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Reactivity in radical polymerization of *N*-substituted maleimides and thermal stability of the resulting polymers

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SUMMARY

The effect of *N*-substituents on the radical polymerization of *N*-substituted maleimides (RMI) was investigated. The polymerization reactivities, i.e. yield and molecular weight of the polymers, were found to change depending on the structure of the *N*-substituents. The poly(RMI)s bearing a bulky *N*-substituent were confirmed to be semiflexible poly(substituted methylene)s which were soluble in many organic solvents, but did not melt below their decomposition temperatures. From thermogravimetric analysis determined in a nitrogen stream, no weight-loss of poly(RMI) was observed at temperature below 300°C, and the maximum decomposition temperature was 400-440°C, except for *N*-*tert*-alkyl substituted derivatives which decomposed at 240-280°C via a two-step reaction.

INTRODUCTION

Maleimide and its *N*-substituted derivatives (RMI) are well-known to polymerize in spite of a 1,2-disubstituted ethylenic structure [1-9]. Thermal properties of the maleimide polymers and copolymers have also attracted great attentions, e.g. excellent thermal stability of poly(*N*-phenyl maleimide) [10-11].

Recently, we have found that dialkyl fumarates with a bulky ester alkyl group such as *tert*-butyl or isopropyl show high polymerization reactivities in the studies on synthesis of poly(substituted methylene)s from maleic and fumaric derivatives [12-16]. The mutual termination between these rigid polymer radicals was considered to be less occuring owing to bulkiness of the substituents, resulting in the increase of the overall polymerization reactivity. Moreover, it was confirmed by the observed ESR spectra of the propagating polymer radicals under usual polymerization conditions [16]. In polymerization of RMI, it was expected that the *N*-substituent influenced its polymerization reactivity as well as dialkyl fumarates. Therefore, RMIs bearing various *N*-substituents were prepared and polymerized, and then the thermal property of poly(RMI)s was investigated in this paper.

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EXPERIMENTAL

RMIs were prepared and purified according to the methods reported in literature [17-19]. Other reagents were used after ordinary purifications.

Polymerizations were carried out in the presence of 2,2'-azobisisobutyronitrile (AIBN) as an initiator in a sealed glass tube. After polymerization, the mixture was poured into a large amount of methanol or ethanol to isolate the polymer. Intrinsic viscosity ($[\eta]$) of the polymers was measured in benzene or dimethylformamide (DMF) at 30°C. Number-average molecular weight ($\bar{M}_n$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) at 38°C in tetrahydrofuran (THF) as an eluent, calibrated with standard polystyrenes. Thermogravimetric analysis was carried out in a nitrogen stream with a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Polymerization of RMIs

Radical polymerizations of various RMIs with AIBN in benzene at 60°C were carried out to elucidate the effect of the *N*-substituents on the polymerization reactivity. The yield, $[\eta]$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ are shown in Tab. 1.

RMIs with *n*-butyl or higher *n*-alkyl substituents gave a high molecular weight polymer in a high yield, when compared with less-reactive MI and EMI. tBMI was also found to show a high polymerization reactivity, as shown in Fig. 1, inspite of its bulky substituent. Similar tendency was also observed in the polymerization in dioxane [6]. However, the introduction of bulkier *tert*-alkyl groups such as *tert*-amyl or *tert*-octyl decreased both its polymerization rate and $\bar{M}_n$ [7]. It was resemble to the tendency for polymerization of dialkyl fumarates [15].

The polymers from IPMI and CHMI had a complicated molecular weight distribution (MWD) with large $\bar{M}_w/\bar{M}_n$ values (6.0 and 4.6) as shown in Fig. 2(b) and (c), respectively. The polymer obtained from the polymerization at high monomer concentration at 70°C was found to contain partly less-soluble fraction which increased with a polymerization time, indicating the formation of branched or cross-linked polymer as the result of chain transfer to the polymer. It was also supported from thermal decomposition behavior of the polymers [8].

