

Radical high polymerization of β -monoalkyl itaconates and characterization of the resulting polymers

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SUMMARY

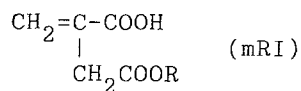
Radical polymerization behavior of itaconates with various β -monoalkyl substituents (mRI) was investigated. mRIs homopolymerize easily in bulk at 60~90°C, to give polymers with molecular weight of 23,000~306,000. The yield and the molecular weight of the resulting polymers were found to be slightly dependent on the alkyl substituents, and apparently higher than those of dialkyl itaconates (DRI). In the copolymerization of β -monoethyl and mono-tert-butyl itaconates with styrene, these monomers exhibited similar reactivity toward polystyryl radical. The solubility of the poly(mRI)s in water and organic solvents varied with the structure of the alkyl substituent. Thermogravimetric analysis in a nitrogen atmosphere revealed that the initial decomposition temperatures for most of poly(mRI)s were observed at about 150°C and poly(mono-tert-butyl itaconate) decomposed at ca. 100°C.

INTRODUCTION

Since 1958, much attention has been paid to the radical polymerization behavior of some polymerizable α -substituted acrylates as 1,1-disubstituted ethylenic monomers [1-6]. Recently, we have also studied on the radical polymerization reactivity of various dialkyl itaconates (DRI) which undergo radical polymerization easily in bulk and the ester alkyl substituents have been confirmed to slightly affect the polymerization reactivities [7].

Within our knowledge, there has been a few publication for thermal properties of some poly(monoalkyl itaconates) [8,9]. However, the radical polymerization reactivity of α -alkoxycarbonylmethylacrylic acid (Scheme I) which has been called the β -monoalkyl ester of itaconic acid (mRI) [10] has not been reported in detail. We have been interested in the radical polymerization of mRIs because they can be expected to polymerize as well as DRIs [7].

In the present study, mRIs bearing various ester alkyl substituents were prepared and polymerized with radical initiation. Furthermore, in order to estimate the reactivities of mRIs, mono-



Scheme I

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ethyl and mono-tert-butyl itaconates were copolymerized with styrene. Characterization of the resulting polymers was performed by IR and NMR spectroscopies. Some properties of the polymers such as solubility and thermal stability were also examined. The results obtained are described in this paper.

EXPERIMENTAL

mRIs were prepared and purified according to the methods reported in the literature [8]. Commercial 2,2'-azobisisobutyronitrile (AIBN) and 1,1'-azobiscyclohexane-1-carbonitrile (ACN) were purified by recrystallization twice from methanol. Other reagents and solvents were used after ordinary purifications.

Polymerizations and copolymerizations were carried out in sealed glass tubes under shaking. After polymerization for a given time, the mixture was poured into a large amount of ethyl ether to isolate the polymer. The polymer was purified by reprecipitation from methanol and a precipitant. Copolymer compositions were determined by measuring the intensity ratio of the specific resonances for the respective monomer units in ^1H NMR spectra.

Number-average molecular weight (\bar{M}_n) calibrated with the standard polystyrene was determined by a Toso 8000 series gel permeation chromatography (GPC) at 38°C using tetrahydrofuran (THF) as eluent. Thermogravimetric analysis (TGA) was carried out by means of Shimadzu TGA-20 thermobalance in a nitrogen steam with a heating rate of 10°C/min. NMR spectra (400 MHz) were taken on a JEOL-GX 400 spectrometer in CDCl_3 at 27°C.

RESULTS AND DISCUSSION

Homopolymerization

Radical polymerizations of mRIs initiated with AIBN or ACN were carried out in bulk at temperatures higher than the melting points (mp) of the monomers. The results of the polymerizations together with mp of the monomers are shown in Tab. 1. The polymerizations in bulk at 60°C gave the high molecular weight polymers in high yields. The bulk polymerizations at temperatures higher than 60°C or the polymerizations in solution proceeded slowly and gave the lower molecular weight polymers. The rates of the polymerizations for mRIs are observed to be considerably higher than those for DRI and the \bar{M}_n of the poly(mRI)s are higher than those of poly(DRI)s.

