Polymer Bulletin 24, 475–480 (1990)

Polymer Bulletin

Radical polymerization of *N*-substituted citraconimides as polymerizable 1,1,2-trisubstituted ethylenes

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SUMMARY

The radical polymerization behavior of N-substituted citraconimides, 1,1,2-trisubstituted ethylenic monomers, was investigated. N-Alkylcitraconimides were found to homopolymerize in bulk at 60°C to give polymers with molecular weight of 6800~10000, except methyl and ethyl derivatives. Polymerization of N-phenylcitraconimides in benzene at 60°C or in bulk at 120°C gave polymers with relatively low molecular weight from 700 to 2000. From thermogravimetric analysis, the initial and maximum decomposition temperatures for poly(N-isopropylcitraconimide) were 309 and 365°C, respectively, and these were lower than those for poly(N-isopropylmaleimide) by about 40°C.

INTRODUCTION

N-Substituted maleimides (RMI) have been known to polymerize easily as well as fumaric acid derivatives, in spite of a 1,2-disubstituted ethylenic structure [1-8]. However, N-substituted citraconimides (α-methylmaleimides) have been attracted little attention [9]. Recently, copolymerizations of N-alkyl and N-(4-substituted phenyl) citraconimides with styrene or methyl methacrylate have been reported by Oishi and coworkers [10-12].

We have interested in the radical polymerization behavior of the isomeric dicarboxylic acid derivatives, itaconic, citraconic and mesaconic acid derivatives. In the course of these studies, we have found that N-substituted citraconimides are noted as the homopolymerizable trisubstituted ethylenes. In order to examine the radical polymerization reactivity of N-alkyl- and N-phenylcitraconimides (RCI and PhCI, respectively), the radical polymerization of these monomers was performed. Furthermore, the polymer obtained was characterized by spectroscopy and thermal stability.

EXPERIMENTAL

RCI was prepared and purified according to the methods reported in the literatures [10-12]. 2,2'-Azobisisobutyro-

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*To whom offprint requests should be sent nitrile (AIBN) was purified by recrystallization twice from methanol. Commercial sec-butyllithium (s-BuLi) diluted with n-hexane was used without further purification. Other initiators and solvents were used after ordinary purifications.

Polymerization was carried out in the presence of radical initiator in a sealed glass tube. After polymerization for a given time, the mixture was poured into a large amount of n-hexane to isolate the polymer. Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) calibrated with standard polystyrenes were determined by gel permeation chromatography (GPC) at 38°C using tetrahydrofuran (THF) as an eluent. Thermogravimetric analysis (TGA) was carried out in a nitrogen stream with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Polymerization of RCIs

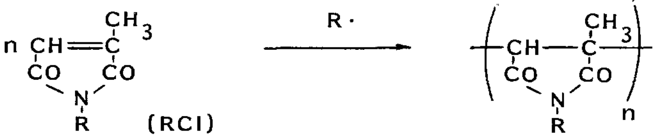
Radical polymerizations of various RCIs with AIBN were carried out in bulk at 60°C. The yield, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ are shown in Tab. 1. RCIs were found to homopolymerize, in spite of their trisubstituted ethylenic structure. RCIs with propyl and n-butyl substitutents gave higher molecular weight polymers than those with methyl and ethyl substitutents. Similar tendency has been observed in the polymerization of RMIs [7]. However, the α-methyl substitution of RCIs apparently decreased the polymerization rate and $\bar{M}_n$ of the polymer.

Tab. 1 Radical Polymerization of RCIs at 60°C for 10h$^{a)}$

RCI	R	Yield(%)	$\bar{M}_n$$^{b)}$x10^{-3}	$\bar{M}_w/\bar{M}_n$
MCI	CH_3	2.7	0.7	2.14
ECI	CH_2CH_3	1.7	1.7	1.43
nPCI	$(CH_2)_2CH_3$	10.0	7.7	2.05
iPCI	$CH(CH_3)_2$	9.2	10.0	1.43
nBCI	$(CH_2)_3CH_3$	5.1	7.4	1.40
iBCI	$CH_2CH(CH_3)_2$	6.7	9.1	1.72
sBCI	$CH(CH_3)CH_2CH_3$	2.8	7.3	1.39
tBCI	$C(CH_3)_3$	0.8	6.8	1.14

a) In bulk, [AIBN] = 0.03 mol/L. b) By GPC in THF.