The polymerization reactivity of RMIs containing a phenyl group in the *N*-alkyl groups was not so high, when they were compared with those from other *N*-alkyl-substituted RMIs. The fact that the reactivity of MBzMI was higher than BzMI was interesting, because the former has a bulkier substituent than the latter. It was found by GPC that poly(BzMI) and poly(MBzMI) with ordinary MWD ($\bar{M}_w/\bar{M}_n$ = 2-3) was formed even in bulk polymerization at 80°C, although they have a benzylic hydrogen atom. In the polymerizations of more sterically hindered RMIs such as DPhMMI and TrMI, their reactivities were lower than that of MBzMI.

The polymerization of PhMI proceeded heterogeneously because of insolubility of poly(PhMI) into benzene similarly as reported. The $[\eta]$ of poly(PhMI) was not so high as those of other RMIs. On the contrary,

Tab. 1 Radical Polymerization of N-Substituted Maleimides in Benzene at 60°C for 5 h$^{a)}$

RMI	R	Yield (%)	$[\eta]^{b)}$ (dL/g)	$\bar{M}_n{}^{c)} \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$
MI	H	34.3	$0.29^{d)}$	$-^{e)}$	$-^{e)}$
EMI	C_2H_5	33.4	$0.24^{d)}$	2.1	2.3
IPMI	$CH(CH_3)_2$	74.0	$0.58^{d)}$	8.8	6.0
nBMI	$\mathrm{+CH_2+_3CH_3}$	78.4	0.76	15.9	2.6
IBMI	$CH_2CH(CH_3)_2$	66.6	0.50	5.9	3.0
sBMI	$CH(CH_3)CH_2CH_3$	70.9	0.53	9.5	2.5
tBMI	$C(CH_3)_3$	82.8	0.68	14.9	2.5
tAMI	$C(CH_3)_2CH_2CH_3$	71.2	0.61	13.0	2.1
CHMI	cyclo-C_6H_{11}	39.1	$0.27^{d)}$	4.3	4.6
nOMI	$\mathrm{+CH_2+_7CH_3}$	$40.1^{f)}$	0.79	17.3	2.0
tOMI	$C(CH_3)_2CH_2C(CH_3)_3$	26.5	0.27	5.0	1.8
DMI	$\mathrm{+CH_2+_{11}CH_3}$	$46.5^{f)}$	0.69	16.2	2.0
ODMI	$\mathrm{+CH_2+_{17}CH_3}$	$44.6^{f)}$	$0.60^{g)}$	17.0	2.0
BzMI	CH_2Ph	20.4	0.13	0.9	2.7
MBzMI	$CH(CH_3)Ph$	47.5	0.30	7.4	2.0
DPhMMI	$CHPh_2$	$20.4^{h)}$	0.12	2.2	1.9
TrMI	CPh_3	$4.9^{i)}$	-	0.3	1.3
PhMI	Ph	78.9	$0.10^{d)}$	$-^{e)}$	$-^{e)}$
2-MPhMI	2-(CH_3)-Ph	27.6	0.17	3.3	1.9
2,6-DMPhMI	2,6-$(CH_3)_2$-Ph	20.4	0.10	1.9	1.6

a) [RMI] = 1.0 mol/L, [AIBN] = 0.005 mol/L. b) In benzene at 30°C. c) By GPC in THF. d) In DMF at 30°C. e) Insoluble. f) Polymerized for 1 h. g) Polymerized for 2 h, yield 67.9 %. h) [DPhMMI] = 0.5 mol/L. i) [TrMI] = 0.2 mol/L.

2-MPhMI and 2,6-DMPhMI were found to polymerize homogeneously in benzene, although the polymer yield decreased owing to the steric hindrance of the *ortho*-methyl groups in the *N*-phenyl substituent. Similar steric interaction was also observed for the other PhMI derivatives bearing some alkyl groups at 2- or 2,6-positions. Furthermore, we have recently found that the alkyl groups on the *N*-phenyl ring influenced importantly on the polymerization reactivity and solubility of the polymers corresponding to the number, position and bulkiness of the substituents [9].