As can be seen from Tab. 1, mtBI polymerized slowly to give the low \bar{M}_n polymer in bulk at 100°C. This is considered to come from the decarboxylation of mtBI as reported for the polymerization of itaconic acid [11]. This consideration is manifested by the IR spectrum of poly(mtBI) prepared at 100°C as shown in Fig. 1(b), in which the absorbance of C=O at 1650~1700 cm^{-1} disappeared partially.

Comparing the results of polymerization for mMI, mEI, and mtBI in dioxane at 60°C, we can conclude that the rate of the polymerization decreases only slightly with increasing bulk-

Tab. 1 Radical Polymerization of mRIs in Bulk

Abb.	Monomer		Initiator (wt.%)	Temp. (°C)	Time (h)	Yield (%)	\bar{M} a) $\times 10^{-4}$
	R	mp(°C)					
mMI	CH ₃	68-70	ACN 1.0	80	4.5	34.2	5.3
mMI	CH ₃	68-70	AIBN ^{b)}	60	12.0	15.6	1.0
mEI	C ₂ H ₅	55-56	AIBN 0.4	60	2.5	59.6	24.1
mEI	C ₂ H ₅	55-56	AIBN ^{b)}	60	12.0	14.5	0.5
mnPI	n-C ₃ H ₇	35-36	AIBN 0.4	60	2.5	57.6	29.5
miPI	i-C ₃ H ₇	45-46	AIBN 0.4	60	2.5	49.8	24.3
mnBI	n-C ₄ H ₉	33-34	AIBN 0.4	60	2.5	58.1	30.6
miBI	i-C ₄ H ₉	46-47	AIBN 0.4	60	2.5	56.0	24.2
mtBI	t-C ₄ H ₉	95-96	ACN 1.0	100	1.5	6.8	-
mtBI	t-C ₄ H ₉	95-96	AIBN ^{b)}	60	12.0	12.6	1.3
mcHI	c-C ₆ H ₁₁	62-63	AIBN 0.4	65	2.0	15.5	9.2
mBzI	CH ₂ C ₆ H ₅	83-85	ACN 1.0	90	4.0	15.8	2.3
mnOI	n-C ₁₈ H ₃₇	88-89	ACN 1.0	90	4.0	36.0	2.3
DEI ^{c)}	C ₂ H ₅	< 0	AIBN 0.3	60	2.5	8.7	4.2
DEI ^{c)}	C ₂ H ₅	< 0	AIBN ^{b)}	60	12.5	8.8	0.4

a) By GPC, the sample was methylated with diazomethane.

b) In dioxane; [M] = 2.0 mol/L, [AIBN] = 0.03 mol/L.

c) Diethyl itaconate.

iness of the ester substituent. Similar conclusion can also be drawn from the time-conversion relations for the bulk polymerization of mRIs with AIBN at 60°C shown in Fig. 2.

Copolymerization

To compare the reactivity of mRIs, copolymerizations of mEI and mtBI (M₂) with styrene (St) (M₁) were performed in dioxane at 60°C with 0.02 mol/L of AIBN. The copolymerizations were found to proceed easily. The compositions of the copolymers obtained were determined by ¹H-NMR spectra measured in CDCl₃ after methylation with diazomethane. Fig. 3 shows the copolymer composition curves obtained. The monomer reactivity ratios evaluated (r_1 and r_2) are summarized in Tab. 2 together with those reported¹ for mMI [12]. Comparing the values of $1/r_1$ in Tab. 2, we can note that the relatively reactivity of mtBI toward polystyryl radical is almost the same as those of mMI

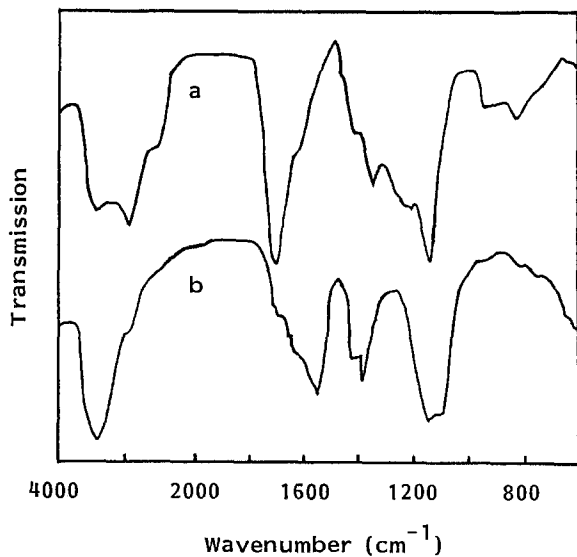


Fig. 1 IR spectra of poly(mtBI) from radical polymerization in dioxane at 60°C (a) and in bulk at 100°C (b).

