

Radical Polymerization of Muconic Acid and Ethyl Muconate

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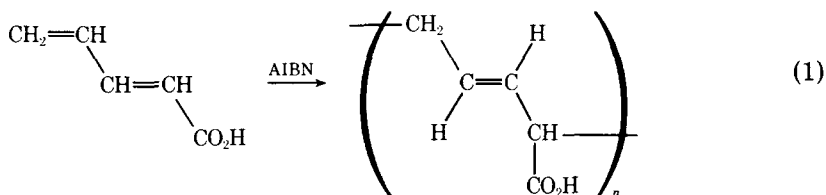
Synopsis

Muconic acid (Mu-acid) was found to polymerize to *trans*-1,4-poly(Mu-acid) with the use of azobisisobutyronitrile (AIBN) as an initiator. Similarly, a muconic acid derivative, ethyl muconate (EMu), was readily polymerized through a *trans*-1,4 addition mechanism by the use of a radical or anionic catalyst, but did not polymerize when a cationic catalyst such as boron trifluoride etherate was used. Moreover, the copolymerization of Mu-acid and EMu with various comonomers such as styrene, acrylonitrile, and 2-vinylpyridine was carried out and *Q-e* values of Mu-acid and EMu are discussed. These substituted diene monomers always polymerized through *trans*-1,4 addition with all catalysts and any comonomers.

INTRODUCTION

Some studies of the polymerization of muconic acid alkyl have been reported¹⁻³ and focused on the preparation and polymerization of new muconic acid derivatives. Recently, Bezdek et al.⁴ reported the preparation and polymerization of 1,2,2,2-tetrachloroethyl muconate. Little attention, however, has been paid to the copolymerizability of muconic acid derivatives with various monomers.

Very recently, the authors reported⁵⁻⁷ the radical polymerization of butadiene 1-carboxylic acid (Bu-1-acid), a monosubstituted butadiene derivative, in various organic solvents. It was mentioned that Bu-1-acid polymerized through a *trans*-1,4 addition with a free-radical initiator, as shown in eq. (1).



Studies dealing with the polymerization of muconic acid and its 1,4-disubstituted butadiene derivatives were carried out. Detailed studies relating to the polymerizability and copolymerizability of muconic acid (Mu-acid) and ethyl muconate (EMu) were performed.

The purpose of this report was to clarify the polymerizability and copolymerizability of Mu-acid and EMu and the microstructure of the resultant polymers.

EXPERIMENTAL

Materials

Muconic acid (Mu-acid), prepared according to the method described by Guha et al.,⁸ had mp 280–290°C (lit.⁸ mp 298°C). Ethyl muconate (EMu) was prepared by the usual method of esterification of Mu-acid, as follows. A mixture of 28 g of Mu-acid, 280 ml of fresh ethanol, and 8 ml of concentrated sulfuric acid was refluxed for 24 hr. After the given reaction time, the reaction mixture was evaporated, and the crude residue was extracted with ether. The ether solution was washed with the 3% potassium carbonate solution to remove the unreacted Mu-acid; the extract was dried (Na_2SO_4), filtered, and evaporated. Recrystallization from methanol yielded 28 g (54%) of the pure product, mp 62°C (lit.⁹ mp 63–64°C). The product had infrared absorption at 1700 cm^{-1} (conjugated $\text{C}=\text{O}$) and at 1610 cm^{-1} (conjugated $\text{C}=\text{C}$). The NMR spectrum of the material had a triplet centered at δ 1.35 ppm (3H, $-\text{C}-\text{CH}_3$), quartuplet peaks centered at δ 4.3 ppm (2H, $-\text{CH}_2-\text{C}$), and complex peaks centered at δ 6.3 ppm (2H, $-\text{CH}=\text{C}$).

ANAL. Calcd for $\text{C}_{10}\text{H}_{14}\text{O}_4$: C, 60.59%; H, 7.12%. Found: C, 59.85%; H, 7.12%.