As is shown later, the polymers obtained were found to consist of the corresponding RCI monomeric units, indicating that RCIs were polymerized through opening their double bond, i.e. an ordinary vinyl polymerization mechanism [eq.(1)].



(1)

Time-conversion relations are shown in Fig. 1 for bulk polymerization of nPCI initiated with AIBN at temperatures ranging from 50 to 70°C. The overall activation energy, E_a, was obtained from the Arrhenius plot of the initial polymerization rate to be 86.2 KJ/mol. Being smaller than that for RMI (ca. 105 KJ/mol) [3], this is close to those for the radical polymerization of conventional vinyl monomers.

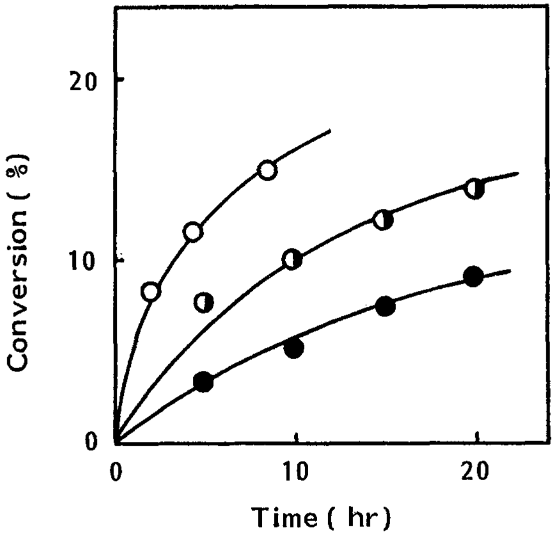


Fig. 1 Time-conversion curves for polymerization of nPCI in bulk at : 50°C (●), 60°C (◑), and 70°C (○). [AIBN] = 0.03 mol/L.

Tab. 2 Homopolymerization of nPCI in Bulk at Various Temperatures

[Initiator]$^{a)}$ (mmol/L)		Temp. (°C)	Time (h)	Yield (%)	$\bar{M}_n$$^{b)}$
s-BuLi	55	$0^{c)}$	75	22.2	450
AVN	30	45	10	8.2	7700
AIBN	30	60	10	10.0	7700
ACN	30	80	10	11.2	9800
DtBPO	54	120	20	16.8	2800

a) AVN: 2,2'-azobis(2,4-dimethylvaleronitrile), ACN: 1,1'-azobiscyclohexane-1-carbonitrile, DtBPO: di-t-butyl peroxide. b) By GPC. c) In THF, [M] = 2.7 mol/L.

Tab. 2 shows the results of polymerization of nPCI under various conditions. nPCI was found to polymerize even at 120°C with DtBPO. nPCI was also found to undergo anionic polymerization with s-BuLi to give relatively low molecular weight polymer at 0°C.

Polymerization of PhCIs

Polymerizations of PhCI and 2- or 4-substituted PhCIs in benzene at 60°C or in bulk at 120°C were found to give polymers with relatively low molecular weight from 700 to 2000 as shown in Tab. 3. However, higher molecular weight polymer was not obtained.

Tab. 3 Radical Polymerization of PhCIs

R	Solvent	[Initiator] (mmol/L)		Temp. (°C)	Time (h)	Yield (%)	$\overline{M}_n$ [a]
Ph	benzene[b]	AIBN	21	60	40	5.9	1450
	none	DtBPO	54	120	20	4.2	710
2-CH_3-Ph	benzene[b]	AIBN	20	60	20	3.0	1170
	none	DtBPO	54	120	20	10.2	700
4-CH_3-Ph	benzene[b]	AIBN	20	60	40	7.3	1920
	none	DtBPO	54	120	20	31.3	1030
4-OCH_3-Ph	benzene[b]	AIBN	20	60	20	2.9	1500
	none	DtBPO	54	120	20	31.5	1280
4-$COOC_2H_5$-Ph	none	ACN	30	80	20	1.6	1520

a) By GPC in THF.
b) [M] = 2.7 mol/L.

Characterization of poly(RCI)s

All poly(RCI)s obtained by radical polymerization were colorless powder and were soluble in common organic solvents such as benzene, acetone, and THF.

Poly(RCI)s were confirmed to consist of the corresponding monomeric unit by IR and NMR as shown in Figs. 2 and 3. The resonances at 127 and 145 ppm (=CH and =C, respectively) in the ^{13}C-NMR spectrum of the monomer (Fig. 3) disappear by polymerization, and new signals at 48 and 56 ppm (-CH and -C) emerge in the spectrum of the polymer. Therefore, it is clear that nPCI polymerized through opening its double bond, i.e. an ordinary vinyl polymerization mechanism.