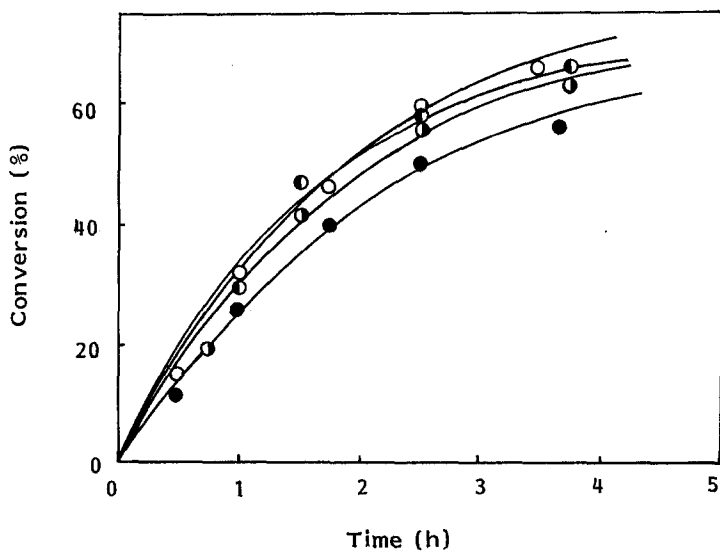


Fig. 2 Time-conversion curves for bulk polymerization at 60°C: mEI (○), mnBI (●), miBI (◐), and miPI (●). [AIBN] = 0.4 wt.%.

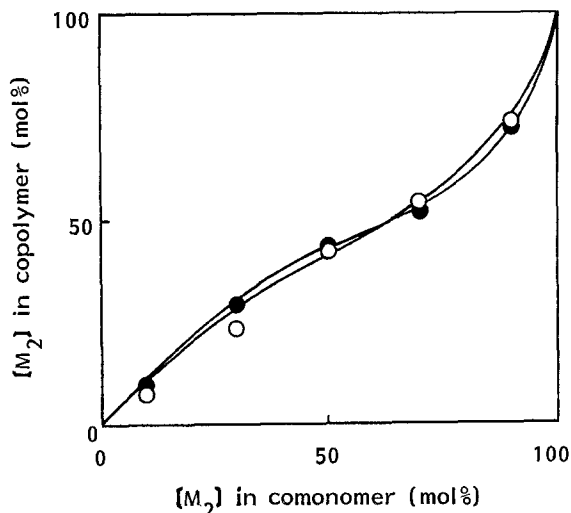


Fig. 3 Copolymer composition curves for copolymerizations of mEI (O) and mtBI (●) (M_2) with St (M_1)

Tab. 2 Radical Copolymerization Parameters of mRI (M_2) with Styrene (M_1)

M_2	r_1	r_2	$1/r_1$	Q_2	e_2	Ref.
mMI	0.55	0.28	1.8	0.61	0.57	12
mEI	0.84	0.26	1.2	0.44	0.44	This work
mtBI	0.68	0.22	1.5	0.49	0.58	This work

and mEI. This finding is in agreement with the results for homopolymerization of mMI, mEI and mtBI in dioxane, suggesting that the reactivity of mRI slightly dependent on the alkyl substituent.

Characterization of poly(mRI)s

Poly(mRI)s were confirmed to consist of the corresponding monomeric unit by IR and NMR spectroscopies. The ^1H NMR spectra of mtBI and its homopolymer obtained by polymerization in dioxane at 60°C are shown in Fig. 4. The resonances at 5.77 and 6.40 ppm due to the olefin protons in the spectrum of the monomer disappeared by polymerization. It is clear that mRI polymerized through an ordinary vinyl polymerization mechanism accompanying opening its carbon-carbon double bond.

Poly(mRI)s obtained by radical polymerization except the polymer prepared by bulk polymerization of mtBI were colorless powder. Tab. 3 shows the solubilities of these polymers in water and some organic solvents. It is confirmed that polymers with different solubilities were obtained as expected.

