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Polymers from 1,2-Disubstituted Ethylenic Monomers. V. Radical Polymerization of Dimethyl Maleate in the Presence or Absence of Isomerization Catalyst

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ABSTRACT

Although dimethyl maleate (DMM) did not give any homopolymer with a radical initiator, it was polymerized in the presence of some amines via a monomer-isomerization radical polymerization mechanism, i.e., DMM isomerized to dimethyl fumarate (DMF) which then homopolymerized. For this polymerization, some primary or secondary aliphatic amines served as isomerization catalysts, and morpholine showed the most efficient activity. The activation energies for the monomer-isomerization radical polymerization of DMM with di-*tert*-butyl peroxide in the presence of morpholine and for the isomerization from DMM to DMF with morpholine were 95.9 and 23.0 kJ/mol, respectively. Morpholine was also observed to act as a retarder in radical polymerization of DMF. Moreover, the relationships between rates or copolymer compositions and the feed monomer compositions in the copolymerization of DMM with styrene in the presence of morpholine were found to become close to those of DMF with styrene, although both relationships were different in the absence of morpholine.

INTRODUCTION

In previous papers [1, 2] it was reported that diethyl fumarate (DEF) was homopolymerized with a radical initiator, but diethyl maleate (DEM) did not give any polymer. Similar results were also observed for other fumarate and maleate monomers [1-4]. However, the latter maleates, including DEM, can homopolymerize in the presence of isomerization catalysts such as morpholine, i.e., in this case maleates isomerized first to fumarates which then homopolymerized according to the monomer-isomerization radical polymerization mechanism [3, 5].

To clarify further the detailed mechanism of these polymerizations dimethyl maleate (DMM) is studied in this paper, and the results obtained are described in comparison with those of dimethyl fumarate (DMF).

EXPERIMENTAL

Materials

Commercial DMM was distilled under reduced pressure. DMF, a commercially available reagent, was recrystallized from benzene.

α, α' -Azobisisobutyronitrile (AIBN) and α, α' -azobiscyclohexanecarbonitrile (ACN) were recrystallized from methanol and dried in vacuum.

Isomerization catalysts such as morpholine, piperidine, diethylamine, n-propylamine, triethylamine, aniline, and pyridine were distilled before use. Benzene and other reagents were used after ordinary purification.

Polymerization Procedure

The polymerizations of DMM and DMF were carried out in a degassed glass tube with ACN or AIBN initiator in the absence or presence of amines as isomerization catalysts in benzene. After polymerization for a given time, the content of the tubes was poured into a large amount of diethyl ether to isolate the polymer. The resulting polymer was washed well with diethyl ether and dried in vacuum at room temperature.

Copolymerizations of DMM and DMF with Styrene (St)

The copolymerizations of DMM and DMF with St were carried out with ACN in the presence or absence of morpholine at 90°C. After the

copolymerizations were performed to a low conversion ($\sim 10\%$), the reaction mixture was poured into excess methanol to isolate the copolymers which were then filtered, washed with diethyl ether, and dried in vacuum. The composition of the copolymers was analyzed by elementary analyses and then calculated from their carbon contents.

Isomerization of DMM to DMF

The isomerizations of DMM to DMF were carried out in benzene in the presence of morpholine. A required amount of the reaction mixture was taken out of the system at regular time intervals, and the ratios of DMF to DMM were determined by gas chromatography.

RESULTS AND DISCUSSION

Radical Polymerizations of DMM and DMF

The radical polymerizations of DMM and DMF with radical initiators in the presence or absence of morpholine, which acts as an isomerization catalyst from maleate to fumarate (as is shown later), are shown in Table 1.

As can be seen from this table, the homopolymerization of DMM did not take place in the absence of morpholine, although homopolymerization of DMF was induced. However, when a small amount of morpholine was added to these systems, the polymerization of DMM was induced and that of DMF was markedly retarded. These observations are in good agreement with the results obtained for DEM and DEF [5], and these effects of morpholine are described later (see Table 3 and Fig. 6).

The unreacted monomer recovered after polymerization of DMM in the presence of morpholine was found to consist of only the DMF monomer, indicating that isomerization of DMM to DMF was performed (see later). In these conditions, however, no isomerization from DMF to DMM was observed. In the absence of morpholine, of course, no isomerization of DMF to DMM and of DMM to DMF occurred under these polymerization conditions. Therefore, this polymerization of DMM was assumed to be that of isomerized DMF (i.e., monomer-isomerization radical polymerization). The IR (Fig. 1) and NMR spectra of the polymers obtained from both DMM and DMF were quite identical, indicating that both polymers consisted of the same structure, i.e., poly(methoxycarbonylmethylene). These polymers were colorless powders and melted at 132-136°C. The glass transition, initial, and maximum degradation temperatures of both polymers were 65, 248, and 398°C, respectively [1].

