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## **Polymers from 1,2-Disubstituted Ethylenic Monomers. IX. Radical High Polymerization of Methyl-tert-butyl Fumarate**

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### **ABSTRACT**

Methyl-tert-butyl fumarate (MtBF) was found to homopolymerize in bulk in the presence of 2,2'-azobisisobutyronitrile (AIBN) at 50-80°C to give a high molecular weight polymer. From IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra, this polymer was assumed to consist of alternating methoxycarbonylmethylene and tert-butoxycarbonylmethylene units, indicating that it was produced from MtBF through an ordinary vinylene polymerization mechanism. Consideration of a molecular model suggested that this polymer had a less flexible rodlike structure with the diameter of about 13.5 Å. The thermal properties of this polymer were also evaluated. Moreover, the bulk polymerization of MtBF initiated by AIBN was investigated kinetically at 60°C. The overall activation energy for this polymerization was determined to be 83.5 kJ/mol. The reaction orders with respect to the monomer and initiator concentrations were obtained as 2.0 and 0.33, respectively.

## INTRODUCTION

In a previous paper [1], various dialkyl fumarates were found to homopolymerize in the presence of a radical initiator to give relatively high molecular weight polymers. In that paper we also reported that some dialkyl fumarates with bulky branched-alkyl ester groups, especially diisopropyl fumarate, were homopolymerized easily. Moreover, the polymers obtained were found to consist of a less flexible rodlike structure [2], and hence to show high softening and glass transition temperatures [1, 2]. Recently, similar results were observed for a series of methylalkyl fumarates [3]. It is worth noting that these monomers having a sterically hindered double bond are highly polymerizable and give a rodlike polymer.

To confirm these observations, we have prepared methyl-tert-butyl fumarate (MtBF) and attempted to polymerize it. As a result, MtBF was found to polymerize readily to give a high molecular weight homopolymer [2]. The present paper describes the kinetic results of radical high polymerization of MtBF and characterizes the resulting polymer.

## EXPERIMENTAL

### Materials

MtBF monomer was prepared as follows: Maleic anhydride was reacted with excess methanol at room temperature, and the resulting monomethyl maleate was then reacted with thionyl chloride in benzene. The fumaryl chloride monomethyl ester thus obtained was allowed to react with tert-butanol in the presence of a catalytic amount of pyridine in dry ether. The resulting MtBF was purified by repeated fractional distillation in a nitrogen atmosphere under reduced pressure, bp 68°C/6 mmHg. From gas chromatographic analysis and IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra (see Figs. 1, 2, and 3), this MtBF monomer was confirmed to be pure (its purity was above 99%).

2,2'-Azobisisobutyronitrile (AIBN), a radical initiator, was used after recrystallization from methanol. The other reagents were also purified by ordinary methods.

### Polymerization Procedure

The bulk polymerizations of MtBF were carried out in the presence or absence of AIBN as an initiator in a sealed glass tube at 50-130°C.

After polymerization for a given time, the contents of the tubes were poured into large amounts of n-hexane to precipitate the polymer.

The polymer was then purified by the reprecipitation method from the benzene-*n*-hexane system, and finally dried in vacuum. The conversion was calculated from the weight of the dry polymer obtained.

### Characterization of the Polymer

The structure of the MtBF polymers was analyzed by their IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectra. The intrinsic viscosities ( $[\eta]$ ) of the polymers were determined by micromelting point apparatus, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) in order to determine softening, glass transition, and thermal degradation temperatures, respectively.

## RESULTS AND DISCUSSION

### Homopolymerization of MtBF

MtBF did not give any polymer in the absence of radical initiator at 100-130°C. When AIBN was added to this system, however, polymerization was easily induced at 50-80°C. The results are shown in Table 1.

From this table it is clear that the polymerization of MtBF occurs easily in the presence of AIBN under ordinary conditions, and the intrinsic viscosity of the polymers obtained is high compared to those (10% and  $[\eta] = 0.2 \text{ dL/g}$ ) for diethyl fumarate (DEF) in bulk at 60°C

TABLE 1. Radical Homopolymerization of MtBF<sup>a</sup>

Temperature (°C)	Time (h)	Yield (%)	$[\eta]^b$ (dL/g)
80	2.5	27.6	0.25
70	4	20.1	0.35
65	8	26.8	0.40
60	10	22.3	0.48
55	10	13.5	0.55
50	8	5.8	0.60

<sup>a</sup>Polymerization conditions:  $[\text{AIBN}] = 2 \times 10^{-2} \text{ mol/L}$  in bulk.