Styrene (St), acrylonitrile (AN), and 2-vinylpyridine (2-Vp) were purified by the usual methods and distilled under reduced pressure.

Solvents

Benzene and toluene were purified by the usual methods and dried over sodium.

Catalyst

Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol; mp 103°C. Commercial samples of boron trifluoride etherate were purified by distillation under reduced pressure. Commercial samples of *n*-butyllithium were used without any purification.

Polymerization

For the radical polymerization of Mu-acid, the required amount of Mu-acid, AIBN, and dimethyl sulfoxide were charged in a Pyrex glass tube, cooled in a Dry Ice-methanol bath, and sealed in a vacuum system. The sealed tubes were placed in a thermostat maintained at a definite temperature. After polymerization for a given time, the contents of the tube were poured into a large amount of ether to precipitate the polymer. The resulting polymer was purified several times reprecipitation with methanol and ether.

For the anionic polymerization, monomer, solvent, and catalyst were intro-

duced under nitrogen into a glass tube. The polymerization was terminated by adding a small amount of methanol. The reaction mixture was then poured into a large amount of methanol containing aqueous HCl. The precipitated polymer was thoroughly washed with methanol and dried under vacuum at room temperature.

Characterization of the Polymer

Intrinsic viscosities were determined in benzene at 30°C by use of a Ubbelohde viscometer. NMR examination was performed with a Hitachi-Perkin-Elmer R-10 high-resolution NMR spectrometer on solutions of polymers in CDCl_3 . Infrared spectra of films obtained by evaporating the appropriate solutions of the polymers on KBr plates were taken with a Jasco IR-A2 infrared spectrophotometer.

RESULTS AND DISCUSSION

Polymerization of Muconic Acid

Muconic acid (Mu-acid) was insoluble in most organic solvents but was slightly soluble in dimethyl sulfoxide (DMSO) and pyridine. The polymerization of muconic acid, therefore, was carried out in DMSO with azobisisobutyronitrile (AIBN) as an initiator. The results and conditions are summarized in Table I.

The resultant polymers were soluble in methanol, tetrahydrofuran, DMSO, and dimethylformamide and insoluble in benzene, petroleum ether, hexane, and ether. This solubility pattern is very similar to that of poly(Bu-1-acid).

Next, to determine the monomer reactivity of Mu-acid, radical copolymerization of Mu-acid (M_1) with styrene (M_2) and with acrylonitrile (M_2) was carried out in DMSO with AIBN as an initiator. Copolymer composition curves are shown in Figure 1.

Based on these curves, the monomer reactivity ratios r_1 and r_2 were determined by the curve-fitting method and Fineman-Ross method.¹⁰ Also, Alfrey-Price Q - e values¹¹ were calculated from them, yielding the following values:

For $M_2 = \text{St}$:

$$r_1 = 0.52, r_2 = 0.15$$

$$Q_1 = 1.8, e_1 = +0.8$$

For $M_2 = \text{AN}$:

TABLE I
Radical Polymerization of Muconic Acid (Mu-acid)

Run	Mu-acid, g	AIBN, mg	DMSO, ml	Temp, °C	Time, hr	Polymer yield, g	$[\eta]^a$
733	0.5	25	2	50	50	0.08	—
734	0.5	25	2	50	140	0.18	0.24
768	1	25	2	50	90	0.12	0.38
736	0.5	25	2	75	69	0.14	0.15
751	0.5	25	2	100	50	0.15	0.06

^a Measured in methanol, 1.5 g/100 ml at 30°C.

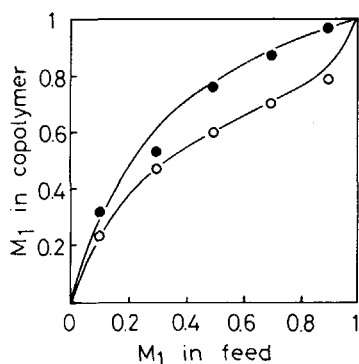


Fig. 1. Copolymerization composition curves for copolymers of (M_1) Mu-acid with (O) styrene and (●) acrylonitrile.

