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Synthesis and characterization of poly(*N-tert*-alkylmaleimide)s

2. Synthesis of high molecular weight polymaleimide by thermolysis of poly(*N-tert*-alkylmaleimide)s

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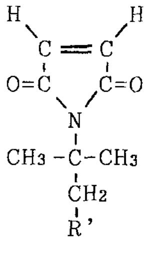
ABSTRACT

N-tert-Butylmaleimide (tBMI), *N-tert*-amylmaleimide (tAMI) and *N-tert*-octylmaleimide (tOMI) were polymerized in the presence of a radical initiator to give high molecular weight polymers. The polymerization reactivity was found to depend on the bulkiness of the *N*-substituent. From thermogravimetric analysis of the polymers obtained, it was revealed that these polymers thermally decomposed via a two-step mechanism, i.e. elimination of olefins at the first step and decomposition of the resulting *N*-unsubstituted polymaleimide (poly(MI)) at the second step. The high molecular weight poly(MI) was isolated by thermolysis of poly(tBMI), poly(tAMI) and poly(tOMI) with elimination of isobutene, 2-methyl-1-butene and 2-methyl-2-butene, and 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene, respectively. It was also confirmed that the resulting poly(MI) had excellent thermal stability.

Introduction

The homo- and copolymers from *N*-phenylmaleimides and its derivatives have excellent thermal stability. In previous papers [1-4], we have reported on radical polymerization of *N*-alkylmaleimides and *N*-(alkyl-substituted phenyl)maleimides with various substituents and on thermal stability of the resulting polymers. These thermally stable polymaleimides are expected to be applied to various fields. For example, Turner et al. reported a new polymer of a high glass transition temperature as a deep-UV resist material, i.e. phenolic copolymers based on *N*-(*p*-hydroxyphenyl)maleimide [5], from which high resolution images exhibiting no deformation on heating to 200°C was obtained in either positive and negative tone by protection of the phenolic group with a *tert*-butoxycarbonyl group [6,7].

In preceding paper [8], *N-tert*-butylmaleimide (tBMI) was observed to polymerize quite easily in the presence of a radical initiator. It has been already found that poly(tBMI) is available for preparation of a high molecular weight polymaleimide (poly(MI)) by olefin elimination from the side chain [4]. In this paper, polymerization reactivity of *N-tert*-alkylmaleimides (tRMI) as shown in Scheme I and thermal decomposition behavior of the resulting poly(tRMI)s are investigated.



R' = H(tBMI)
CH_3 (tAMI)
$C(CH_3)_3$ (tOMI)

tRMI

Scheme I

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Experimental

tRMIs were prepared from maleic anhydride and a corresponding *tert*-alkylamine by the method described in previous papers [1-3]. *N*-*tert*-Amylmaleimide (tAMI) (*N*-(1,1-dimethylpropyl)maleimide): yield 24%, bp 82°C/9 mmHg, ^{13}C NMR($CDCl_3$) δ 172.5(C=O), 133.8(C=C), 60.8($-\overset{|}{\underset{|}{C}}-$), 33.0($CH_2$), 26.9($CH_3$), 25.6($CH_3$); ^{1}H NMR($CDCl_3$) δ 6.43(s, 2H, CH=), 1.87(q, J = 7.2 Hz, 2H, CH_2), 1.52(s, 6H, CH_3), 0.77(t, J = 7.2 Hz, 3H, CH_3). *N*-*tert*-Octylmaleimide (tOMI) (*N*-(1,1,3,3-tetramethylbutyl)maleimide): yield 39%, bp 91°C/5 mmHg, mp 54.5°C, ^{13}C NMR($CDCl_3$) δ 172.3(C=O), 133.9(C=C), 60.5($-\overset{|}{\underset{|}{C}}-$), 50.6($CH_2$), 31.3($-\overset{|}{\underset{|}{C}}-$), 30.9($CH_3$), 29.8($CH_3$); ^{1}H NMR($CDCl_3$) δ 6.48(s, 2H, CH=), 1.86(s, 2H, CH_2), 1.62(s, 6H, CH_3), 0.91(s, 9H, CH_3).

