

Radical High Polymerization of Di-tert-Butyl Fumarate and Novel Synthesis of High Molecular Weight Poly(Fumaric Acid) from Its Polymer*

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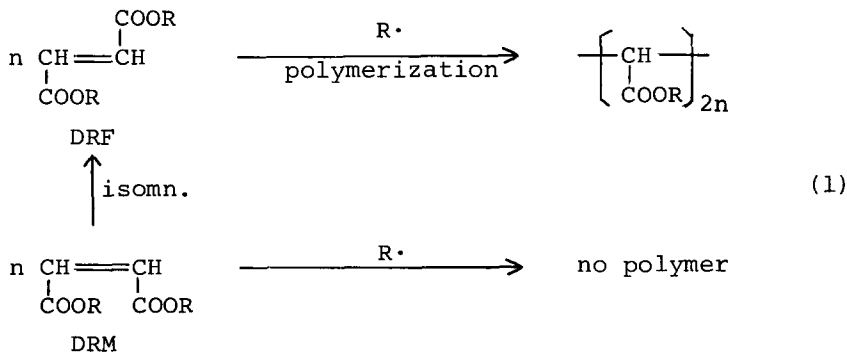
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Summary

Di-tert-butyl fumarate (DtBF) was found to homopolymerize easily with 1,1'-azobisisobutyronitrile and benzoyl peroxide as radical initiators at 50~80°C to give a nonflexible rod-like polymer, poly(tert-butoxycarbonylmethylene) with number-average molecular weight of more than 100,000. The colorless powder-like polymer thus obtained was soluble in benzene, toluene, carbon tetrachloride and tetrahydrofuran, and gave a transparent film or fiber from its toluene solution. This polymer did not melt, but it underwent degradation with a quantitative elimination of isobutene at 180~190°C. The remaining polymer was confirmed to be a pure poly(fumaric acid), poly(hydroxycarbonylmethylene). Therefore, the degradation of poly(DtBF) in solution at 180~190°C was found to be a new route for synthesizing of a high molecular weight poly(fumaric acid).

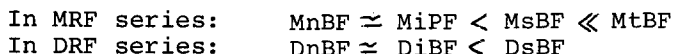
Introduction

In previous papers of this series (1~10), we have found that various dialkyl fumarates (DRF) and dialkyl maleates (DRM), typical 1,2-disubstituted ethylenic monomers which have been known to be not homopolymerized to give high polymer, can undergo homopolymerization in the absence and presence, respectively, of isomerization catalysts such as morpholine, according to Eq. (1):



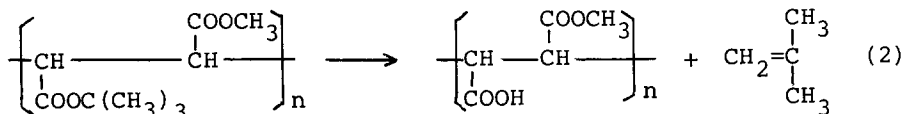
* Polymers from 1,2-Disubstituted Ethylenic Monomers. XI. Parts I~X of this series are Refs. 1~10.

More detailed studies on radical homopolymerization of various DRF including methylalkyl fumarates (MRF) showed that those with bulky ester alkyl substituents such as diisopropyl fumarate (DiPF) (2,8~10) and methyl-tert-butyl fumarate (MtBF) (7,9) could homopolymerize quite easily to yield high molecular weight homopolymers. Further, it was found that when the bulkiness of the butyl ester substituents in both DRF and MRF increased, the homopolymerization reactivities (yield and intrinsic viscosity) increased simultaneously, in spite of increased steric effect of the substituent, as in the following order (10):



Therefore, DtBF which has the most bulky substituent was expected to homopolymerize easier than di-sec-butyl fumarate (DsBF). As will be shown in this paper, DtBF was observed to homopolymerize quite readily to give a high molecular weight polymer.