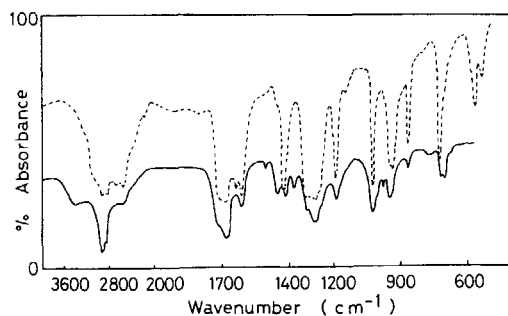


Fig. 2. Infrared spectra of (—) homopoly(Mu-acid) and (- -) its copolymer with styrene.

$$r_1 = 4.0, r_2 = 0.2$$

$$Q_1 = 1.7, e_1 = +0.73$$

The Q - e values obtained from styrene were in good agreement with those obtained from acrylonitrile.

Microstructure of Poly(Mu-acid) and Its Copolymers

In the preceding papers,⁵ the authors reported on elucidation of the structure of poly(Bu-1-acid) and its copolymers from their infrared spectra. In the present work, the same procedures were used for poly(Mu-acid) and its copolymers. The

TABLE II
Polymerization of EMu Using Various Catalysts

Catalysts			Solvent		Temp, °C	Time, hr	Polymer yield, %	$[\eta]^a$
Type	Amt, mmole	EMu, mmole	Type	Vol, ml				
AIBN	0.04	4	benzene	1.2	50	24	9.7	0.15
<i>n</i> -BuLi	0.6	2.6	toluene	1.0	-28	18	34.5	0.25
BF ₃ OEt ₂	0.05	2.6	toluene	1.5	20	18	0	—

^a In benzene, 0.5 g/100 ml, at 30°C.

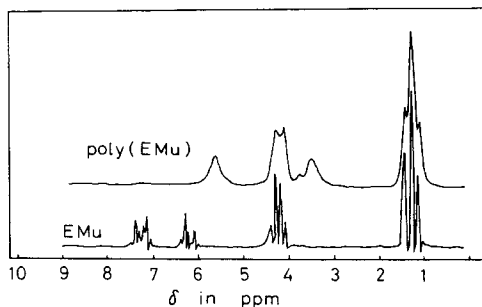
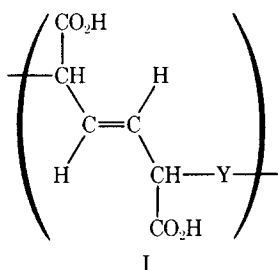


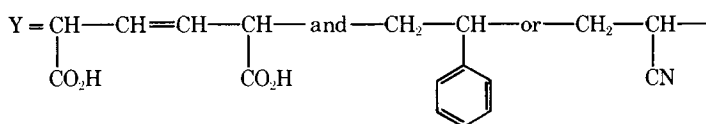
Fig. 3. NMR spectra of EMu monomer and poly(EMu).

infrared spectra of poly(Mu-acid) homopolymer and its copolymers with styrene are shown in Figure 2.

The respective infrared spectra showed no absorption bands at 1600 cm^{-1} which is characteristic of diene group and had absorption bands at 1720 cm^{-1} ($-\text{CO}_2\text{H}$). In addition, the strong absorption band at 950 cm^{-1} was assigned to the stretching frequency of *trans*-disubstituted ethylene. Also, similar results were obtained from the spectra of the copolymer with acrylonitrile. Therefore, these results showed that Mu-acid units were composed of *trans*-1,4 bonds in the homopolymer or copolymers (I):



where



This conclusion was in good agreement with results for poly(Bu-1-acid) and its copolymers.⁶

Polymerization of Ethyl Muconate (EMu)

In order to determine the polymerizability of EMu, polymerizations were carried out with various kinds of catalysts. The conditions and results are shown in Table II.