As described above, it was found that RMI with a bulky *N*-substitu-

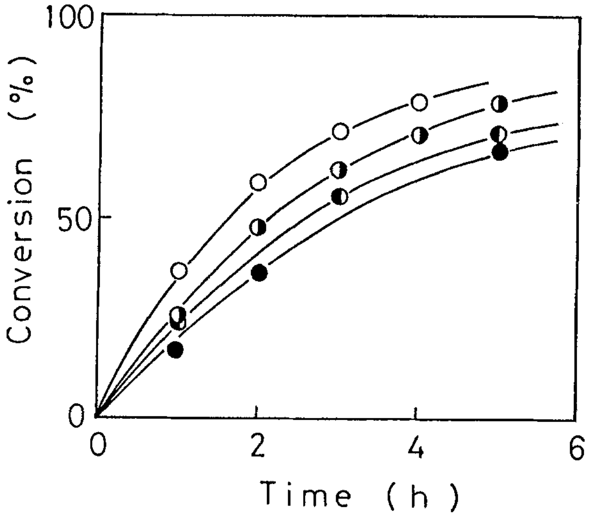


Fig. 1 Radical polymerization of N-butylmaleimides in benzene at 60°C: [RMI]=1.0 mol/L, [AIBN]=0.005 mol/L, (○) tBMI, (◑) nBMI, (◐) sBMI, (●) IBMI.

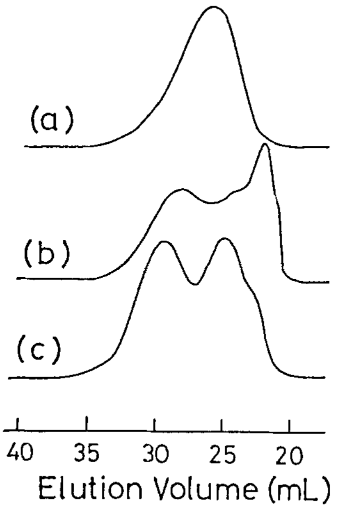


Fig. 2 GPC elution curves of (a) poly(tBMI), (b) poly(IPMI), (c) poly(CHMI).

ent such as *tert*-butyl can polymerize to give a high polymer in a high yield, but the relation between the polymerization reactivity and the bulkiness of the substituents was not observed, as was seen in the polymerization of dialkyl fumarates [16], i.e. the reactivity increased with increasing of bulkiness of the ester substituentsd. The high reactivity of maleimides with a strained five-membered ring may veil the effect of their *N*-substituents.

Poly(RMI) was considered to be a relatively rigid polymer due to an imide ring restricting the rotation of its C-C bond and a bulky substituent to induce slow termination between its polymer radicals. Since an ESR spectrum of the propagating polymer radicals from dialkyl fumarates could be observed [16], the ESR measurement of the polymerization mixture of tBMI in benzene was attempted under irradiation of UV light. A spectrum was observed at a room temperature, but its intensity was not enough to examine further under such a condition.

Characterization of Poly(RMI)s

The poly(RMI)s thus obtained were confirmed by IR and NMR to consist of poly(substituted methylene) structure formed via an opening carbon-to-carbon double bond as shown in Figs. 3 and 4.

All polymers were colorless powder. Poly(MI) and poly(PhMI) were soluble in DMF, dimethyl sulfoxide and nitrobenzene, and insoluble in other many organic solvents. The other poly(RMI)s were soluble in benzene, chloroform and THF except for poly(EMI) which was insoluble in benzene. Poly(CHMI) and poly(IPMI) were partly insoluble as stated before.

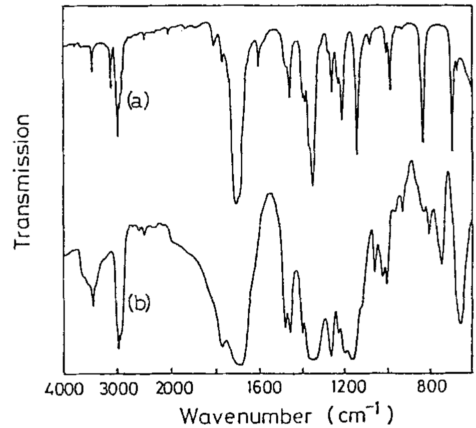


Fig. 3 IR spectra of (a) tBMI and (b) poly(tBMI).