Polymerization was carried out with 2,2'-azobisisobutyronitrile (AIBN) or dimethyl 2,2'-azobisisobutyrate (MAIB) an a similar way to those in previous papers. The polymers were purified by reprecipitation.

Gel permeation chromatography (GPC) was performed in THF at 38°C, and number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calibrated with standard polystyrenes. Intrinsic viscosity ([η]) was measured in benzene for poly(tRMI)s and in dimethylformamide (DMF) for poly(MI) at 30°C. Thermogravimetric analysis (TGA) was carried out with ca. 1.5 mg of a polymer sample in a nitrogen stream with a heating rate of 10°C/min.

Results and Discussion

Radical polymerization reactivity of tRMIs

Radical polymerization of tRMIs was carried out with AIBN in benzene at 60°C. The results of the polymerization are shown in Fig. 1 and Tab. I. It was found that all tRMIs polymerized readily to give a high molecular weight polymer as well as other *N*-alkylmaleimides such as *N*-*n*-butylmaleimide (nBMI) [1]. However, the polymerization reactivity, i.e. polymerization rate, [η] and $\bar{M}_n$ of the polymer were observed to decrease, as the bulkiness of the alkyl substituents increased, especially in the case of polymerization of tOMI bearing the bulkiest *N*-substituent. It was different from the fact that the introduction of higher *n*-alkyl substituents such as *n*-octyl and octadecyl groups did not interfere the polymerization at all [1,9]. It may be interpretted with the steric hindrance by the introduction of a bulky substituent in the propagation. On the other hand, *N*-unsubstituted maleimide (MI) showed a low polymerization reactivity, compared with other maleimides [1].

Tab. I Radical Polymerization of tRMIs in Benzene[a]

tRMI	*N*-Substituent	Yield (%)	[η][b] (dL/g)	$\bar{M}_n$[c] x 10^{-4}	$\bar{M}_w/\bar{M}_n$[c]
tBMI	*tert*-butyl	82.8	0.68	14.9	2.50
tAMI	*tert*-amyl	71.2	0.61	13.0	2.14
tOMI	*tert*-octyl	26.5	0.27	4.95	1.83
nBMI	*n*-butyl	78.4	0.76	15.9	2.55
MI	none	34.3	0.29[d]	-	-

[a] [tRMI] = 1.0 mol/L, [AIBN] = 5 x 10^{-3} mol/L at 60°C for 5 h. [b] In benzene at 30°C. [c] By GPC in THF. [d] In DMF at 30°C.

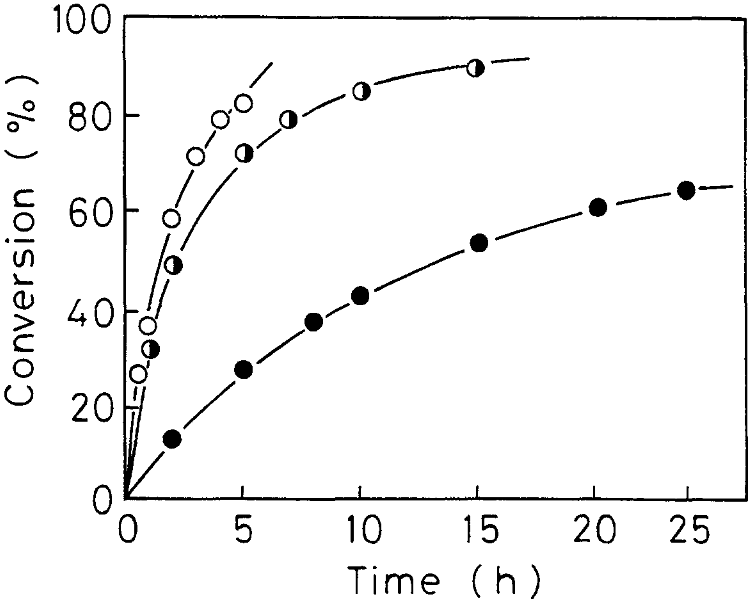


Fig. 1 Time-conversion curves for radical polymerization of tRMIs in benzene at 60°C, [tRMI] = 1 mol/L, [AIBN] = 5 x 10^{-3} mol/L: (○) tBMI, (◑) tAMI, (●) tOMI.