In a previous paper (7), it was also observed by thermogravimetric analysis that thermal degradation of poly(MtBF) was performed by a two-step reaction. The first degradation observed at about 190°C was recently confirmed to be a quantitative elimination of isobutene (11) [Eq. (2)].



Similarly, the thermal degradation of poly(DtBF) at 180 ~ 190°C was found to proceed to give a pure poly(fumaric acid). Since fumaric acid did not undergo radical high polymerization and the hydrolysis of high molecular weight poly(DiPF) occurred very hardly (10), this method is considered to be an excellent route for synthesizing of high molecular weight poly(fumaric acid).

The present paper is described the results of radical high polymerization of DtBF and of synthesis of high molecular weight poly(fumaric acid) through thermal degradation of its polymer.

Experimental

Synthesis of DtBF

DtBF was synthesized by the reaction of fumaroyl chloride with potassium tert-butoxide in benzene. After separation of potassium chloride precipitated, the benzene solution of the crude DtBF was purified by passing twice into a silicagel column and then it was recrystallized from isopropanol. The pure DtBF was obtained as a colorless needle: Yield 32.3%, mp 69 ~ 70°C. Anal. obs., C 62.99%, H 8.77%; calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_4$ (MW 228.16), C 63.12%, H 8.77%. From NMR spectral data (Figs. 3, 4), this DtBF was also shown to be pure.

Other Reagents

1,1'-Azobisisobutyronitrile (AIBN), 1,1'-azobiscyclohexane-

carbonitrile (ACN) and benzoyl peroxide (BPO) were used after recrystallization. Benzene and other reagents were purified according to ordinary methods.

Homopolymerization

Bulk or benzene-solution polymerization was carried out in ordinary sealed tube in the presence or absence of radical and anionic initiators. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to isolate the polymer. The polymer yield was calculated from the weight of the polymer dried.

Characterization

The structure of the polymers obtained was confirmed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra. The intrinsic viscosities, $[\eta]$ of the poly(DtBF) were measured viscometrically in benzene at 30°C . Thermal degradation behavior was determined by thermogravimetric analysis (heating rate $10^\circ\text{C}/\text{min}$. in N_2) and pyrolysis gas chromatography.

Synthesis of Poly(Fumaric Acid) and its Dimethyl Ester [Poly(DMF)] from Poly(DtBF)

The polymer of fumaric acid (FA) was synthesized by thermal degradations of powder-like poly(DtBF) and in dispersed solution of poly(DtBF) in *o*-dichlorobenzene or tetralin in sealed tube at $175\sim 180^\circ\text{C}$ for 1.5~2.0 hours. The polymer thus obtained was purified by extraction with benzene and methanol to eliminate the impurities. The colorless polymer obtained after purification and drying was confirmed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra to be pure poly(FA).

The poly(FA) was then converted to poly(DMF) by methylation with diazomethane in diethyl ether at room temperature. The resulting poly(DMF) was also a colorless powder.

Results and Discussion

Homopolymerization of DtBF

The results of radical polymerization of DtBF in bulk are summarized in Table 1.

As is seen from this table, DtBF does not polymerize thermally and photochemically, but it can polymerize quite easily in the presence of radical initiators to give homopolymers with high intrinsic viscosities. If the number-average molecular weight (\bar{M}_n)- $[\eta]$ relationship for poly(DiPF) (10),

$$[\eta] = 7.67 \cdot 10^{-6} \bar{M}_n^{1.0}$$

is applied, the \bar{M}_n of poly(DtBF) with $[\eta] = 0.8 \text{ dl/g}$ is calculated to be 100,000. Therefore, it is clear that the polymer obtained by AIBN at 40°C for 31 hours consists of \bar{M}_n of 170,000.