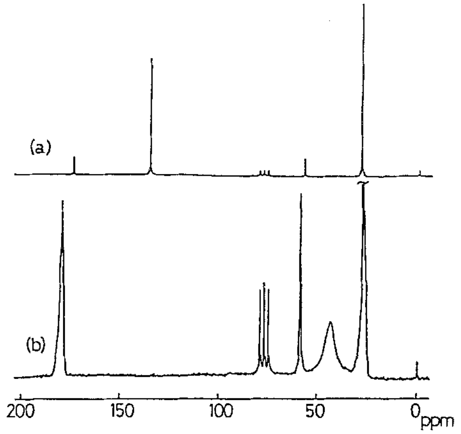


Fig. 4 ^{13}C NMR spectra of (a) tBMI and (b) poly(tBMI).

A transparent thin-film was obtained by casting from the solution of poly(RMI). The polymers bearing a higher alkyl chain, i.e. poly(nBMI), poly(nOMI) and poly(DMI) gave a tough film. However, the film from the polymers with a bulky *N*-alkyl group such as *tert*-butyl or *sec*-butyl was very brittle. The glass transition temperature (T_g) was determined by differential scanning calorimetry; 200, 180 and 115°C for poly(IBMI), poly(nBMI) and poly(DMI), respectively. This observation that the T_g decreased when a higher alkyl chain was introduced in the *N*-substituents was in agreement with that reported [20]. No T_g was observed for poly(RMI)s bearing *tert*-alkyl substituents below its decomposition temperature.

Thermogravimetric Analysis of Poly(RMI)s

To examine thermal stability of poly(RMI)s, thermogravimetric analysis was carried out in a nitrogen stream. In Fig. 5, the thermograms obtained are shown, and the initial decomposition temperature (T_{init}), the maximum decomposition temperature (T_{max}) and the residue at 500°C are summarized in Tab. 2.

The thermal decomposition of poly(RMI) proceeded via a one-step reaction and no weight-loss was observed below ca. 300°C, except for polymers bearing *N*-*tert*-alkyl groups. Especially, poly(CHMI), poly(ODMI), poly(PhMI) and poly(2,6-DMPhMI) showed excellent thermal stability (T_{init} > 360°C, T_{max} ~ 430°C). The residue at 500°C of poly(*n*-alkylmaleimide)s were lower than those of the polymers containing a *tert*-alkyl or phenyl group in the *N*-substituents.

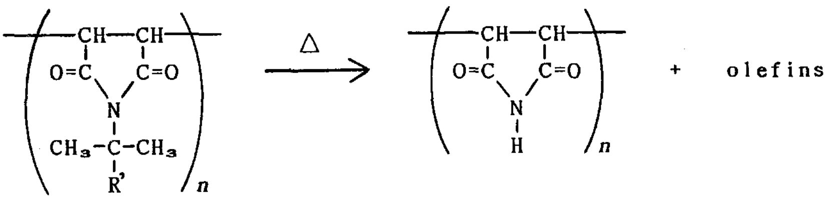
The decomposition of poly(tBMI) and the other poly(RMI)s with *tert*-alkyl groups proceeded via a two-step reaction [5,7], i.e. the first started at 240-280°C and the second decomposition occured over 400°C. Similar two-step decompositions were already observed on poly(*tert*-alkyl fumarate)s [14-16] and poly(*tert*-alkyl methacrylate)s [21-23]. The first weight-loss cor-

Tab. 2 Thermogravimetric Analysis for Poly(N-substituted maleimide)s$^{a)}$

Polymer	T_{init} (°C)	T_{max} (°C)	Residue at 500°C (%)
Poly(IPMI)	349	403	2.2
Poly(nBMI)	291	402	1.8
Poly(IBMI)	347	413	1.4
Poly(sBMI)	284	400	4.2
Poly(tBMI)	281	328, 432$^{b)}$	26.0
Poly(tAMI)	255	310, 426$^{b)}$	23.4
Poly(CHMI)	362	430	4.6
Poly(tOMI)	242	285, 430$^{b)}$	16.8
Poly(ODMI)	368	445	5.2
Poly(BzMI)	348	408	22.6
Poly(MBzMI)	338	412	12.3
Poly(TrMI)	227	308	33.7
Poly(PhMI)	364	422	21.5
Poly(2,6-DMPhMI)	393	435	11.3
Poly(MI)$^{c)}$	380	426	41.3

a) Heating rate of 10°C/min in a nitrogen stream. b) Decomposed via a two-step reaction. c) Prepared by olefin elimination from poly(tBMI).