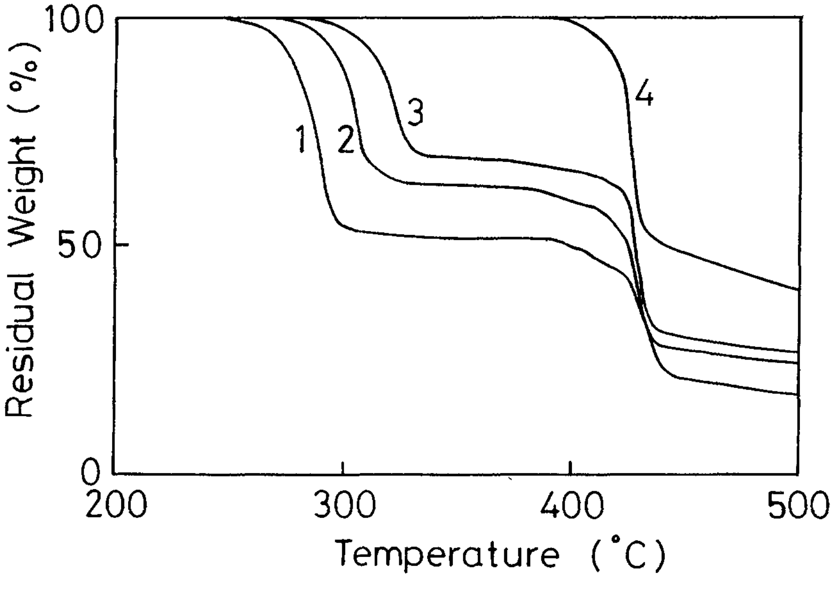


Fig. 2 Thermogravimetric analysis of poly(tRMI)s in a nitrogen stream with a heating rate of 10°C/min: (1) poly(tOMI), (2) poly(tAMI), (3) poly(tBMI), (4) poly(MI) derived from poly(tBMI).

Tab. II Results for Thermogravimetric Analysis of Poly(tRMI)s[a]

Polymer	First-step decomposition				Second-step decomposition		
	T_{init} (°C)	T_{max} (°C)	Weight loss(%) found	Weight loss(%) calcd.[b]	T_{init} (°C)	T_{max} (°C)	Residue at 500°C (%)
Poly(tBMI)	281	328	34.1	36.6	386	432	26.0
Poly(tAMI)	255	310	39.3	42.0	385	426	23.4
Poly(tOMI)	242	285	49.1	53.6	388	430	16.8
Poly(MI)[c]	-	-	-	-	388	426	41.3

[a] In a nitrogen stream with a heating rate of 10°C/min. [b] Elimination of olefins from the side chain. [c] Prepared by thermolysis of poly(tBMI) (see text).

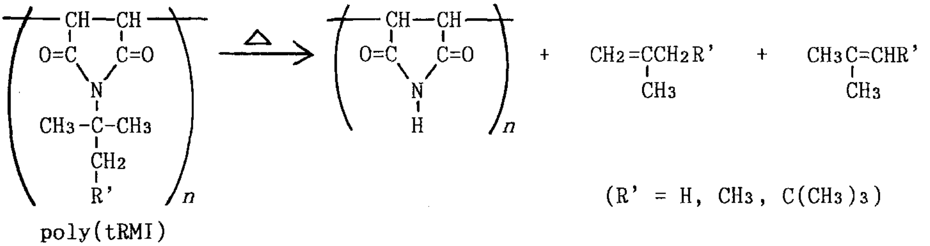
Thermal decomposition of the polymers

As reported in previous communication [4], poly(tBMI) can be converted thermally into poly(MI) with elimination of isobutene. Therefore, the thermal decomposition behaviors of poly(tRMI)s including poly(tBMI) were investigated by TGA.

