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

1. Radical polymerization of *N-tert*-butylmaleimide leading to a less-flexible poly(substituted methylene)

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ABSTRACT

N-tert-Butylmaleimide (tBMI) polymerized readily in the presence of a radical initiator in spite of its bulky *N*-substituent to give a high molecular weight and less-flexible poly(substituted methylene). From kinetic investigation for the polymerization of tBMI with 2,2'-azobisisobutyronitrile (AIBN) in benzene, it was revealed that the rate of polymerization (R_p) was expressed as $R_p = k\,[\text{AIBN}]^{0.51}[\text{tBMI}]^{1.4}$, and the overall activation energy was 99.6 kJ/mol. The high polymerization of tBMI was assumed to result from the decrease in the rate of bimolecular termination between rigid polymer radicals bearing a bulky substituent. The flexibility of the polymer chain was examined by the viscometric and light scattering methods, and the effect on the polymerization reactivity was discussed.

Introduction

In previous papers [1-5], we have reported that dialkyl fumarates (DRF), *N,N,N',N'*-tetraalkylfumaramides and alkyl *N,N*-diethylfumaramates polymerize with a radical initiator to give high molecular weight polymers consisting of rigid poly(substituted methylene)s, in which all carbons of the main chain are substituted.

Maleimide and its *N*-substituted derivatives, one of 1,2-disubstituted ethylenes, are well-known to polymerize easily. We have already reported on the polymerization of *N*-alkylmaleimides or *N*-(alkyl-substituted phenyl)-maleimides bearing various substituents, and on the thermal properties of the polymers [6-9]. The polymaleimides with a bulky group as *N*-substituent were expected to have a relatively rigid conformation [10,11], as well as poly(DRF) [3-5]. The formation of less-flexible vinyl polymers with bulky substituents influences polymerization behavior, i.e. it decreases the bimolecular termination rate, resulting in easy observation of an ESR spectrum of the propagating polymer radical because of the increasing radical concentration at a stationary state, as observed in the polymerization of DRF [3].

As reported in previous papers [6,7], *N-tert*-butylmaleimide (tBMI) had a high polymerization reactivity, and a benzene-soluble and high molecular weight polymer was obtained from polymerization in bulk or in benzene with a high yield. Moreover, poly(tBMI) is interesting as a precursor for the synthesis of *N*-unsubstituted polymaleimide by thermolysis as will be described in the subsequent paper.

In this paper, radical polymerization of tBMI is investigated kinetically in detail, and the polymer chain flexibility estimated from the viscosity and light scattering data in its dilute solution is discussed in the view of the effects on the polymerization reactivity.

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Experimental

tBMI was prepared according to the method in literature [12]. Yield 30%, bp 54°C/3.5 mmHg, d^{25} 1.061, ^{13}C NMR(CDCl$_3$) δ 171.1(C=O), 133.3(C=C), 56.2(-$\overset{|}{C}$-), 28.1(CH$_3$); ^1H NMR(CDCl$_3$) δ 6.55(s, 2H, CH=), 1.55(s, 9H, CH$_3$). The purity of tBMI was checked by NMR spectroscopy and high performance liquid chromatography. Other reagents and solvents were purified according to ordinary methods.

Polymerization was carried out in the presence of 2,2'-azobisisobutyro-nitrile (AIBN) in a sealed glass tube. After a given time, the polymeriza-tion mixture was poured into a large amount of methanol to precipitate the polymer. The yield of polymers dried was determined gravimetrically.

Intrinsic viscosity ([η]) was measured in benzene at 30°C by using an Ubbelohde viscometer. The number-average molecular weight ($\bar{M}_n$) was deter-mined in toluene at 38°C with a membrane osmometer (Knauer). Light scat-tering measurement was performed with a Union Giken LS-601 spectrometer. The specific refractive index increment of poly(tBMI) was 0.107 mL/g in tetrahydrofuran (THF). Gel permeation chromatography (GPC) was carried out in THF at 38°C, and number- and weight-average molecular weights ($\bar{M}_{n,GPC}$ and $\bar{M}_{w,GPC}$) were calibrated with standard polystyrenes.