With a free-radical initiator, EMu was polymerized to give viscous oligomers which were soluble even in methanol. The anionic polymerization system showed orange-red coloration, indicating that the carbanion was formed; a white solid polymer was obtained. No crosslinked polymer was produced under our polymerization conditions. The polymer obtained with the use of radical ini-

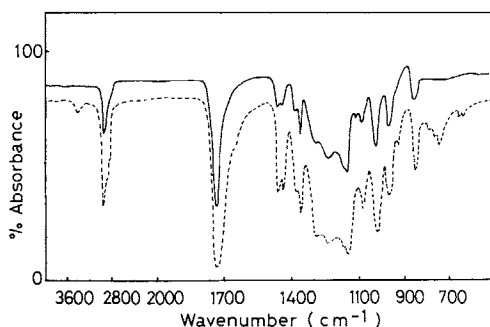


Fig. 4. Infrared spectra of (—) poly(EMu) obtained with AIBN and (---) poly(EMu) obtained with *n*-BuLi as initiator.

tiator was soluble in methanol, acetone, benzene, and chloroform and insoluble in petroleum ether. The polymer obtained with the use of anionic catalyst was soluble in chloroform and benzene and insoluble in methanol, acetone, and petroleum ether.

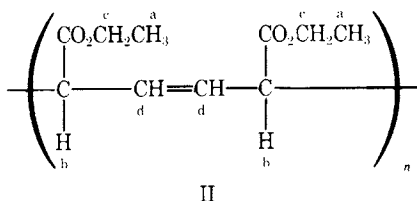
No polymer was obtained in the cationic polymerization.

Microstructure of Poly(ethyl Muconate)

NMR spectra of the polymer obtained in the radical polymerization are shown in Figure 3, together with that of the monomer EMu.

Triplet peaks centered at δ 1.3 ppm ($-\text{C}-\text{CH}_3$) correspond to the proton of methyl group a. The peak centered at δ 3.5 ppm corresponds to the methyne proton b ($-\text{HC}-\text{CO}_2$). The peak centered at δ 4.2 ppm corresponds to the methylene protons c ($-\text{CO}_2-\text{CH}_2-$).

The singlet peak at δ 5.7 ppm corresponds to the olefinic proton d ($\text{HC}=\text{C}$). The area ratios of a, b, c, and d were 2.9, 1.0, 2.0, and 1.0. These results were in good agreement with the theoretical values (6, 2, 4, and 2) for the polymer structure II.



It seemed of interest that this polymer was the perfect alternating copolymer from acetylene and ethyl maleate, ethyl fumarate. Actually, it is very difficult to prepare alternating copolymers from these monomers.

TABLE III
Copolymerization of EMu with Styrene with Various Catalysts^a

Catalysts (0.1 mmole)	Solvent (1 ml)	Temp, °C	Time, hr	Yield, %	EMu units, mole-%
AIBN	benzene	50	24	18.5	60.1
<i>n</i> -BuLi	toluene	-28	15	37.5	98.5
BF ₃ OEt ₂	bulk	20	0.4	80.0	0

^a EMu = St = 2.6 mmole.

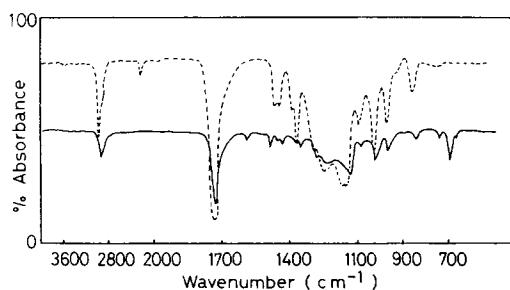


Fig. 5. Infrared spectra of (—) copoly(EMu-St) and (---) copoly(EMu-AN).

The infrared spectrum of the polymer is shown in Figure 4, together with that of polymer obtained in anionic polymerization. The two spectra were similar to each other.

The infrared spectra of both polymers had no absorption in the region of $675\text{--}730\text{ cm}^{-1}$, where *cis*-disubstituted ethylene absorbed; an absorption band at 975 cm^{-1} , characteristic of *trans*-disubstituted ethylene, was present.