When the results obtained for DtBF were compared with those of DiPF and MtBF under similar conditions ($[\text{AIBN}] = 20 \text{ mmol/l}$ in bulk at 80°C for 6 hours), the polymerization reactivities (yield and $[\eta]$) were in the order: MtBF (60.3% and 0.45) < DiPF (68.0% and 0.51) < DtBF (84.6% and 0.63). This order was the same as that of the mean bulkiness of the ester alkyl substituents. Similar

Table 1 Radical Polymerization of DtBF in Bulk

[DtBF] (mol/l)	[Initiator] (mmol/l)	Temp. (°C)	Time (hr)	Yield (%)	$[\eta]^c$ (dl/g)
0.22 ^{a)}	————	80	6	~0	—
0.22 ^{b)}	————	21	7	~0	—
4.38	AIBN, 20	80	1	50.3	0.71
4.38	AIBN, 20	80	6	84.6	0.63
2.19 ^{a)}	AIBN, 20	60	10	38.4	0.78
2.19 ^{a)}	AIBN, 29	40	31	34.8	1.28
4.38	BPO, 20	80	3	95.0	0.63
4.38	ACN, 20	80	4	77.8	0.84
4.38	ACN, 20	90	4	83.0	0.61

a) Polymerized in benzene.

b) Polymerized under irradiation of Toshiba SHL-100 UV lamp from a distance of 10 cm.

c) Determined in benzene at 30°C.

tendencies were observed for DRF with butyl ester substituents under identical conditions in bulk: $DnBF(6.4\% \text{ and } 0.15) \approx DiBF(5.4\% \text{ and } 0.12) < DsBF(16.4\% \text{ and } 0.41) < DtBF(38.4\% \text{ and } 0.84$ when polymerized even in benzene)(Table 1)(9). It must be noted that the polymerization reactivities of these monomers are reversely correlated with the bulkiness of their substituents. This may also be a characteristic of 1,2-disubstituted ethylenic monomers, i.e. contrary to mono- and 1,1-disubstituted monomers, the increased bulkiness may result in the decreased flexibility of the growing polymer chain, and hence it may also diminish the rate of mutual termination. More detailed discussion for such effects will be described in a later publication.

The time-conversion relations for radical polymerization of DtBF in benzene at 50~70°C are shown in Fig. 1, from which the polymerization was observed to proceed linearly with reaction time. From Table 1, the \bar{M}_n of the polymers seem to be almost kept constant independent of the time. Anionic polymerization of DtBF with n-butyllithium was not found to give any polymer.

Characterization of Poly(DtBF)

The poly(DtBF) obtained was a colorless powder, soluble in benzene, toluene, carbon tetrachloride and tetrahydrofuran, but insoluble in n-hexane and methanol. A transparent brittle film or fiber was obtained from its toluene solution. The poly(DtBF) did not melt up to 400°C, although its degradation occurred(Fig.6).

IR, ¹H-NMR and ¹³C-NMR spectra of the poly(DtBF) are shown in Figs. 2, 3 and 4, in which those of DtBF monomer and poly(FA) are also indicated. As is seen from these figures, the absorption bands due to the double bond, i.e. those at 970 cm⁻¹(trans-C=C), 6.6 ppm(=CH proton) and 134.4 ppm(=CH carbon) observed in DtBF monomer disappear from the spectra of the polymer, and the new band around 3.0 ppm(-CH- proton) is observed. However, a broad absorption band due to -CH- carbon was observed around 45 ppm (Fig. 4). Therefore, it is clear that DtBF was polymerized by an opening of its double bond, i.e. an ordinary vinylene polymerization mechanism, to give the polymer with a poly(tert-

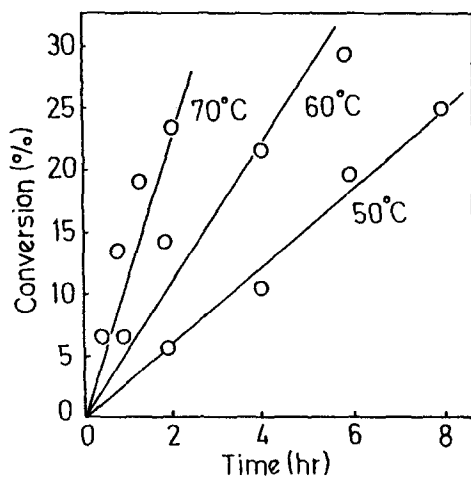


Fig. 1 Time-conversion relations for the polymerization of DtBF with AIBN in benzene at 50~70°C; [DtBF]= 2.2 mol/l, [AIBN]= 20 m mol/l.