Results and Discussion

Radical polymerization of tBMI

Radical polymerization of tBMI was carried out in benzene or in bulk with AIBN. As shown in Tab. I, polymerization of tBMI proceeded rapidly in spite of the 1,2-disubstituted ethylenic structure and its bulky N-substi-tuent, as well as other N-substituted maleimides [7].

The time-conversion relations of polymerization of tBMI was examined at 40-80°C. The results are shown in Fig. 1. The overall activation energy for the polymerization was calculated to be 99.6 KJ/mol from an Arrhenius

Tab. I   Results of Radical Polymerization of tBMI and Determination of Intrinsic Viscosity and Molecular Weights of Poly(tBMI) Obtained

Polymerization[a]			VIS[b]	GPC[c]		OS[d]		LS[e]
Temp. (°C)	Time (h)	Yield (%)	[η] (dL/g)	$\bar{M}_{n,GPC}$ x 10^{-5}	$\dfrac{\bar{M}_{w,GPC}}{\bar{M}_{n,GPC}}$	$\bar{M}_n$ x 10^{-5}	A_2x10^4 (mL/g^2)	$\bar{M}_w$ x 10^{-5}
80	0.3	57.8	0.367	0.752	1.88	1.09	4.94	1.62
70	0.75	62.1	0.487	0.938	1.94	1.76	4.00	2.92
50	7.0	51.1	0.558	2.07	1.65	2.15	3.32	3.81
50[f]	6.0	54.8	0.937	3.21	2.06	2.45	2.75	3.71
30[f]	161	49.8	3.23	12.0	2.43	11.3	1.47	18.1

[a] [tBMI] = 1 mol/L, [AIBN] = 5 x 10^{-3} mol/L in benzene.   [b] In benzene at 30°C.   [c] Gel permeation chromatography in THF, calibrated with standard polystyrenes.   [d] Membrane osmometry in toluene.   [e] Light scattering in THF.   [f] Polymerized in bulk, [AIBN] = 3.7 x 10^{-2} mol/L.
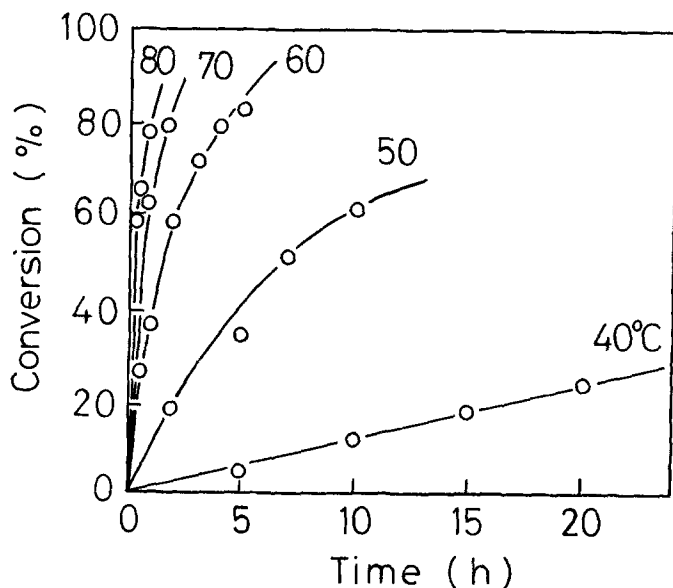
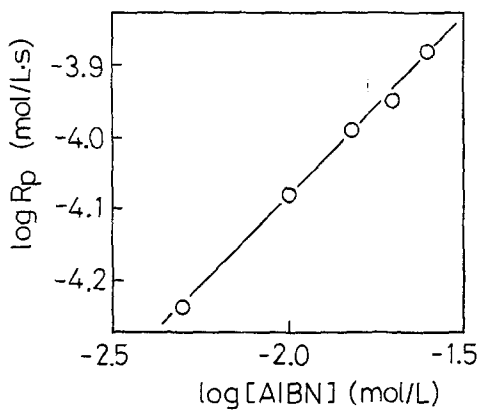Fig. 1 Time-conversion relations for radical polymerization of tBMI in benzene at various temperatures, [tBMI] = 1 mol/L, [AIBN] = 5 x 10⁻³ mol/L.