Fig. 2 shows the thermograms for poly(tBMI), poly(tAMI) and poly(tOMI) in a nitrogen stream. The decomposition behaviors of poly(tRMI)s were different from the other polymaleimides bearing primary and secondary alkyl or phenyl substituents, e.g. poly(*N*-*n*-alkylmaleimide)s, poly(*N*-cyclohexylmaleimide) and poly(*N*-phenylmaleimide)s, which showed very high performance for thermal stability [1-3]. As seen in the figure, all poly(tRMI)s decomposed via a two-step mechanism. The initial decomposition temperature (T_{init}) and the maximum decomposition temperature (T_{max}) are summarized in Tab. II.

The first-step decomposition of poly(tBMI) strarted at 281°C and the maximum rate showed at 328°C, and the second started at 386°C. The similar two-step decomposition was also observed for poly(tAMI) and poly(tOMI). The T_{init} and T_{max} of the first-step decomposition were found to decrease as the *N*-substituent was larger. The all second-step decomposition started from 385-388°C and the T_{max} were 426-432°C, agreeing well with each other.

The weight loss of the polymers after the first-step decomposition were 34.1, 39.3 and 49.1% for poly(tBMI), poly(tAMI) and poly(tOMI), respectively, agreeing with the theoretical values which were calculated based on the quantitative elimination of olefins yielding poly(MI) (Scheme II).



Scheme II

The olefin elimination, i.e. two-step decomposition was also observed for not only homopolymers, but also copolymers of tRMI with vinyl monomers. In the thermogram of alternating copolymer of tBMI with styrene [3], the weight-loss started at 292° C, and T_{max} were observed at 375 and 411° C.

Similar thermal decompositions accompanying olefin elimination from the side chain of the polymer have been also reported for polymers bearing *tert*-alkoxycarbonyl or *tert*-alkoxycarbonyloxy groups, e.g. poly(di-*tert*-alkyl fumarate)s [10-13], poly(*tert*-butyl methacrylate) [14-16], poly(1,1-dimethylbenzyl methacrylate) [17], poly(*tert*-butyl acrylate) [18], poly(*N*-(*p*-*tert*-butoxycarbonyloxyphenyl)maleimide) [5], poly(*4*-*tert*-butoxycarbonyloxystyrene) [6,7] and poly(vinyl *tert*-butyl carbonate) [19,20].

Synthesis of high molecular weight poly(MI)

The preparation and isolation of high molecular weight poly(MI) by thermolysis of poly(tRMI) with olefin elimination was carried out in vacuum on heating at 280-320° C. The results are shown in Tab. Ⅲ. The colorless and powdery polymers were recovered quantitatively in the all cases. The reaction at the temperature over 320° C for a long period induced coloration of the polymer recovered.

The generated gaseous material from poly(tBMI) was confirmed to be isobutene by gas chromatography and NMR spectroscopy. The formation of poly(MI) was confirmed directly from the ^{13}C NMR and IR spectra. The peak of carbonyl and methine carbons were detected at δ 178 and 40, respectively, but no absorption of *tert*-alkyl groups were observed in the spectrum of poly(MI) as shown in Fig. 3(a). In the IR spectrum (Fig. 3(b)), the absorbance of the *N*-*tert*-alkyl groups disappered and was replaced by that of the N-H group. These spectra were identical to those of poly(MI) which were prepared by polymerization. When the reaction temperature was risen over 350° C, poly(MI) was not isolated because of further decomposition of the resulting poly(MI).

When poly(tAMI) was heated in vacuum at 300° C, the evolution of 2-methyl-1-butene and 2-methyl-2-butene was observed, and a molar ratio of the olefins was determined to be 48 to 52 from peak intensity of the olefinic protons (δ4.66-4.70 for $C\underline{H}_2=C(CH_3)CH_2CH_3$ and δ5.15-5.21 for $(CH_3)_2C=C\underline{H}CH_3$) in the ^1H NMR spectrum (Fig. 4). Any other gaseous products were not detected in the spectrum. Similar results were obtained from thermolysis of poly(tOMI) at 280° C, i.e. evolution of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (77:23 in a molar ratio) was detected, indicating de-

Tab. Ⅲ Synthesis of Poly(MI) by Thermolysis of Poly(tRMI)s[a]