TABLE 1. Radical Polymerization of DMF and DMM in Xylene

Monomer (mol/L)	Initiator ^a (mol/L × 10 ³)	[Morpholine] (mol/L × 10 ³)	Temperature (°C)	Time (h)	Yield (%)	[η] ^b (dl/g)
DMF (2.1)	AIBN (0.3) ^c	0	60	28	0.5	-
DMF (5.3)	ACN (3.0)	0	90	4	10.5	0.05
DMF (5.3)	ACN (3.0)	0	90	12	21.9	-
DMF (5.3)	ACN (3.0)	4.3	90	12	9.3	-
DMF (6.4)	DBPO (4.2)	0	130	2	10.8	-
DMM (2.1)	AIBN (0.3) ^c	0	60	28	0	-
DMM (5.3)	ACN (3.0)	0	90	12	0	-
DMM (5.3)	DBPO (4.2)	0	130	6	0	-
DMM (4.3)	ACN (3.0)	7.0	90	8	8.2	0.01
DMM (4.3)	ACN (3.0)	7.0	95	4	4.5	-

^aDBPO: di-tert-butyl peroxide.

^bDetermined in benzene at 30°C.

^cPolymerized in benzene.

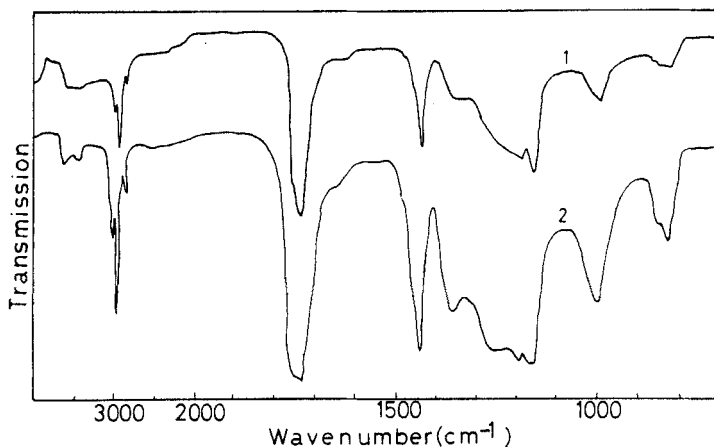


FIG. 1. IR spectra of the polymers obtained from DMM (1) and DMF (2).

Kinetic Study of Monomer-Isomerization Radical Polymerization of DMM

To clarify these polymerizations kinetically, the monomer-isomerization radical polymerization of DMM was investigated in detail.

Figure 2 represents the relationship between the polymer yield and the polymerization time in the polymerization of DMM with ACN in the presence of morpholine in benzene. According to this figure, a short induction period appears in the initial stage for all cases, and then the polymerization proceeds linearly up to 5% conversion at 80–95°C. The observed induction periods shortened with an increase of temperature, indicating that they corresponded to the times necessary to isomerize from DMM to DMF.

From the slopes of the straight lines shown in Fig. 2, the rates of polymerization (R_p) were determined. The Arrhenius plots between $\log R_p$ and the reciprocals of the absolute polymerization temperatures are shown in Fig. 3, from which the activation energy for the monomer-isomerization radical polymerization of DMM was calculated to be 95.9 kJ/mol. This value was somewhat larger than that (91.9 kJ/mol) [5] obtained for DEM at 60–80°C. This seems to be due to the differences in temperatures and initiators evaluated.

Isomerization of DMM to DMF with Morpholine

The isomerization of DMM to DMF catalyzed by morpholine in benzene at 40–60°C was determined by gas chromatography. The amount of isomerization from DMM to DMF was plotted against the

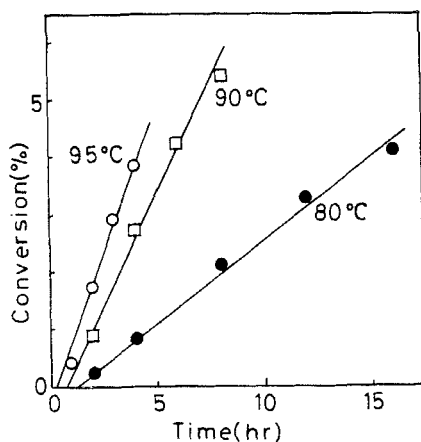


FIG. 2. Time-conversion relationships for radical polymerization of DMM in the presence of morpholine in xylene: $[DMM] = 4.30$, $[ACN] = 3.0 \times 10^{-2}$, $[morpholine] = 7.0 \times 10^{-2}$ mol/L.