Fig. 2 The dependence of AIBN concentration on R_p for polymerization of tBMI in benzene at 60°C, [tBMI] = 0.69 mol/L.

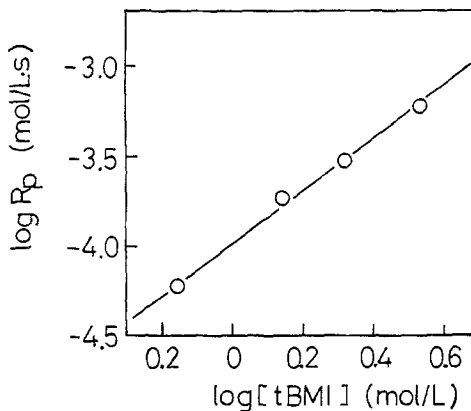Fig. 3 The dependence of tBMI concentration of R_p for polymerization of tBMI in benzene at 60°C, [AIBN] = 5 x 10⁻³ mol/L.

plot of the polymerization rate (R_p), which was determined from the each initial slope of the curves in Fig. 1. This value was similar to those for the other maleimides [13,14].

The dependence of the concentrations of tBMI and AIBN on R_p was also determined. The results obtained are shown in Figs. 2 and 3, from which the slope of the lines was determined to be 0.51 and 1.4, respectively. As a result, the R_p was expressed as follows: $R_p = k[\text{AIBN}]^{0.51}[\text{tBMI}]^{1.4}$. The order of 0.5 with respect to the AIBN concentration indicates that ordinary bimolecular termination occurs in this polymerization. On the other hand, the high order beyond unity was observed with respect to the tBMI concentration. Similar tendency has been reported for polymerizations of other maleimides [13,14] and dialkyl fumarates [3]. It was considered that slow initiation and propagation of these monomers by steric hindrance due to the 1,2-disubstituted ethylenic structure might be important for the kinetics.

In the radical polymerization of 1,2-disubstituted ethylenes such as DRF, the polymerization reactivity increases with the introduction of bulky substituents in the side chain, because the propagation rate decreases by a steric factor, but the bimolecular termination rate between propagating polymer radicals decreases further as a result of the formation of rigid polymer chains bearing bulky substituents. The poly(tBMI) was also expected to have less-flexible structure because of the five-membered ring in the main chain and the bulky N-substituent in the side chain. When an ESR spectrum of the propagating polymer radical from tBMI was tried to be detected under the polymerization conditions, it was found that the polymerization of tBMI in benzene in the presence of an initiator at 60-80°C gave a three-line spectra, which were resemble to that observed for polymerization of N-cyclohexylmaleimide reported [15]. The intensity of the spectra increased as the increasing temperature from 60°C to 80°C. A similar spectrum was also observed when the polymerization mixture was irradiated with UV light at room temperature. The easy observation of the spectrum under usual polymerization conditions suggests considerably high concentration of the propagating radical at a stationary state. The ESR study of the polymerization of maleimides including tBMI is now in progress, and the detailed results will be shown in future.

Characterization of poly(tBMI)

Poly(tBMI) was colorless powder, soluble in benzene, toluene, chloroform and THF, and insoluble in n-hexane, dimethyl sulfoxide and methanol. A transparent and brittle film was obtained by casting of the solution of poly(tBMI).