<sup>b</sup>Determined in benzene at 30°C.

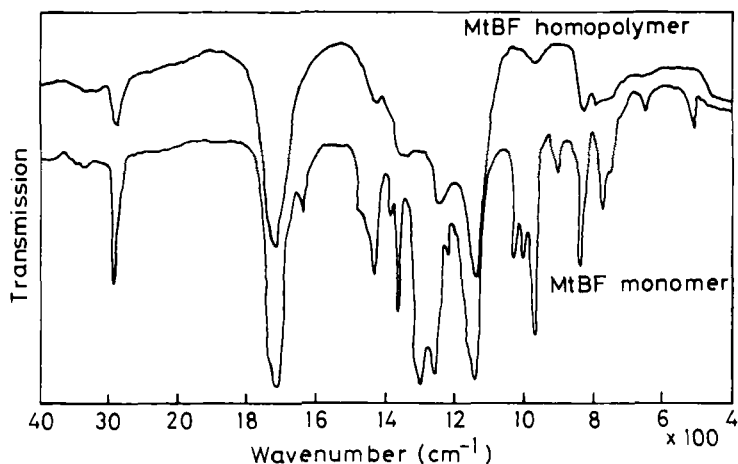


FIG. 1. IR spectra of MtBF monomer and homopolymer.

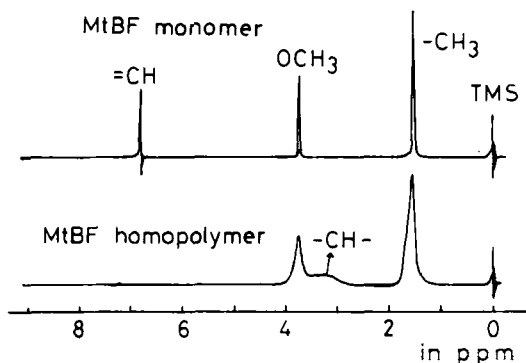


FIG. 2.  $^1\text{H-NMR}$  spectra of MtBF monomer and homopolymer.

[ 1 ]. A similar high polymerization reactivity was found for diisopropyl fumarate (DiPF) (29.1% and  $[\eta] = 0.86 \text{ dL/g}$ ) [ 1 ]. However, comparison of the homopolymerization reactivity of MtBF with that of ethyl acrylate or methyl methacrylate shows that both the yield and the molecular weight are low because of the increased steric effect of the 1,2-disubstituents.

The IR spectra of the MtBF monomer and its polymer are shown in Fig. 1, from which the absorption bands at  $1630\text{-}1640$  and  $980 \text{ cm}^{-1}$  due to the double bond of the monomer are found to disappear from the spectrum of the polymer. Similar results are also observed for

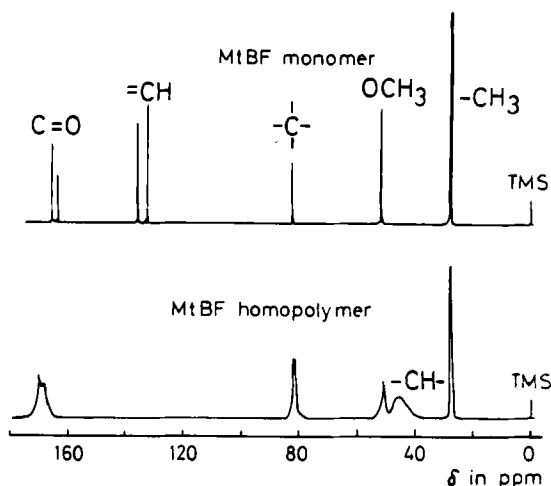


FIG. 3.  $^{13}\text{C}$ -NMR spectra of MtBF monomer and homopolymer.

the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra which are shown in Figs. 2 and 3, respectively, i.e., the absorption bands at 6.8 ppm ( $=\text{CH}$  proton), and 135.7 and 132.3 ppm ( $=\text{CH}$  carbons) observed in the monomer disappear from the spectra of the polymer, and new bands at around 3.0 ppm ( $-\text{CH}-$  proton) and 46 ppm ( $-\text{CH}-$  carbon) are observed. Therefore, it is clear that MtBF (**1**) was polymerized through an opening of its double bond, i.e., an ordinary vinylene polymerization mechanism (see Eq. 1).

