The Copolymerization of Trimethylethylene and Tetramethylethylene with Maleic Anhydride*

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In a previous paper,[1] it was reported that *cis*-butene-2 was more reactive than the *trans*-isomer in the copolymerization with maleic anhydride (MAn). We wish now to report the copolymerization behavior of trimethylethylene and tetramethylethylene with MAn in comparison with that of butene-2. Trimethylethylene was readily copolymerized with MAn to give a copolymer with a relatively high molecular weight, whereas tetramethylethylene gave practically no copolymer with MAn.

Momoners were copolymerized at 60°C in benzene in the presence of 2, 2'-azobisisobutyronitrile as an initiator. Conversions were less than 5% in all cases. Copolymers were purified by repeated reprecipitation from an acetone solution with dry ether. The copolymer compositions were calculated from the analysis with correction for absorbed water. Specific viscosities were measured in acetone at 30°C, using an Ostwald viscometer. The results are shown in Fig. 1.

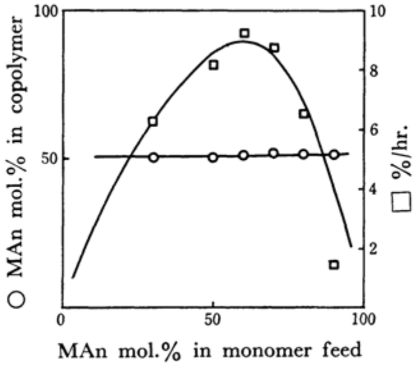

Fig. 1. Copolymerization of trimethylethylene (M_2) with MAn (M_1). $[M_1+M_2]=2.0$ mol./l., [AIBN]$=0.01$ mol./l. in benzene at 60°C.

The resulting copolymers of trimethylethylene with MAn were found to have a 1 : 1 molar composition and almost identical specific viscosities (0.14—0.18, $c=0.3$ g./dl.), independent of the monomer compositions. It was observed that

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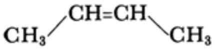
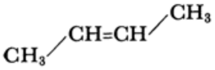
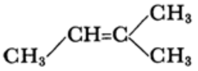
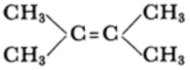
* Paper VIII in a series on "The Polymerization of Internal Olefins." For the preceding paper, see S. Murahashi, S. Nozakura, T. Okamoto and Y. Kotake, *Chem. High Polymer* (*Kobunshi Kagaku*), in press.

[1] S. Murahashi, S. Nozakura and K. Yasufuku, This Bulletin, **38**, 2082 (1965).

TABLE I. COMPARISON OF THE REACTIVITIES OF BUTENE-2, TRIMETHYLETHYLENE (M_2) AND TETRAMETHYLETHYLENE IN THE COPOLYMERIZATION WITH MAn (M_1)
$[M_1]=[M_2]=1.0$ mol./1., $[AIBN]=0.01$ mol./1. in C_6H_6, 60°C

M_2	Rate %/hr.	$\eta_{sp/c}$	Soft p. °C	r_1
	0.8	0.08	185—190	0.016 ± 0.005
	0.6	0.07	175—185	0.030 ± 0.009
	10.0	0.18	245—250	0.005 ± 0.002
	0	—	~150	—

* $c=0.3$ g./dl.

the rate of copolymerization reached a maximum value at the monomer composition of about 60 mol.% of MAn. A distinct yellow coloration was observed on mixing tetramethylethylene with MAn, suggesting the formation of a charge transfer complex between monomers. However, this system did not give an appreciable amount of copolymer by the usual procedure. A very slow polymerization was recognized from the facts that a slight volume contraction was observed in a dilatometric measurement and that a trace of colored noncrystalline powder (soft. p. ~150°C) was obtained by the careful treatment of the contents of the dilatometer.

Table I gives a comparison of the copolymerization behavior of trimethylethylene, tetramethylethylene, *cis*- and *trans*-butene-2[1] with MAn under similar conditions. Trimethylethylene, in comparison with butenes, copolymerized with a higher rate and with a greater tendency to alternation with MAn, yielding copolymers of higher specific viscosities. This result was rather unexpected, but it was rationalized as follows. The higher reactivity of trimethylethylene compared with butene-2 may be due to the increase in the electron density of the C=C double bond by the substitution of one more methyl group, since the MAn radical is partially positive in character. Also, the increase in the resonance stability of the resulting radical might have contributed to the reactivity. The increase in steric hindrance due to the additional methyl group might not play a significant role in this case.

The introduction of the fourth methyl group resulted in a further increase in the electron density, as is shown in the yellow coloration of a charge transfer complex. The low reactivity of tetramethylethylene, however, suggests the overwhelming effect of the steric inhibition of four methyl groups. Similar behavior of the multi-substituted ethylenes had been found in the copolymerizations of chlorinated ethylenes with various monomers.[2]

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[2] K. W. Doak, *J. Am. Chem. Soc.*, **70**, 1525 (1948).