From the NMR and IR spectra of poly(tBMI), polymerization of tBMI was confirmed to perform via an opening of the double bond to give a poly(substituted methylene) [7]. This polymer was observed to decompose without any softening or melting by heating in a nitrogen atmosphere, i.e. quantitative elimination of isobutene from the side chain at 280°C, and decomposition of the resulting N-unsubstituted polymaleimide at ca. 400°C [6,7] (see also the subsequent paper). It indicates that poly(tBMI) has a high glass transition temperature which is more than its decomposition temperature.

Flexibility of the polymer chain

Considering that poly(tBMI) consists of successive 2,5-dioxopyrrolidone-3,4-diyl rings with a bulky tert-butyl group, the backbone seems to
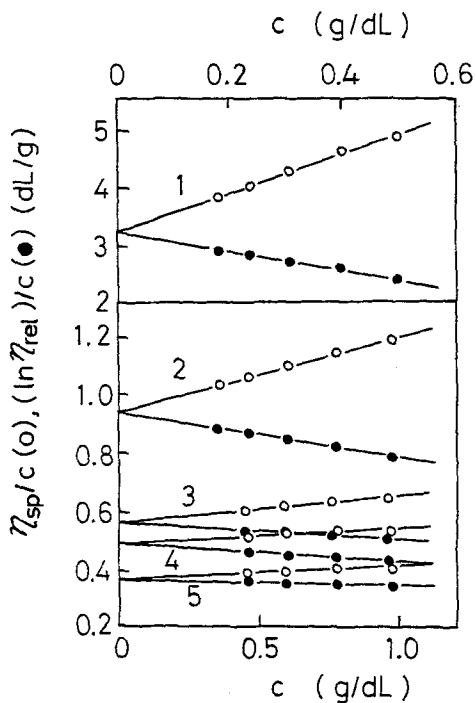
Fig. 4 $c - \eta_{sp}/c$ (o) and $(\ln \eta_{rel})/c$ (●) relations for poly(tBMI) in benzene at 30° C: Polymerization conditions, (1) 80° C in benzene, (2) 70° C in benzene, (3) 50° C in benzene, (4) 50° C in bulk, (5) 30° C in bulk.
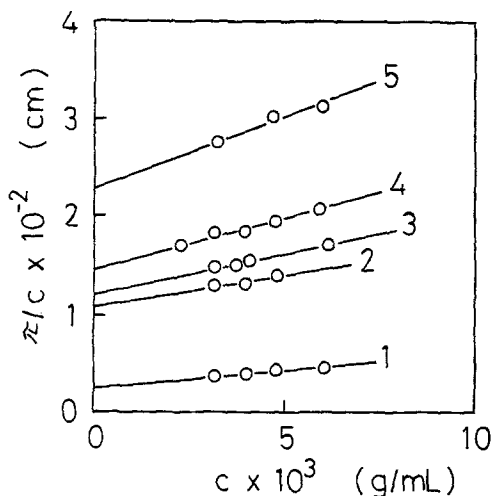
Fig. 5 $c - \pi/c$ relations for poly-(tBMI) in toluene at 38° C: Polymerization conditions, see Fig. 4.

have an appreciable rigid conformation. In order to estimate flexibility of the poly(tBMI) chain in solution, viscometric and light scattering measurements were carried out. The results of the molecular weight determination by viscometry, GPC, membrane osmometry and light scattering are also summarized in Tab. I.

The $[\eta]$ value in benzene at 30° C was determined by extrapolation with both Huggins [16] and Mead-Fuoss [17] equations (eqs. 1 and 2):

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \tag{1}$$

$$(\ln \eta_{rel})/c = [\eta] - k''[\eta]^2 c \tag{2}$$

where η_{sp} is a specific viscosity, η_{rel} is a relative viscosity, and c is the concentration of the polymer. Typical plots for determination of $[\eta]$ are shown in Fig. 4. The both extrapolations to $c = 0$ by eqs. 1 and 2 gave the $[\eta]$ values from 0.367 to 3.23 dL/g in good agreement.