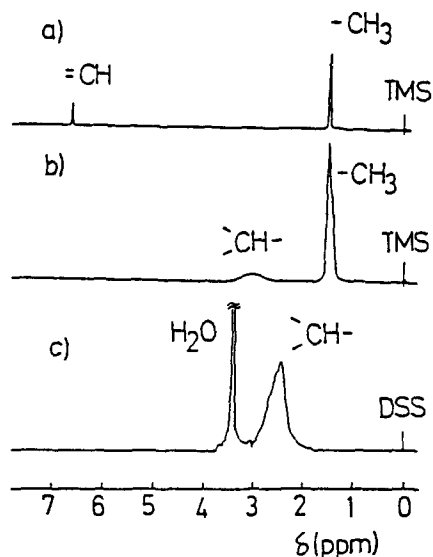


Fig. 3 ¹H-NMR spectra of a) DtBF monomer in CDCl₃ at room temp., b) poly(DtBF) in CDCl₃ at 50°C and c) poly(FA) in D₂O at 80°C.

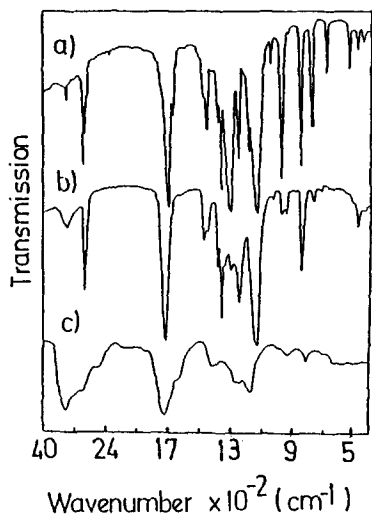


Fig. 2 IR spectra of a) DtBF monomer, b) poly(DtBF) and c) poly(FA).

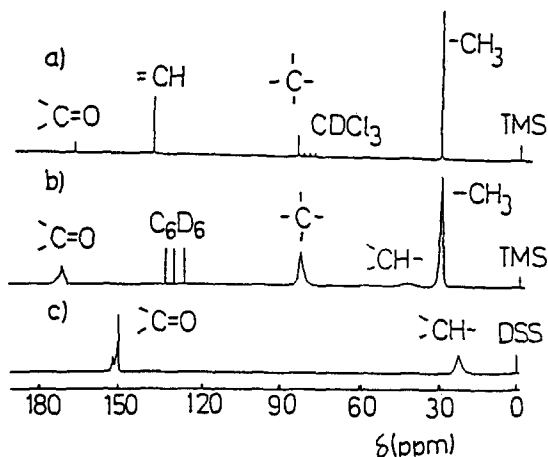


Fig. 4 ¹³C-NMR spectra of a) DtBF monomer in CDCl₃, b) poly(DtBF) in C₆D₆ and c) poly(FA) in D₂O at room temperature.

butoxycarbonylmethylene) structure [R= C(CH₃)₃ in Eq.(1)]. Similar conclusions were obtained for poly(DEF) (8), poly(DiPF) (8,9) and poly(MtBF) (7).

