, the optical purity of which was 75%, was resolved by using brucine from (±)-Et-MEB, and the monomer reactivity ratios, r_1 and r_2, in the copolymerization of (+)-Et-MEB with VAc were compared with those in the same reaction of (±)-Et-MEB with VAc. The results obtained are given in the following table.

Monomer Reactivity Ratio within the Limits of [VAc]/[Et-MEB]=1-3

In the case of	Monomer reactivity ratio
(±)-Et-MEB and VAc	$r_1=k_1/k_2=3.2\pm0.5$, $r_2=k_3/k_4=0.3\pm0.2$
(+)-Et-MEB and VAc	$r_1=k_1/k_2=2.2\pm0.4$, $r_2=k_3/k_4=0.1\pm0.1$

where k_1, k_2, k_3 and k_4 indicate the rate constant of the reactions (1), (2), (3) and (4), respectively.

$$\cdots\cdots\text{VAc}\cdot + \text{VAc} \xrightarrow{k_1} \cdots\cdots\text{VAc}\cdot \quad (1)$$

$$\cdots\cdots\text{VAc}\cdot + \text{Et-MEB} \xrightarrow{k_2} \cdots\cdots\text{Et-MEB}\cdot \quad (2)$$

$$\cdots\cdots\text{Et-MEB}\cdot + \text{Et-MEB} \xrightarrow{k_3} \cdots\cdots\text{Et-MEB}\cdot \quad (3)$$

$$\cdots\cdots\text{Et-MEB}\cdot + \text{VAc} \xrightarrow{k_4} \cdots\cdots\text{VAc}\cdot \quad (4)$$

The data in the table suggest that the reactivity of (+)-Et-MEB on the radical of VAc-type may be about 1.5 times as large as that of (±)-Et-MEB in the reaction (2), because no steric effect will appear on the rate of reactions (1) and (4).

Assuming that the acetyl group of polyvinyl acetate is arranged over five to six units of vinyl acetate at least in such an orientation as has been recognized in that of hydroxyl group of polyvinyl alcohol, a similar orientation will also be given to the acetyl group of the growing copolymeric radicals.

Then it may be possible that the reactivity of (+)-Et-MEB on the growing radical of VAc-type is different from that of (±)-Et-MEB.

The details of this study will be reported in a separate paper.

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* The physical properties of the ester were found as follows: b.p.$_{50}$ 82.0°C., d_4^{20} 0.89423, n_D^{20} 1.4290.