responds to the elimination of olefins from the side chain to result in the formation of poly(MI) as shown in a following scheme;



R' = CH_3, CH_2CH_3, $CH_2C(CH_3)_3$

The gaseous material formed by heating of poly(tBMI) at 320°C in vacuum was found to be isobutene by NMR and gas chromatography. It was also confirmed that the corresponding olefins evolved from poly(tAMI) and poly(tOMI) [9]. The high molecular weight poly(MI) isolated after thermal treatment of poly(tBMI) also showed high thermal stability. Poly(TrMI) had the lowest T_{init} among the all poly(RMI) examined and its weight-loss curve was complicated.

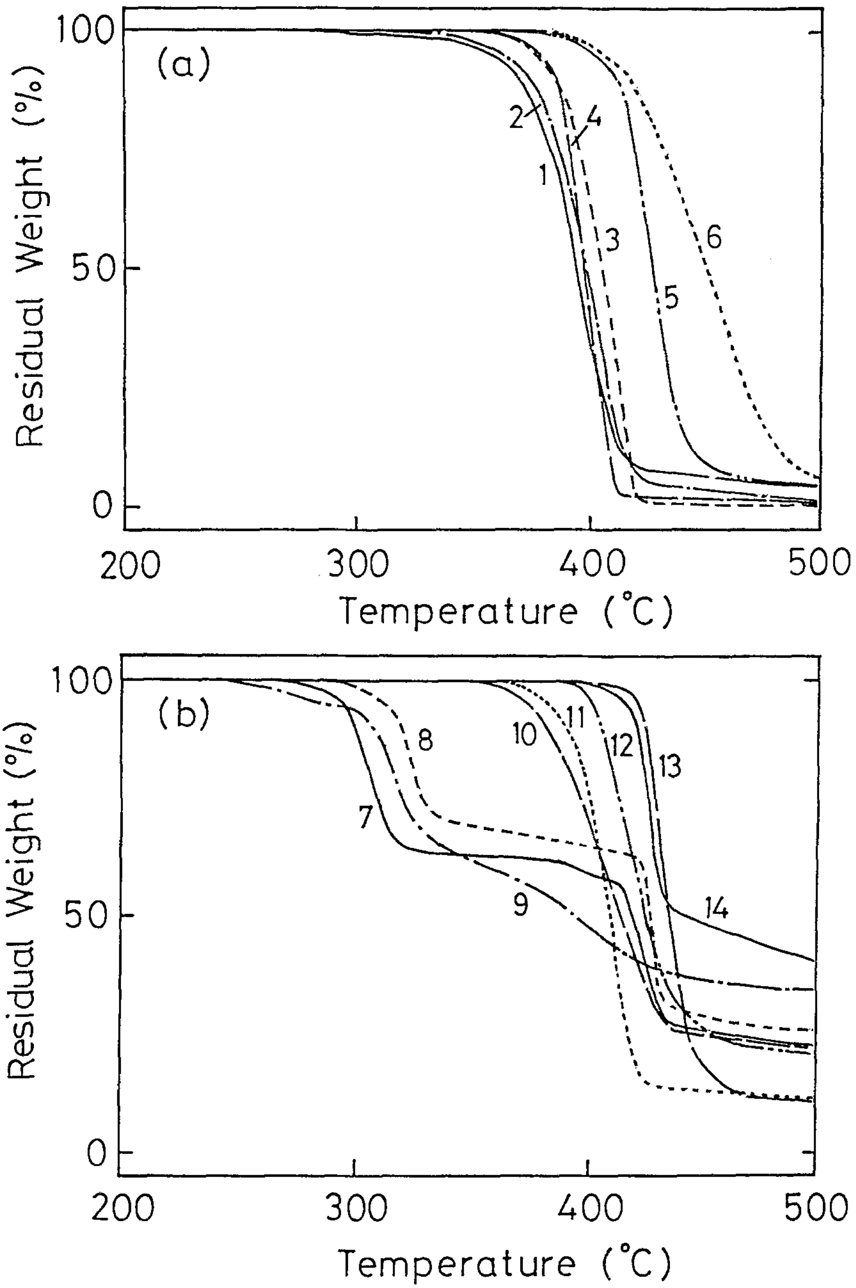


Fig. 5 Thermogravimetric analysis in a nitrogen stream with a heating rate of 10°C/min: (1) poly(sBMI), (2) poly(nBMI), (3) poly(IBMI), (4) poly(IPMI), (5) poly(CHMI), (6) poly(ODMI), (7) poly(tAMI), (8) poly(tBMI), (9) poly(TrMI), (10) poly(BzMI), (11) poly(MBzMI), (12) poly(PhMI), (13) poly(2,6-DMPhMI), (14) poly(MI).

Thus, the poly(RMI)s with primary and secondary alkyl groups as *N*-substituents were found to show high thermal stability as well as poly-(PhMI). As RMI can copolymerize with many vinyl monomers, the thermal properties of vinyl polymers will be improved without imparing the solubility [8].

REFERENCES

1. P.O. Tawney, R.H. Snyder, R.P. Conger, K.A. Leibbrand, C.H. Stiteler and A.R. Williams, *J. Org. Chem.*, 26, 15 (1961).
2. R.C.P. Cubbon, *Polymer*, 6, 419 (1965).
3. M. Yamada and I. Takase, *Kobunshi Kagaku*, 22, 626 (1965); M. Yamada, I. Takase and T. Mishima, *ibid.*, 26, 393 (1969).
4. T. Oishi and N. Kimura, *Kobunshi Ronbunshu*, 33, 685 (1976); T. Oishi and H. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, 16, 129 (1978).