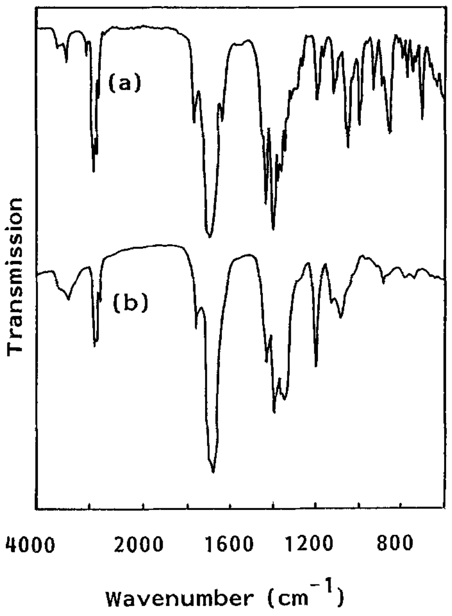


Fig. 2 IR spectra of nPCl (a) and poly(nPCl) (b).

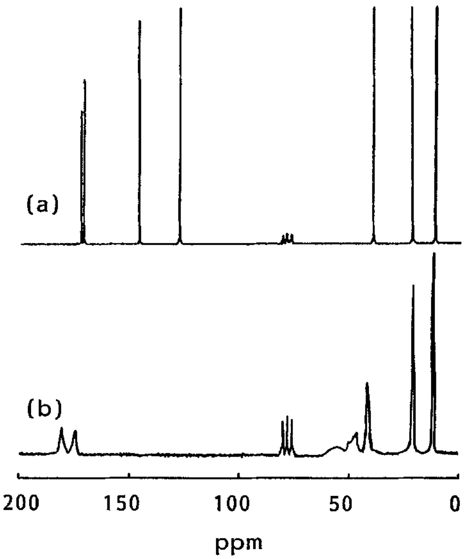


Fig. 3 ^{13}C NMR spectra of nPCl (a) and poly(nPCl) (b).

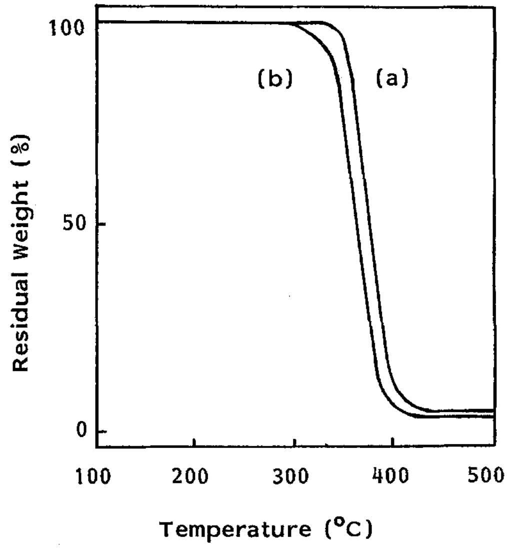


Fig. 4 Thermogravimetric analysis in a nitrogen steam with a heating rate of 10°C / min : poly(iPCl) (a) and poly(nBCl) (b).

To examine thermal stability of poly(RCI), TGA was carried out in a nitrogen stream with a heating rate of 10°C/min. Fig. 4 shows the thermograms for poly(iPCI) and poly(nBCI). The initial decomposition temperature ($T_{init.}$), maximum decomposition temperature ($T_{max.}$), and residual amount at 500°C are summarized in Tab. 4 together with those for poly(RMI)s [7]. The lower $T_{init.}$ and $T_{max.}$ for poly(RCI)s than those of poly(RMI)s by about 40°C evidence that the α-methyl substitution of poly(RMI) considerably decreases thermal stability.

Tab. 4 Thermogravimetric Analysis for Poly(RCI)s

Polymer	$T_{init.}$ (°C)	$T_{max.}$ (°C)	Residue at 500°C (%)	Reference
Poly(iPCI)	309	365	3.9	This work
Poly(iPMI)[a]	349	403	2.2	7
Poly(nBCI)	265	355	3.4	This work
Poly(nBMI)[b]	291	402	1.8	7

a) Poly(N-isopropylmaleimide). b) Poly(N-n-butylmaleimide).

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Accepted August 16, 1990 S