Precursor[b]			Temp.	Yield (g)		$[\eta]^e$
Poly(tRMI)	$\bar{M}_n{}^c \times 10^{-4}$	$[\eta]^d$(dL/g)	(° C)	found	calcd.	(dL/g)
Poly(tBMI)	110.1	-	320	0.064	0.0634	0.347
Poly(tAMI)	94.1	3.13	300	0.063	0.0580	0.667
Poly(tOMI)	72.2	2.36	280	0.050	0.0464	0.795

[a] Poly(tRMI) (0.1 g) was heated in vacuum for 2 h. [b] Polymerized in bulk with MAIB (1×10^{-3} mol/L) at 60° C for 12 h. [c] By GPC. [d] In benzene at 30° C. [e] Poly(MI) in DMF at 30° C.

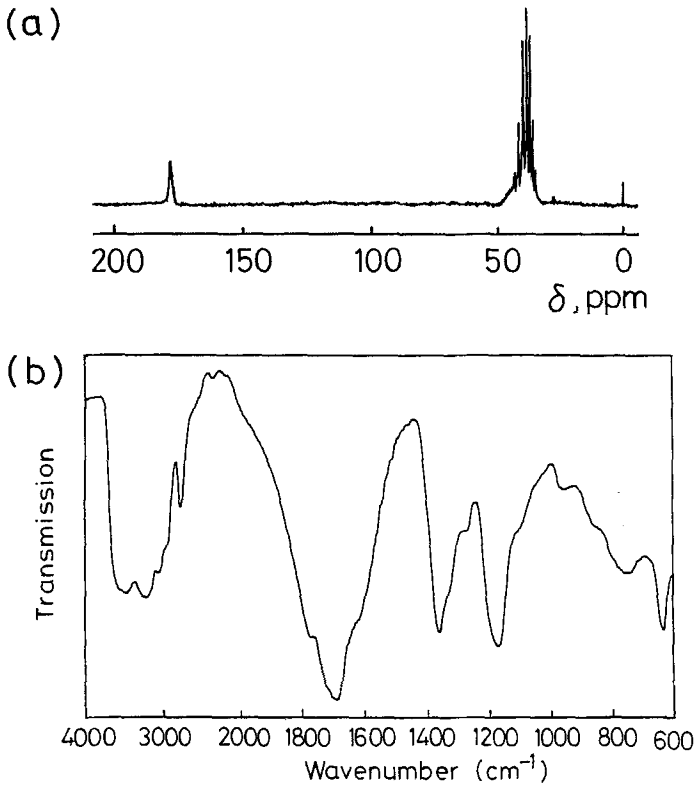


Fig. 3 ^{13}C NMR spectrum in DMSO-d_6 (a) and IR spectrum (b) of poly(MI) prepared by thermolysis of poly(tBMI) at 320°C for 2 h.

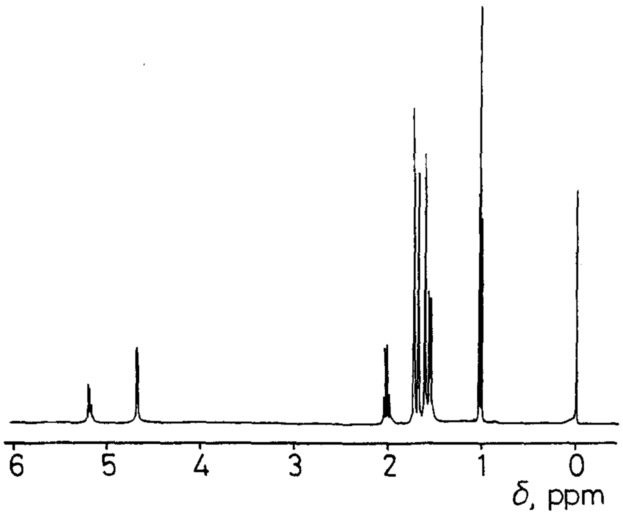


Fig. 4 ^{1}H NMR spectrum of gaseous materials evolved from poly(tAMI) by heating at 300°C.