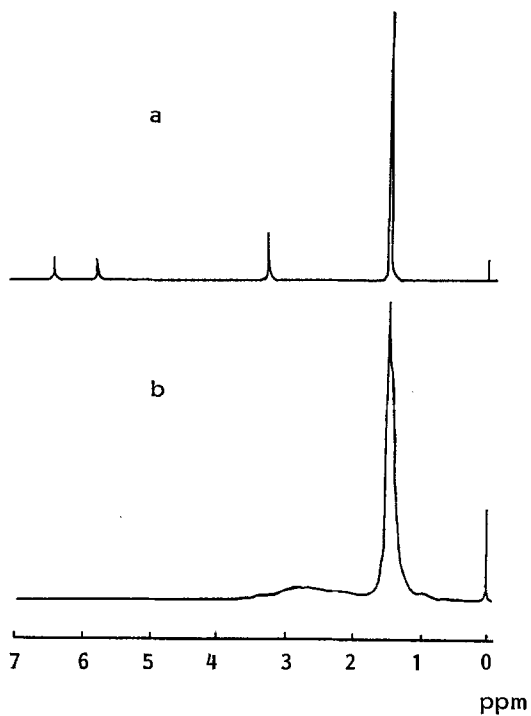


Fig. 4 ^1H NMR spectra of mtBI (a) and poly(mtBI) (b) in CHCl_3 at 27°C .

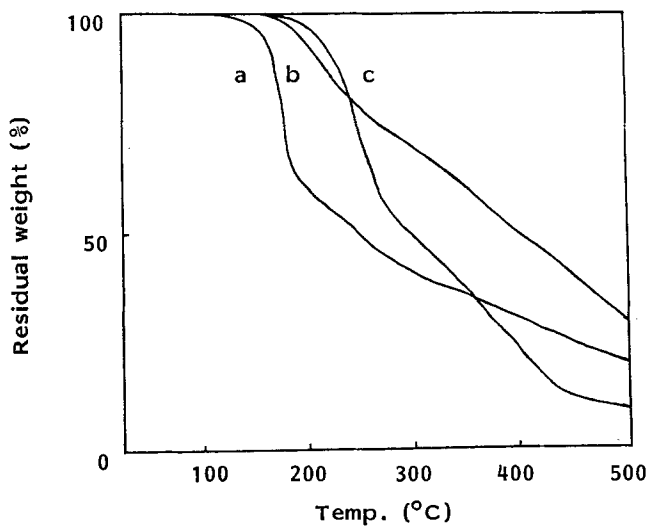


Fig. 5 Thermogravimetric analysis in a nitrogen steam with a heating rate of $10^\circ\text{C}/\text{min}$: poly(mtBI) (a), poly(mMI) (b), and poly(mnOI) (c).

Tab. 3 Solubility of Poly(mRI)s^{a)}

Polymer	Benzene	THF	CHCl ₃	Acetone	CH ₃ OH	H ₂ O
Poly(mMI)	sw	i	sw	i	s	s
Poly(mnOI)	sw	s	s	i	i	i
Poly(mtBI)	s	s	s	s	s	i

a) s: soluble, sw: swelling, i: insoluble.

To examine thermal stability of poly(mRI)s, TGA was carried out in a nitrogen stream with a heating rate of 10°C/min. Fig. 5 shows the thermograms for poly(mMI), poly(mOI), and poly(mtBI). Initial decomposition temperature ($T_{init.}$) and maximum decomposition temperature ($T_{max.}$) are summarized in Tab. 4.

Tab. 4 Thermogravimetric Analysis for Poly(mRI)s

Polymer	$T_{init.}$ (°C)	$T_{max.}$ (°C)	Residue at 500°C (%)
Poly(mMI)	157	196,337	31.3
Poly(mnOI)	155	282,387	9.5
Poly(mtBI)	100	167,260	22.2

The decomposition behavior of poly(mMI) observed is in good agreement with that reported by Cowie and coworkers [9]. The initial decomposition of poly(mnOI) is almost the same as that of poly(mMI), indicating that the length of the ester side chain has little influence on the thermal stability of the polymers.

The decomposition of poly(mtBI) began at a relatively lower temperature (ca. 100°C) than the others with n-alkyl groups. This seems to come from the ease of elimination of the tert-butyl group.

All the decomposition temperatures of the poly(mRI)s were found to be lower than those of poly(DRI)s [7,9]. This is presumably due to that the carboxylic acid functions as a catalyst for the decomposition.

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