The molecular model of the poly(DtBF) is shown in Fig. 5, in which that of poly(FA) derived is also indicated. From Fig. 5a, the poly(DtBF) is observed to consist of a nonflexible rod-like polymer chain more rigid than poly(DiPF) (8,10) and poly-(MtBF) (7). This result is in agreement with the fact that the poly(DtBF) did not melt on heating and showed no melting and glass transition temperatures. Moreover, since the molecular model of this polymer can be constructed only when it consists of a threediisotactic structure, it may also be considered that DtBF polymerizes probably through a repeated cis-opening reaction of its double bond.

The TGA thermogram of the poly(DtBF) is shown in Fig. 6, from which this polymer is found to reveal thermal behavior that initial and maximum degradation temperatures are 190°C and 290~310°C, respectively, and the residue at 500°C is 10.1%. Moreover, this degradation is noted to proceed via a two-step reaction, i.e. the first degradation occurs rapidly at 190°C and the second degradation starts from 290°C.

The pyrogram of the poly(DtBF) at 200°C showed almost one peak, although a very minor peak was observed. Furthermore, from the observed weight loss at 190°C and the gas chromatographic analysis of the evolved gaseous main product at 190°C, the first degradation was confirmed to be a quantitative elimination of isobutene [Eq.(3)].

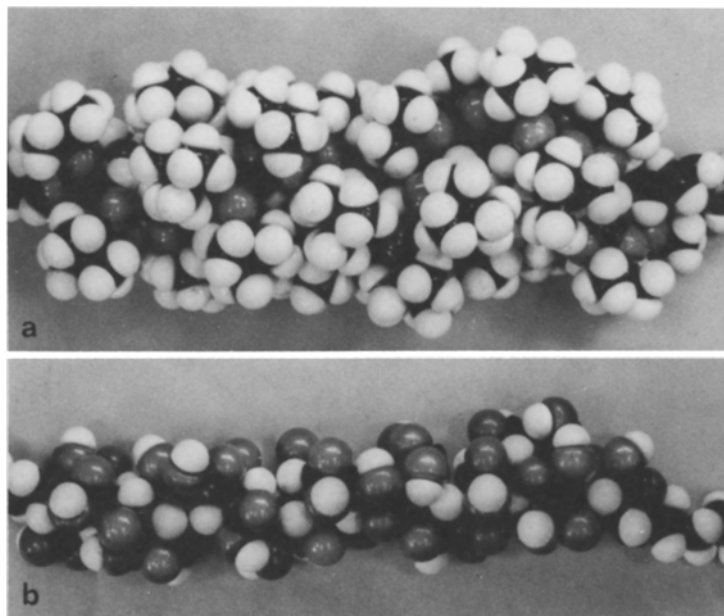
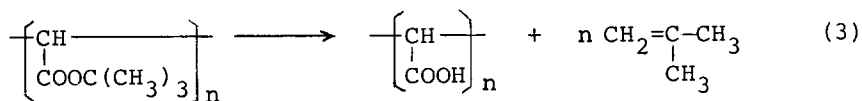


Fig. 5 Molecular models for a) Poly(DtBF) and b) poly(FA).

Similar degradation behavior was also observed for poly(MtB F) (7), and the gaseous product evolved at 190°C was recently confirmed to be isobutene (11). It is a characteristic of poly(DRF)s with tert-alkyl ester group, contrary to that consisting of primary and secondary esters. An easy elimination of isobutene from poly(tert-butyl methacrylate) (12) and poly(tert-butyl acrylate) (13) on heating has been also reported since 1960.

Moreover, the polymer obtained after degradation of the poly(DtBF) at 190°C for 2 hours was confirmed by IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra (Figs. 2, 3 and 4, respectively) to be a pure poly(FA), poly(hydroxycarbonylmethylene), as shown in Eq. (3) and Fig. 5b.

Novel Synthesis of Poly(FA) from Poly(DtBF)

Fumaric acid has been known to be not homopolymerized to give any high polymer under similar conditions reported in the studies of this series. Therefore, the thermal degradation of the poly(DtBF) is expected to afford a novel synthetic route for high molecular weight poly(FA).