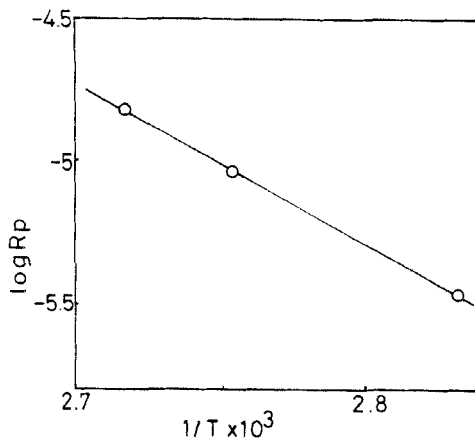


FIG. 3. Arrhenius plot for the radical polymerization of DMM.

reaction time (Fig. 4). In this figure the isomerization of DMM to DMF is shown to be easily performed even at relatively low temperature.

From this figure the pseudo-first-order rate constants (k) of isomerizations were also calculated, as is shown in Table 2. The Arrhenius plots of $\log k$ versus the reciprocals of absolute temperature

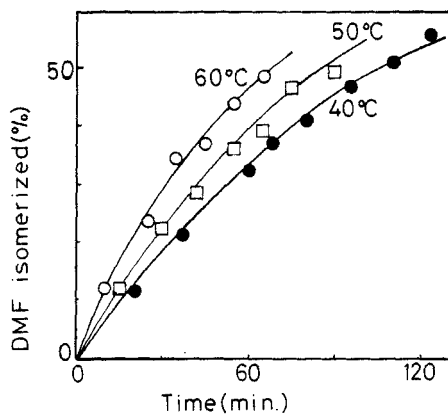


FIG. 4. Isomerization from DMM to DMF with morpholine in benzene: $[DMM] = 0.73$, $[morpholine] = 0.03$ mol/L.

TABLE 2. Pseudo-First-Order Rate Constants (k) for Isomerization of DMM to DMF

Amine	Temperature ($^{\circ}C$)	$k \times 10^{-4}$ (s^{-1})
Morpholine	40	1.08
Morpholine	50	1.39
Morpholine	60	1.84
Diethylamine	40	0.29
Di-n-propylamine	40	0.69

are shown in Fig. 5, from which the activation energy for this isomerization was calculated to be 23.0 kJ/mol. This value is very close to that (24.7 kJ/mol) reported for the isomerization of DEM to DEF [5].

Therefore, although the isomerization from DMM to polymerizable DMF is performed at a relatively fast rate, this step seems to result in a short induction period in the early stages of polymerization (see Fig. 2).

In general, the isomerization from maleates to fumarates has been known to be catalyzed by primary or secondary amines and to proceed via the following three steps [6-8]: 1) reversible attack of the amine to the double bond, 2) rotation of the intermediate formed, and 3) elimination of the amine used. Therefore, when morpholine, a secondary amine, is added, the isomerization of DMM to DMF seems to proceed in a similar way.

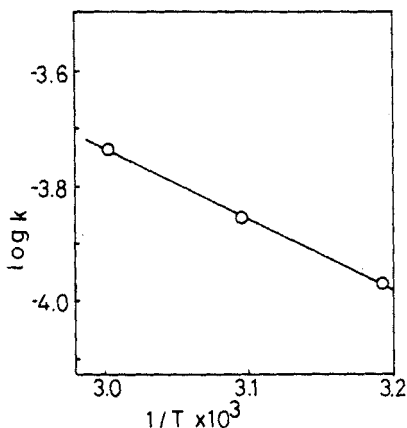


FIG. 5. Arrhenius plot for isomerization of DMM with morpholine.

Effects of Morpholine on Isomerization and Polymerization

The effects of morpholine on the radical polymerization of DMF and on the monomer-isomerization radical polymerization of DMM at 90°C are shown in Fig. 6. When the concentration of morpholine was increased in the radical polymerization of DMF, the polymer yields decreased gradually, indicating that morpholine acts as a retarder of this polymerization. As has been pointed out in the retardation by amines [9], this seems to come about because the polymer radical of DMF abstracts the hydrogen atom from morpholine, and the resulting nitrogen-centered radical does not participate in the reinitiation reaction of the less reactive DEF monomer.

In the case using DMM as the starting monomer, morpholine can act as both the catalyst of isomerization of DMM to DMF and the retarder of radical polymerization of DMF as stated above. Therefore, when a concentration of morpholine above 5×10^{-2} mol/L was used, the curves approached a merged curve (Fig. 6).