From these assignments of infrared and NMR spectra, it was concluded that the resultant poly(EMu) was composed of *trans*-1,4 units. This structure is the same as that of the polymer of muconic acid.

In a previous study,⁵ the radical polymerization of butadiene 1-carboxylic acid was carried out. It was established that the resultant polymer was composed of *trans*-1,4 units and suggested that the *trans* form of the electron crowds of the propagating radical conjugated with an allyl group and a polar group would be most stable in the case of the polymerization of the butadiene derivatives substituted by polar groups. The present work established that this idea was correct.

Copolymerizability of EMu with Styrene with Various Catalysts

In order to determine the copolymerizability of EMu with styrene by various catalysts, the copolymerization of EMu (M_1) was carried out with the use of *n*-BuLi, BF_3OEt_2 , and AIBN as initiators. The results and conditions are shown in Table III. The copolymer compositions were determined from their NMR spectra and elementary analysis.

In the radical copolymerization, the resultant polymer was composed of nearly equimolar quantities of EMu and St. However, in the anionic copolymerization, the resultant polymer was considered to be composed mainly of EMu units. In the cationic copolymerization, no EMu units were incorporated in the polymer and only styrene homopolymer was obtained.

Similar phenomena have been observed in the ionic copolymerization of styrene with methyl methacrylate.¹²

Radical Copolymerization of EMu with Various Comonomers

Radical copolymerizations of EMu (M_1) with styrene (St), acrylonitrile (AN), and 2-vinylpyridine (2-Vp) were carried out by the conventional method. The results and conditions of radical copolymerization of EMu with styrene are shown in Table IV.

The infrared spectrum of the resultant copolymer is shown in Figure 5, together with that of copolymer with acrylonitrile. As shown in Figure 5, in each spectrum, an intense absorption at 975 cm^{-1} which is characteristic of *trans*-disubstituted ethylene is present. This absorption indicates that the EMu unit in the copolymer has a *trans*-1,4 structure. The same result was obtained in the copolymerization of EMu with 2-Vp.

Foster et al.¹³ reported the effect of comonomer on the microstructure of butadiene copolymer. They mentioned that the percentage of *trans*-1,4 addition increases, the 1,2 addition decreases, and the *cis*-1,4 addition decreases as the styrene content is increased.

However, in the case of ethyl muconate copolymer, the microstructure did not vary. All the copolymers were composed of *trans*-1,4 units at all compositions of the copolymer. Similar phenomena have been observed in the copolymerization of muconic acid with styrene.

Table IV summarizes copolymer composition determined from the NMR and elementary analysis. The results determined from NMR measurement were in good agreement with those obtained from C and H elementary analysis.

The copolymerization of EMu (M_1) with acrylonitrile (M_2) and 2-vinylpyridine (M_2) was carried out by the same method. Copolymer composition curves are shown in Figure 6.

Monomer reactivity ratios r_1, r_2 were determined both by the Fineman-Ross and the curve-fitting method, and the Alfrey-Price Q and e values were calculated from them. The following values were obtained.

For $M_2 = \text{St}$: $r_1 = 0.56, r_2 = 0.12$

$Q_1 = 2.0, e_1 = 0.8$

For $M_2 = 2\text{-Vp}$: $r_1 = 0.80, r_2 = 0.40$

$Q_1 = 2.0, e_1 = 0.6$

For $M_2 = \text{AN}$:

TABLE IV
Results of Radical Copolymerization of EMu (M_1) with Styrene (M_2)^a

M ₁ in feed, mole %	Copolymer					[η] ^b
	Yield, %	Analysis		M ₁ determined from C content, mole %	M ₁ determined from NMR analysis, mole %	
		C, %	H, %			
100	9.7	60.47	7.28	100	100	0.15
80	12.8	64.81	7.18	76.7	77.5	0.17
65	16.2	64.92	7.09	63.0	64.1	0.18
50	18.5	69.01	7.29	58.6	60.1	0.19
30	22.5	71.15	7.35	50.8	50.7	0.18
10	21.7	75.32	7.32	37.8	30.2	0.13
0	24.4	92.02	7.79	0	0	0.21

^a [Total monomer] = 2 mole/l.; [AIBN] = 2.0×10^{-2} mole/l.; in benzene at 50°C ; 24 hr.