The degradation of poly(DtBF) was carried out in a degassed sealed tube as a powderlike polymer and in a 2% polymer solution dispersed in *o*-dichlorobenzene or tetralin at 175~180°C for 1.5~2.0 hours.

The polymers obtained from both methods were pure poly(FA) (see Figs. 2, 3 and 4). These polymers were colorless powder soluble in alkaline aqueous solution. The reactions were not induced at temperatures below 170°C. However, when reactions were carried out at temperatures above 185°C and for prolong periods more than 2 hours even at 175~180°C, the colored poly(FA) was obtained. In some polymers especially obtained by degradation of the powdered poly(DtBF), a part of anhydride group contaminated, but it could easily be converted to the acid group with water.

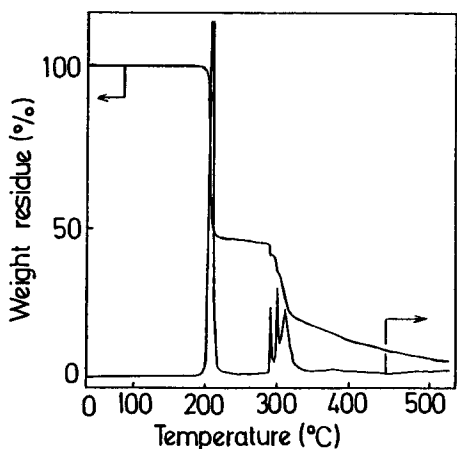


Fig. 6 TGA and DTA thermograms of poly(DtBF): heating rate 10° C/min. in nitrogen.

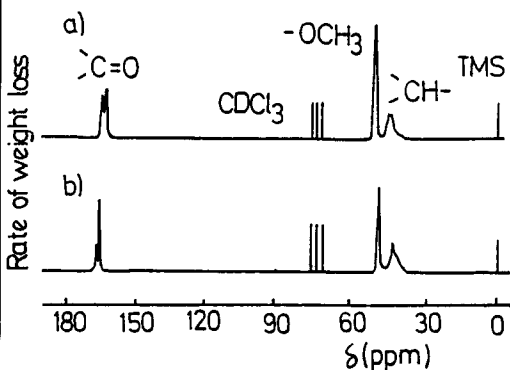
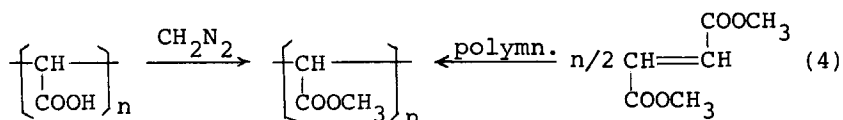


Fig. 7 $^{13}\text{C-NMR}$ spectra of poly(DMF) in CDCl_3 at room temp.: a) obtained from DMF, and b) obtained from poly(FA).

As reported in previous papers (2,4,8), DMF showed the lowest homopolymerization reactivity among DRFs, and the high molecular weight polymer was not produced from its polymerization. Therefore, high molecular weight poly(DMF) was expected to be obtained through methylation of the poly(FA) with diazomethane [Eq. (4)].



The ^{13}C -NMR spectrum of the resulting poly(DMF) is shown in Fig. 7, in which that obtained from radical polymerization of DMF is also indicated as comparison. The spectra observed for both polymers are quite identical, and they are found to be pure poly(DMF). However, the intrinsic viscosity (0.19 dl/g) of the poly(DMF) derived from poly(FA) is about four times higher than that (0.05 dl/g) obtained by DMF.

The thermal properties of both poly(DMF) by TGA were identical: $T(\text{init})$ 245°C, $T(\text{max})$ 390°C for poly(DMF) derived from poly(FA), and $T(\text{init})$ 246°C, $T(\text{max})$ 395°C for poly(DMF) obtained from DMF. Similar solubilities were also observed for both poly(DMF).

Acknowledgement

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