The $\bar{M}_n$ were determined by osmometrically in toluene. The plots of π/c against c for the same polymers used in viscosity measurements are shown in Fig. 5, where π is an osmotic pressure. From the interception and slope of

Tab. II   Results for Light Scattering of Poly(tBMI) in THF

Polymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_w/\bar{M}_n$ [a]	$\bar{M}_z$ [b]$\times 10^{-5}$	$\bar{P}_z$ [c]$\times 10^{-3}$	$A_2 \times 10^4$ (mL/g^2)	R_g (nm)
Poly(tBMI)	2.92	1.66	4.08	2.97	2.44	34.5
Poly(TBC) [d]	3.51	1.11	3.86	2.71	1.46	32.6
Polystyrene [e]	3.42	<1.06	–	3.28	4.12	24.0(16.8) [f]

[a] By light scattering and osmometry. [b] Calculated by assuming the Schulz-Zimm distribution: $\bar{M}_n/h = \bar{M}_w/(h+1) = \bar{M}_z/(h+2)$. [c] z-Average number of the repeating monomer unit. [d] Poly(*tert*-butyl crotonate) in ethyl acetate at 25°C reported [19]. [e] In benzene at 30°C reported [21]. [f] In cyclohexane at 34.6°C.

the lines in Fig. 5, $\bar{M}_n$ and a second virial coefficient (A_2) were calculated, respectively. The $\bar{M}_n$ of 1-11 x 10^5 were obtained, and the A_2 values decreased as increasing of $\bar{M}_n$, as shown in Tab. I.

    The stiffness of polymer chains can be estimated with the value of index a in Mark-Houwink-Sakurada equation (eq. 3).

$$[\eta] = K \cdot \bar{M}_n{}^a \tag{3}$$

    Fig. 6 shows the relationship between $\log[\eta]$ and $\log\bar{M}_n$ of poly(tBMI) obtained from polymerization in bulk or in benzene, where the value of $\bar{M}_n$ was adopted as those determined osmometrically. The a and K values were determined to be 1.0 and 2.98 x 10^{-6} (in dL/g) from the slope and intercept of the line, respectively. The large a value suggests that poly(tBMI) has an extended conformation in benzene, because of its inherent less-flexible chain structure. Recently, we have reported the large a value for poly(di-isopropyl fumarate): $a = 0.98$ in benzene at 30°C [3,4]. Nagasawa and co-workers [18,19] have reported the synthesis and characterization of semi-flexible poly(*tert*-butyl crotonate) (poly(TBC)) with a narrow molecular weight distribution: $a = 0.96$ in toluene at 25°C. The a value for poly-(tBMI) is resemble to those for the these semiflexible polymers.

    The light scattering measurements were also taken. The $\bar{M}_w$ was determined by Berry's square root plot [20] as shown in Fig. 7 (eqs. 4 and 5).

$$(Kc/\Delta R_\theta)^{1/2}{}_{\theta \to 0} = (1/\bar{M}_w)^{1/2}(1 + A_2\bar{M}_w c) \tag{4}$$

$$(Kc/\Delta R_\theta)^{1/2}{}_{c \to 0} = (1/\bar{M}_w)^{1/2}(1 + (8\pi^2 n^2/3\lambda^2)R_g{}^2\sin^2(\theta/2)) \tag{5}$$

where K is the optical constant of the system, ΔR_θ is the excess Rayleigh's ratio, n is the refractive index of the solvent, and λ is the wavelength of incident light. The values of $\bar{M}_w$ determined are listed in Tab. I, and it was found that the $\bar{M}_w/\bar{M}_n$ which were determined by light scattering and osmometry, respectively, were 1.5-1.7.

