

Group Transfer Polymerization of Methyl Crotonate

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Methyl crotonate [(*E*-) CH₃CH=CHCO₂CH₃] has long been considered as a monomer that can hardly be polymerized. As a commonly observed feature of crotonates, methyl crotonate gives no polymer by a free radical mechanism.^{1,2} Typical anionic initiators such as alkylolithium or Grignard reagents are ineffective for the polymerization of methyl crotonate,^{1–4} whereas branched alkyl crotonates including *t*-butyl crotonate and triphenylmethyl crotonate are polymerized in good yield^{1–10} and in a living manner¹¹ by these initiators. The only compound that has been known to polymerize methyl crotonate in a substantial yield is calcium zinctetraethyl complex. The polymerization of methyl crotonate with this complex in toluene at –78°C for 96 h affords polymer in a 28% yield.⁴

Though the reason for the reluctance of methyl crotonate to polymerize is not clear, it seems reasonable to suppose that side reactions such as intra- and intermolecular carbonyl addition of the active species should take place in preference to propagation. If this is the case, group transfer polymerization (GTP), a convenient method to prepare polymethacrylates and polyacrylates with controlled molecular weight,^{12–14} would be useful for the polymerization of methyl crotonate.

Our early attempts to polymerize methyl crotonate by GTP were unsuccessful. No polymerization proceeded in tetrahydrofuran (THF) when 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) and tris(dimethylamino)sulfonium bifluoride were used as an initiator and as a nucleophilic catalyst, respectively. Only a small amount of oligomer was obtained (yield, 12.5%) by the GTP using MTS and ZnI₂ in CH₂Cl₂ at 20°C.¹⁵ These results suggest that Lewis acid catalysts and nonpolar solvents should be preferable for the GTP of this monomer.

Recently, the GTP of acrylates using MTS as an initiator and HgI₂ as a catalyst in toluene at room temperature has been found to give a very good control of molecular weight and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.2$).^{16,17} Detailed kinetic studies on this polymerization system revealed that the use of iodotrimethylsilane as a co-catalyst and CH₂Cl₂/toluene mixtures as a solvent drastically accelerates the polymerization.^{18,19} On the basis of the above findings, we have reinvestigated the GTP of methyl crotonate to achieve quantitative formation of poly(methyl crotonate)s with

controlled molecular weight.

The GTP was initiated by adding a solution of MTS in CH₂Cl₂ to a stirred mixture of 10 mmol methyl crotonate, 0.016 mmol HgI₂, 0.048 mmol iodotrimethylsilane, and 8 ml CH₂Cl₂ under a dry argon atmosphere. The reaction mixture was homogeneous throughout the polymerization. After a predetermined period of polymerization, a small amount of methanol was added to the mixture, and then the volatile components were removed by evaporation under reduced pressure. The residue was dissolved in toluene, and the solution was poured into a large amount of methanol. The precipitated polymer was collected by filtration, washed several times with methanol, and dried at 40°C *in vacuo* for 6 h (“methanol-insoluble part”). The filtrate was stripped of solvent, re-dissolved in acetone, and poured into a 50 : 50 v/v mixture of methanol and water. The insoluble fraction was recovered by centrifugation and designated as “methanol-soluble part”. The oligomer soluble in methanol–water (50 : 50) was discarded because of the difficulty in separating highly poisonous mercuric compounds.

Table I shows the yield and molecular weight of poly(methyl crotonate) formed in the GTP. The variation in polymerization temperature greatly affected the total yield of methanol-insoluble and methanol-soluble polymers when the polymerization was allowed to proceed for 24 h using 0.20 mmol MTS (the feed ratio of methyl crotonate to MTS being 50 mol mol⁻¹). The maximum yield was obtained at –40°C.

In the polymerization at –40°C with 0.10 mmol MTS, the yield and molecular weight of methanol-insoluble polymer increased with increasing polymerization time from 24 to 96 h. The total yield in the polymerization for 96 h reached 85%. All of the polymers had fairly narrow molecular weight distributions. The initiator efficiency, *f*, in the polymerization at –40°C ranged from 0.70 to 0.92. The deviation of the *f* values from unity is partly due to the exclusion of the oligomers soluble in methanol/water from calculation of *f*.

When the GTP was carried out in toluene (data not shown) or without iodotrimethylsilane, the polymerization was too slow to yield a detectable amount of polymer in 24 h.