Effect of Other Amines

In order to find the isomerization catalyst without retardation in the radical polymerization of DMF, the monomer-isomerization polymerization of DMM and the radical polymerization of DMF were carried out in the presence of various amines. The results are shown in Table 3.

From Table 3 the polymerizations of DMM as observed in the pres-

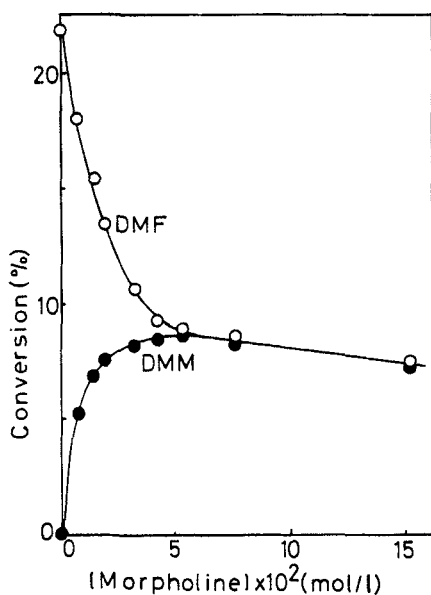


FIG. 6. Effects of morpholine on radical polymerizations of DMF and DMM in benzene at 90°C for 8 h: [DMF] = [DMM] = 5.3, [ACN] = 3.0×10^{-2} mol/L.

TABLE 3. Monomer-Isomerization Polymerization of DMM and Radical Polymerizations of DMF and ACN with Various Amines^a

Catalyst	Polymer yield (%) from	
	DMM	DMF
None	0	21.9
Morpholine	8.5	9.3
Piperidine	7.5	7.8
Di-n-propylamine	3.4	6.8
Diethylamine	2.1	9.2
Triethylamine	0	-
Aniline	0	-
Pyridine	0	-
Hydrochloric acid	8.1	8.0

^aPolymerization conditions: [ACN] = 3.0×10^{-2} , [Amine] = 4.3×10^{-2} , [HCl] = 0.4, [DMM] = [DMF] = 5.3 mol/L in benzene at 90°C for 12 h.

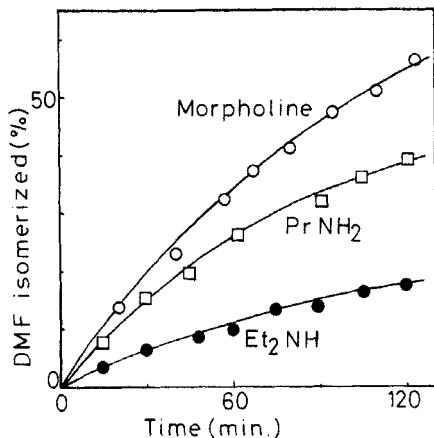


FIG. 7. Isomerization from DMM to DMF with amines in benzene at 40°C: [DMM] = 0.73, [amine] = 0.03 mol/L.

ence of morpholine, piperidine, diethylamine, and di-*n*-propylamine are presented. In these cases the isomerizations of DMM to DMF were also found, as shown in Fig. 7, and the observed pseudo-first-order rate constants are summarized in Table 2.

According to Table 3, primary and secondary amines are effective as isomerization catalysts but tertiary amines and aromatic amines, pyridine, and aniline do not serve as catalyst, indicating that a hydrogen atom is necessary to isomerization of DMM to DMF. Similar results were found for the isomerization and polymerization of DEM [5].

Hydrochloric acid will also serve as an isomerization catalyst (Table 3), but such other compounds as tertiary amine hydrochloride have no effect on this isomerization. Moreover, retardation in the radical polymerization of DMF is observed for the all compounds examined, as is shown in Table 3.

Effect of DMM on Radical Polymerization of DMF

In order to investigate whether DMM can participate in the radical polymerization of DMF, the polymerizations of DMF (i.e., copolymerizations of DMF with DMM) were carried out in various concentrations of DMM at 90°C. The results are shown in Fig. 8.

In the absence of morpholine, the polymer yield decreases linearly with an increase of the feed DMM concentration, probably indicating that the DMM acts only as an inert solvent in the polymerization of DMF. In fact, the ratio of reactivities of DMF (or DEF) to DMM (or DEM) toward the polystyryl radical is calculated from the copolymerization parameters (see Table 4) to be 23.6 (or 27.5), i.e., the fumarate monomers are 20-30 times more reactive than the maleate monomers.