    The A_2 and z-average radius of gyration (R_g) determined are listed in Tab. II, in which the results reported about poly(TBC) [19] and polystyrene [21] as typical semiflexible and flexible polymers, respectively, are also contained. Because poly(tBMI) obtained in this study did not have a narrow molecular weight distribution, the z-average molecular weight ($\bar{M}_z$) and the z-average number of the repeating monomer unit ($\bar{P}_z$) were calculated from
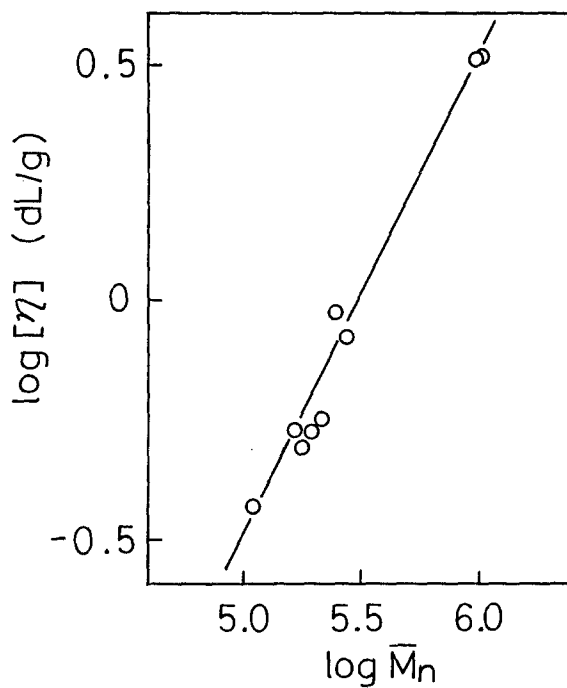
Fig. 6 Relationship between log[η] and log$\overline{M}_n$ for poly(tBMI) in benzene at 30° C.
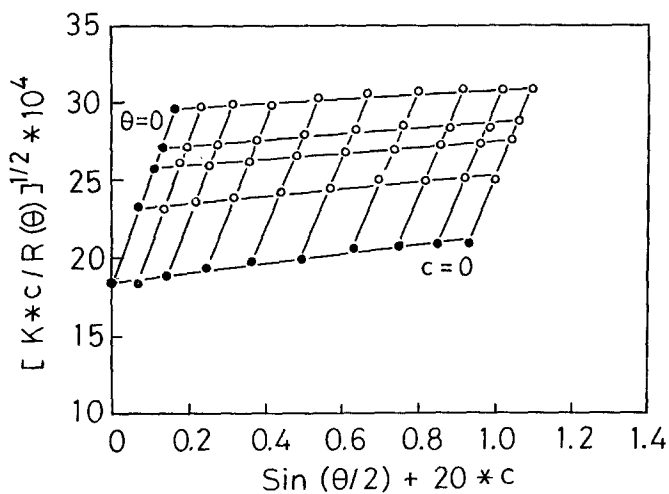

Fig. 7 Typical Berry's square root plot for poly(tBMI) in THF. The open circles are experimental data and the closed circles are the values obtained by extrapolations to zero angle and zero concentration. Poly(tBMI) was prepared by polymerization in benzene at 70°C, $\overline{M}_w$ = 2.92 x 10⁵.

their $\bar{M}_n$ and $\bar{M}_w$ with Schulz-Zimm distribution in order to compare their R_g values with each other. It is clear that R_g of poly(tBMI) is larger than a random coil of polystyrene in benzene as a good solvent, and similar to poly(TBC) in ethyl acetate. It indicates directly the expanded conformation of less-flexible poly(tBMI) in solution. The measurements for other poly(tBMI)s bearing various molecular weights also gave a similar conclusion. The decreasing in flexibility of the resulting polymer chain may take an important role for high polymerization of 1,2-disubstituted ethylenes (decreasing in bimolecular termination rate) mentioned above.

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