The poly(methyl crotonate)s obtained by the GTP were soluble in CH₂Cl₂, chloroform, toluene, and THF. In contrast, highly stereoregular poly(methyl crotonate)s, which are prepared by transesterification of *threodiisotac-*

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Table I. Polymerization of methyl crotonate with 1-methoxy-1-(trimethylsilyloxy)-2-methyl-1-propene (MTS) in dichloromethane in the presence of mercuric iodide and iodotrimethylsilane^a

MTS mmol	Temp °C	Time h	MeOH-insoluble part			MeOH-soluble part ^b		<i>f</i> ^c
			Yield/%	$\bar{M}_n \times 10^3$	\bar{M}_w/\bar{M}_n	Yield/%	$\bar{M}_n \times 10^3$	
0.20	0	24	3.1	6.3	1.30	27.5	3.5	0.42
0.20	-20	24	25.2	8.6	1.27	36.6	4.4	0.56
0.20	-40	24	40.1	6.2	1.18	38.0	4.3	0.77
0.20	-60	24	trace			5.5	1.6	0.17
0.20 ^d	-40	24	0			trace		
0.10	-40	24	12.2	6.9	1.20	28.4	5.4	0.70
0.10	-40	48	46.0	11.6	1.21	25.8	5.5	0.87
0.10	-40	96	61.0	12.9	1.30	23.5	5.3	0.92

^a Methyl crotonate, 10 mmol; HgI₂, 0.016 mmol; iodotrimethylsilane, 0.048 mmol; CH₂Cl₂, 8 ml. \bar{M}_n and \bar{M}_w/\bar{M}_n were determined by vapor pressure osmometry and GPC, respectively. ^b This polymer is soluble in methanol and insoluble in a 50:50 v/v mixture of methanol and water. ^c The initiator efficiency calculated in the following way: $f = [\text{The total yield in mol of MeOH-insoluble and MeOH-soluble polymers}] / [\text{The amount in mol of MTS in feed}]$. ^d Without iodotrimethylsilane.

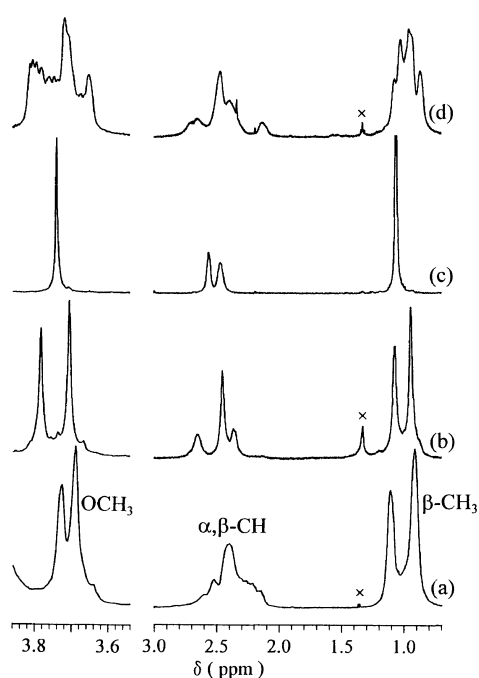


Figure 1. ¹H NMR spectrum of poly(methyl crotonate) prepared by GTP at -40°C (a). The spectra of highly diheterotactic (b), highly threodiisotactic (c), and atactic-like (d) poly(methyl crotonate)s are also shown. All spectra were measured in (CF₃)₂CHOH-C₆D₆ (95:5, v/v) at 55°C and 500 MHz. The strong resonances due to solvent appear in the spectral region from 3.8 to 4.4 ppm. (x) Signals due to impurities.

tic poly(triphenylmethyl crotonate)⁸ and *diheterotactic* poly(*t*-butyl crotonate),¹⁰ are insoluble in the organic solvents other than 1,1,1,3,3,3-hexafluoro-2-propanol. ¹H NMR spectroscopy showed that the stereoregulation of the poly(methyl crotonate)s formed in the GTP was quite different from that of the poly(methyl crotonate) converted from *atactic*-like poly(*t*-butyl crotonate) (*cf.* Figures 1a and 1d). Each of the β -CH₃ and OCH₃ resonances in Figure 1a appears as a doublet, and their chemical shifts disagree with those of *diheterotactic* (Figure 1b) or *threodiisotactic* poly(methyl crotonate)

(Figure 1c). Accordingly, the polymer obtained by the GTP is considered to comprise the two kinds of ditactic sequences which are still unidentified, *i.e.*, *erythrodiisotactic* and *disyndiotactic* sequences.

The present work has shown that poly(methyl crotonate) can be prepared directly and efficiently by the GTP of methyl crotonate. The use of CH₂Cl₂ as solvent together with HgI₂ and iodotrimethylsilane as catalyst extends the scope of GTP to crotonates which is another family of acrylates and methacrylates.

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