From the observed NMR spectra of the polymer, it is still not possible to know the exact sequential structure. However, a qualitative consideration by a molecular model (see Fig. 9) suggests that this polymer consists of alternating methoxycarbonylmethylene and tert-butoxycarbonylmethylene units (**2** in Eq. 1). Therefore, the propagation reaction may be performed by selective addition of a growing radical having a bulky tert-butyl ester group to the carbon atom with a less-bulky methyl ester group of the vinylene bond of **1** as shown in Eq. (2).

In order to clarify the feature of this polymerization, some kinetic investigations were attempted. The time-conversion relations obtained are shown in Fig. 4. From this figure the polymerization is found to occur 2.35 times easier than that of DEF [**1**], and to proceed with straight line relations between the conversion and the reaction time up to  $\sim 30\%$ .

The time-intrinsic viscosity relations for this polymerization are also shown in Fig. 5, from which the molecular weight of the polymers produced is almost constant, independent of the reaction time.

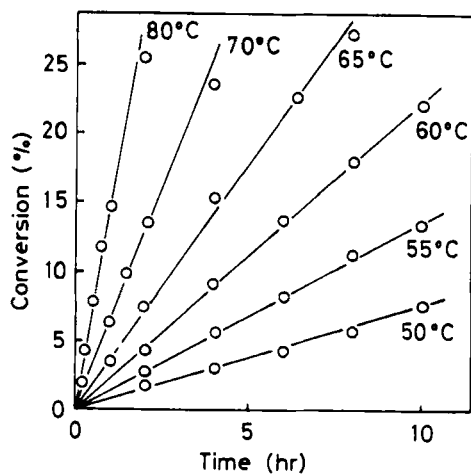
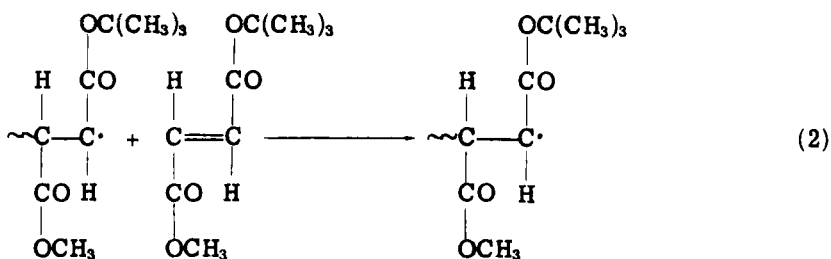
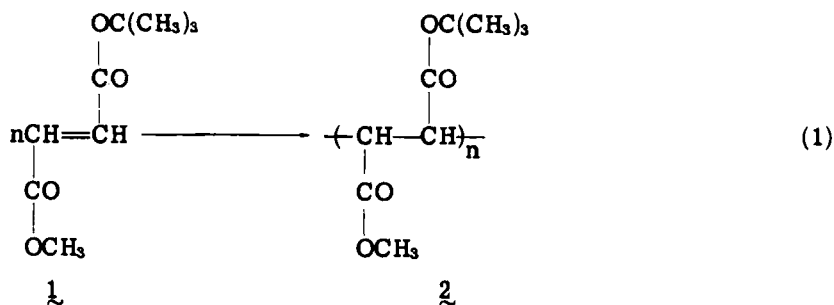


FIG. 4. Time-conversion relations for homopolymerization of MtBF with AIBN in bulk:  $[\text{AIBN}] = 2 \times 10^{-2}$  mol/L.

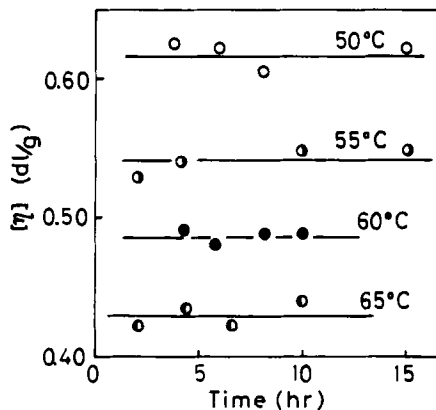


FIG. 5. Relationship between intrinsic viscosities and reaction time in homopolymerization of MtBF with AIBN.

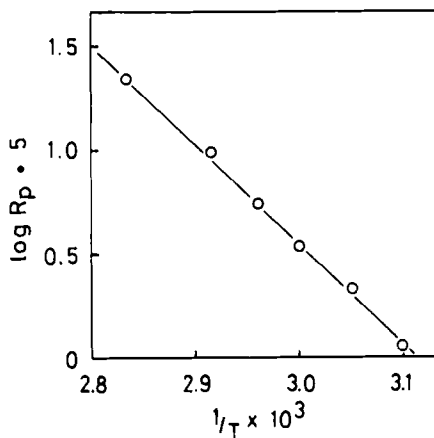


FIG. 6. Arrhenius plot of  $\log R_p$  with  $1/T$  for homopolymerization of MtBF.