5. T. Otsu, A. Tatsumi and A. Matsumoto, *J. Polym. Sci., Part C: Polym. Lett.*, 24, 113 (1986).
6. T. Otsu and A. Matsumoto, *Acta Polymerica*, 39, 5 (1988).
7. A. Matsumoto, T. Kubota, A. Tatsumi and T. Otsu, in preparation.
8. A. Matsumoto, T. Kubota, S. Mori and T. Otsu, in preparation.
9. A. Matsumoto, T. Kubota and T. Otsu, in preparation.
10. M. Urushizaki, H. Aida and S. Matsui, *Kobunshi Kagaku*, 27, 474 (1970); H. Aida, M. Urushizaki, H. Maegawa and S. Okazaki, *Kobunshi Ronbunshu*, 45, 333 (1988).
11. J.M. Barrales-Rienda, J.I.G. De la Campa and J.G. Ramos, *J. Macromol. Sci.-Chem.*, A11, 267 (1977).
12. T. Otsu, O. Ito, N. Toyada and S. Mori, *Makromol. Chem., Rapid Commun.*, 2, 725 (1981).
13. T. Otsu, H. Minai, N. Toyoda and T. Yasuhara, *Makromol. Chem., Suppl.*, 12, 133 (1985).
14. T. Otsu, T. Yasuhara, K. Shiraishi and S. Mori, *Polym. Bull.*, 12, 449 (1984).
15. T. Otsu, K. Shiraishi, A. Matsumoto, T. Yasuhara, N. Amaya and S. Mori, *Polym. Commun.*, 26, 367 (1985).
16. T. Otsu, T. Yasuhara and A. Matsumoto, *J. Macromol. Sci.-Chem.*, A25, 537 (1988).
17. N.B. Mehta, A.R. Phillips, F.F. Lui and R.E. Brooks, *J. Org. Chem.*, 25, 1012 (1960).
18. L.E. Colleman, Jr., J.F. Bork and H. Donn, Jr., *J. Org. Chem.*, 24, 185 (1959).
19. A.L. Schwartz and L.M. Lerner *J. Org. Chem.*, 39, 21 (1974).
20. J.M. Barrales-Rienda, J.G. Ramos and M.S. Chaves, *Bri. Polym. J.*, 9, 6 (1977).
21. D.H. Grant and N. Grassie, *Polymer*, 1, 445 (1960).
22. J.R. Schaefgen and I.M. Sarasohn, *J. Polym. Sci.*, 58, 1049 (1962).
23. H. Ito and M. Ueda, *Macromolecules*, 21, 1475 (1988).

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