^b In benzene, 0.5 g/100 ml, at 30°C .

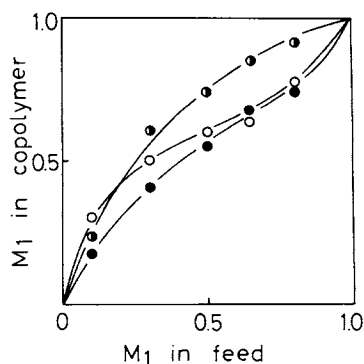


Fig. 6. Copolymer composition curves for copolymers of EMu (M_1): (O) St; (◐) AN; (●) 2-Vp.

$$r_1 = 3.2, r_2 = 0.30$$

$$Q_1 = 1.6, e_1 = 1.0$$

Discussion of Q - e Values of Mu-acid and EMu

Table V summarizes the average Q - e values of Mu-acid and EMu obtained in the present work, together with those of related more common monomers reported in the literature.¹⁵ In general, Q and positive e values of free acid monomer are larger than those of their alkyl ester, as is clear from Table V. However, in the case of Mu-acid and EMu monomer, respective Q - e values were very similar to each other were obtained.

As mentioned in the previous paper,⁶ the Q - e value of free acid monomer is markedly altered by the polymerization solvents. Moreover, it was mentioned that Q value and the positive e value decreased with an increase of basicity of used solvents.

In the copolymerization of Mu-acid, dimethyl sulfoxide (DMSO) was selected as a good solvent because of the low solubility of Mu-acid in other organic solvents. DMSO is a strongly basic solvent.

Therefore, it was thought that the chance agreement of Q - e values of Mu-acid with those of EMu resulted from the decrease of Q and positive e values for Mu-acid owing to the strong basicity of DMSO.

Next, as is clear from Table V, the Q values of Mu-acid and EMu are larger

TABLE V
 Q - e Values of Muconic Acid, Ethyl Muconate, and Related Monomers

Monomer	Q	e	Reference
Muconic acid	1.8	+0.77	Present work
Ethyl muconate	1.9	+0.8	Present work
Butadiene 1-carboxylic acid	6.0	+0.11	Bando and Minoura ⁵
Glycidyl β -vinyl acrylate	4.79	-0.05	Iwakura et al. ¹⁴
Acrylic acid	1.15	+0.77	Brandrup and Immergut ¹⁵
Methyl acrylate	0.42	+0.60	Brandrup and Immergut ¹⁵
Methacrylic acid	2.34	+0.65	Brandrup and Immergut ¹⁵
Methyl methacrylate	0.74	+0.40	Brandrup and Immergut ¹⁵

than those of vinyl monomers such as acrylic acid and alkyl acrylate. This is due to the stability of the allyl radical involving the participation of polar groups, as mentioned in the previous paper.⁵

The e value of Mu-acid was near those of the corresponding vinyl monomers as in the case of EMu.

Consequently, it was thought that Mu-acid and EMu were readily polymerized owing to their sufficiently high Q value and that the ready anionic polymerization and absence of cationic polymerization of EMu occurred because of this positive e value.

CONCLUSION

Mu-acid was polymerized with the use of free-radical initiators to give *trans*-1,4-poly(Mu-acid). Similarly, its derivative (EMu) was oligomerized with free-radical or anionic catalysts, to give *trans*-1,4-poly(EMu). From the results of the copolymerization of Mu-acid and EMu with various comonomers, it was found that their Q value had a larger value than that of corresponding vinyl monomers. Moreover, it was found that Mu-acid and EMu were electron-poor monomers in spite of the presence of diene group in the molecule.

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