This result strongly suggests that polymerization proceeds via an ordinary chain reaction mechanism.

Figure 6 shows the Arrhenius plots of the logarithms of the rates of polymerization ( $R_p$ ) determined from the slopes of the straight lines shown in Fig. 4 with the reciprocal absolute temperatures. The apparent activation energy for this polymerization is calculated as 83.5 kJ/mol, which is somewhat lower than that (89 kJ/mol [4]) and



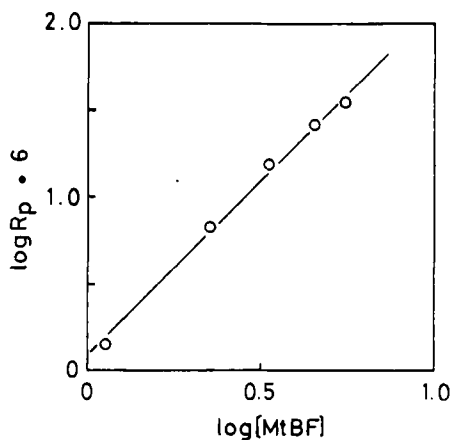


FIG. 7. Log-log plots of  $R_p$  with the monomer concentration:  $[AIBN] = 2 \times 10^{-2}$  mol/L in benzene at  $60^\circ\text{C}$ .

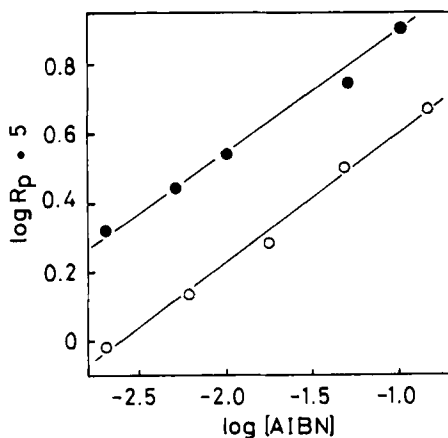
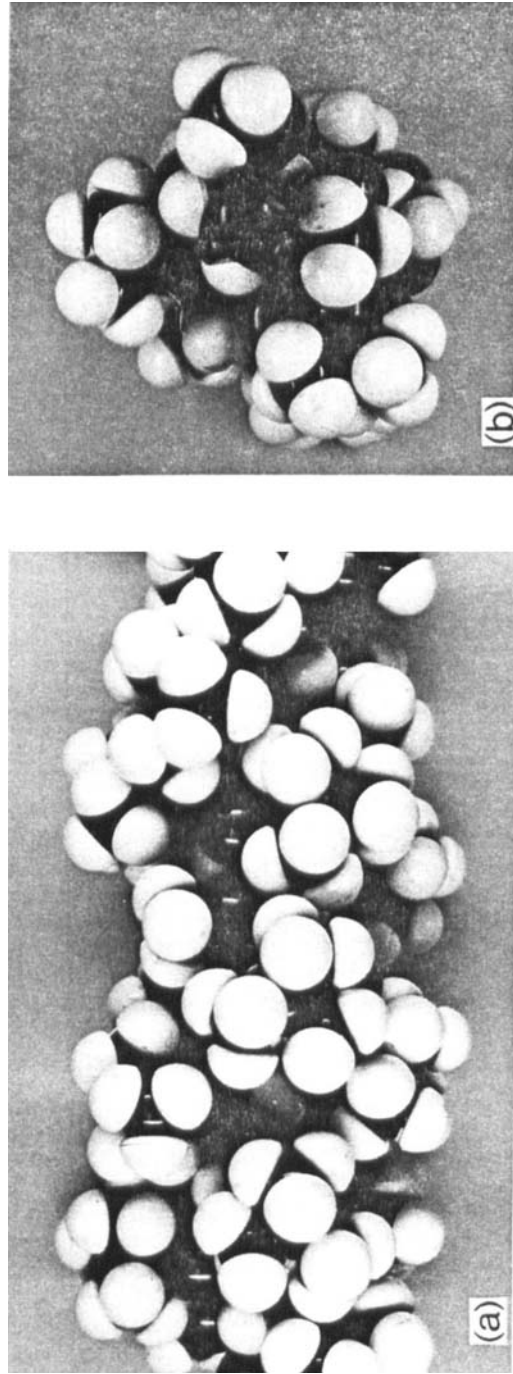


FIG. 8. Log-log plots of  $R_p$  with the AIBN concentration in the polymerization of MtBF. In bulk:  $[MtBF] = 5.55$  mol/L (●). In benzene:  $[MtBF] = 4.44$  mol/L (○).