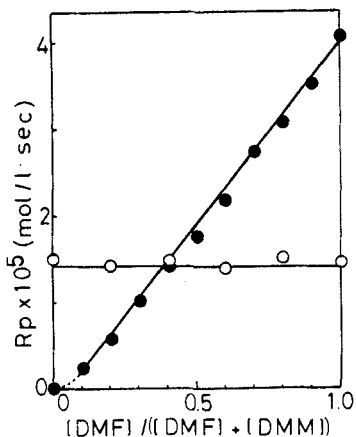


FIG. 8. Effect of DMM on radical polymerization of DMF in benzene at 90°C: $[DMM] + [DMF] = 5.3$, $[ACN] = 2.1 \times 10^{-2}$ mol/L. (○) $[Morpholine] = 6.5 \times 10^{-2}$ mol/L. (●) $[Morpholine] = 0$.

TABLE 4. Monomer Reactivity Ratios (r_1 and r_2) and Q_2 , e_2 Values of Copolymerizations of Styrene (M_1) with DMF, DMM, DEF, and DEF (M_2)

M_1	M_2	[Morpholine] (mol/L)	r_1	r_2	Q_2	e_2	Ref.
St	DMM	0	8.6	0.05	0.056	1.19	This work
St	DMM	0.07	0.50	0.01	0.317	1.50	"
St	DMF	0	0.39	0.03	0.475	1.31	"
St	DEM	0	8.0	0.07	-	-	5
St	DEM	0.28	0.35	0.02	-	-	"
St	DEF	0	0.29	0.02	-	-	"

^aDEF: diethyl fumarate, DEM: diethyl maleate.

In the presence of morpholine, however, the polymer yields are almost constant, independent of the feed DMM concentrations, and these yields are lower than that obtained from the bulk polymerization of DMF. These results are explained from the fact that the morpholine acts both as an efficient isomerization catalyst and as a retarder for the radical polymerization of DMF, as stated above.

Radical Copolymerization of Styrene with DMM and DMF

The results of the copolymerizations of styrene (M_1) with DMM (M_2) in the absence or presence of morpholine are shown in Figs. 9 and 10, respectively. When morpholine is added to the styrene-DMM

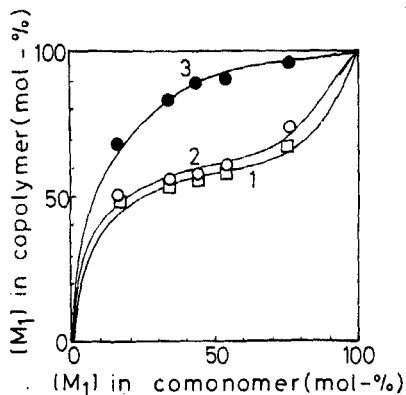


FIG. 9. Monomer-copolymer composition curves for the copolymerization of styrene (M_1) with DMM and DMF (M_2) in the presence or absence of morpholine. (1) Styrene-DMF. (2) Styrene-DMM in the presence of morpholine. (3) Styrene-DMM in the absence of morpholine.

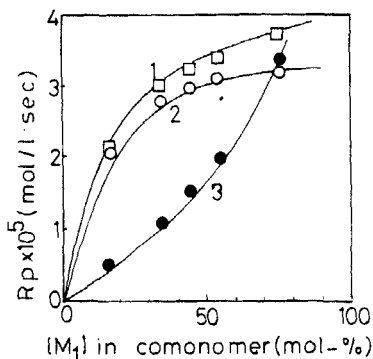


FIG. 10. Rate curves for copolymerization of styrene (M_1) with DMM and DMF (M_2) in the presence or absence of morpholine. (1) Styrene-DMF. (2) Styrene-DMM in the presence of morpholine. (3) Styrene-DMM in the absence of morpholine.

system, the copolymer compositions and the copolymerization rates become close to those of the styrene-DMF system, although in the absence of morpholine both curves for the styrene-DMM system are different from those obtained from the styrene-DMF system. The monomer reactivity ratios determined for these copolymerization systems are summarized in Table 4, in which the results obtained in the styrene-DEM (or DEF) systems [5] are also indicated.

In the absence of morpholine, it is observed that DMF is 23.6 times more reactive than DMM toward attack of the polystyryl radical as stated above, but in the presence of morpholine DMM shows the same reactivity as DMF. Similar results were also found for the copolymerization rates observed in these systems (see Fig. 10). Therefore, the results obtained from these copolymerizations are explained satisfactorily by the monomer-isomerization radical polymerization mechanism of DMM as described above. We propose calling this type of copolymerization "monomer-isomerization radical copolymerization."

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