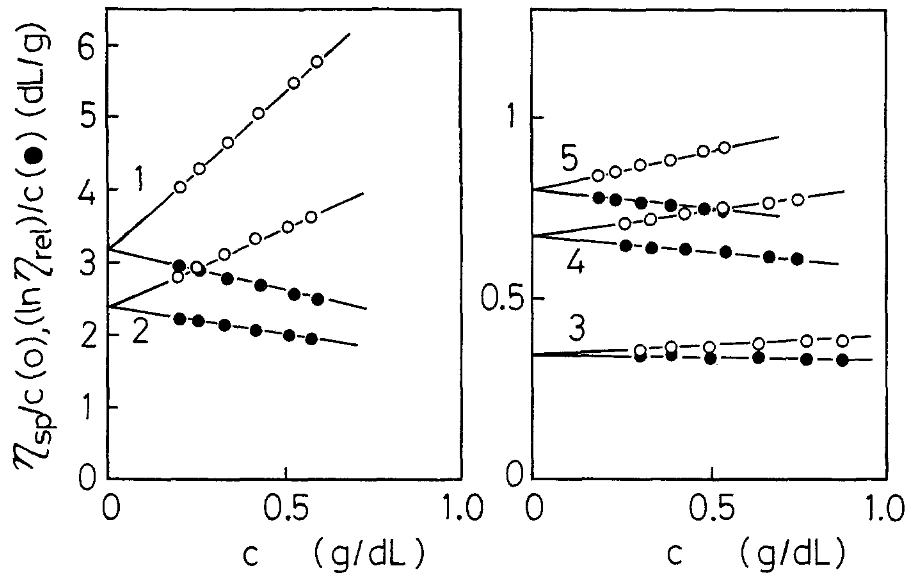


Fig. 5 Intrinsic viscosity of poly(tRMI) in benzene and poly(MI) in DMF at 30°C: (1) poly(tAMI), (2) poly(tOMI), (3) poly(MI) from poly(tBMI), (4) poly(MI) from poly(tAMI), (5) poly(MI) from poly(tOMI).

Tab. IV Solubility of Poly(tRMI)s and Poly(MI)[a]

Polymer	DMF	DMSO	Nitro-benzene	Ben-zene	THF	$CHCl_3$	Ace-tone	*n*-Hex-ane
Poly(tBMI)	sw	i	sw	s	s	s	s	i
Poly(tAMI)	i	i	sw	s	s	s	i	i
Poly(tOMI)	i	i	i	s	s	s	i	s
Poly(MI)[b]	s	s	i	i	i	i	i	i

[a] s: soluble , sw: swelling, i: insoluble. [b] Prepared from poly(tRMI).

pressing of the formation of an internal olefin.

As shown in Tab. III and Fig. 5, poly(MI) obtained by thermolysis was found to have a larger $[\eta]$ value, compared with that prepared from polymerization (Tab. I). These poly(MI)s prepared from poly(tRMI)s were considered to have a high molecular weight more than 10^5. However, the scission of the main chain might also occur during the reaction, because the molecular weight of these poly(MI)s was lower than those of the precursors ($\bar{M}_n \sim 10^6$). The increase in the reaction temperature induced more significantly the decrease in the molecular weight of the resulting poly(MI).

In Tab. IV, comparison of the solubility of poly(tRMI)s and the resulting poly(MI) are summarized. Poly(MI) prepared by the olefin elimination was soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and in soluble in other many organic solvents and water, identical to the solubility of poly(MI) prepared by polymerization. Poly(MI) did not melt and not any transition temperature by differential scanning calorimetry below its decomposition temperature. It was confirmed to have high thermal stability, i.e. T_{init} and T_{max} were 388 and 426°C, respectively, and the residue at 500°C was 41.3% (Fig. 2 and Tab. II).

This procedure via thermolysis of poly(tRMI) will be a new useful route for the synthesis of high molecular weight poly(MI). The difference in solubility between the poly(tRMI) as a precursor and the resulting poly(MI) may open a possibility of application to thermally stable resist materials with aid of acid-catatalyzed thermolysis [21].

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