**FIG. 9.** Molecular model for MtBF homopolymer: (a) from front and (b) from side.

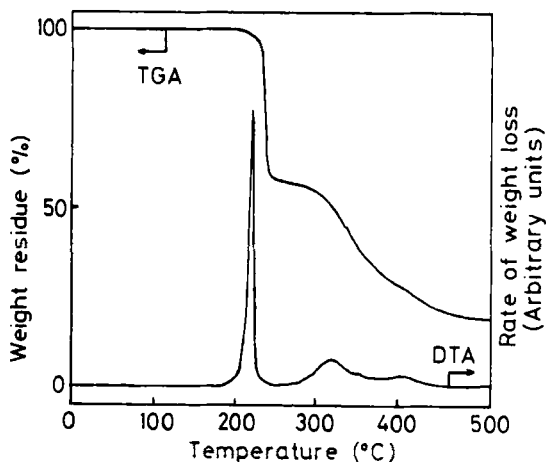


FIG. 10. TGA and DTA thermograms of MtBF homopolymer.

90.6 kJ/mol [5]) obtained for DEF, and also that (85 kJ/mol) for methyl methacrylate.

Moreover, to determine the rate equation in this polymerization and to compare it with that observed for other monomers, the polymerization of MtBF initiated by AIBN was investigated kinetically at 60°C.

Figure 7 shows log-log plots of  $R_p$  with the monomer concentration.

From the slope of the straight line, the reaction order with respect to the monomer concentration was determined to be 2.0, which is larger than that (1.6-1.7) observed for DEF [5] and that (1.0-1.5) for the usual vinyl monomers. Similar results were observed for other 1,2-disubstituted monomers such as vinylene carbonate [6], N-alkylmaleimides [7] and dimethyl fumarate (DMF) [8]. These observations seem to originate generally from the low reactivities of 1,2-disubstituted monomers in initiation, propagation, and termination reactions.

The log-log plots of  $R_p$  with AIBN initiator concentration in bulk polymerization are also shown in Fig. 8, from which the reaction order with respect to the initiator concentration is calculated to be 0.33. This order is somewhat lower than that (0.5) observed for DMF [8] or DEF [5] and other vinyl monomers at 60°C. To confirm this point, the experiment was attempted again in a 80 vol% benzene solution, but the observed order was still 0.38, indicating that in this MtBF polymerization, primary radical termination becomes important.

Therefore, the kinetic features of radical polymerization of MtBF were assumed to be almost similar to those of an ordinary vinyl

monomer, except for the reaction orders with respect to monomer and initiator concentrations. Although the solution viscosity (10.3 cP) of the MtBF monomer was about 4.5 times higher than that (2.3 cP) of DEF, such a viscosity effect may act partly on the increased polymerization reactivity of MtBF.

### Characterization of the MtBF Polymer

The homopolymer obtained from the radical polymerization of MtBF with AIBN was a white powder, soluble in methanol, benzene, chloroform, and tetrahydrofuran, but insoluble in n-hexane and water.

As described above, it was assumed from IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectra that this polymer consisted of Structure 2 in Eq. (1). Figure 9 shows the molecular model for this polymer. As can be seen from this figure, the polymer consists of a less flexible rodlike structure. The diameter and the end-to-end distance of the rodlike polymer with a molecular weight of 100,000 are about 13.5 and 1500 Å, respectively. Similar results were found for the DiPF polymer [2].

In relation to this observation, the softening and glass transition temperatures of the MtBF polymer were found to be as high as 220-250 and 84°C, respectively, and these values were much higher than those (62-70 and 40°C) of DEF polymer. However, the initial and maximum degradation temperatures determined by TGA and differential thermal analysis (DTA), shown in Fig. 10, were lower [196°C and 226 (322)°C, respectively] than those (243 and 382°C) of DEF polymer [1]. Recent results by pyrolysis gas chromatography showed that the amount of tert-butanol produced by thermolysis of MtBF polymer became larger than that of ethanol from DEF polymer.

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