Polymer Vol. 37 No. 24, pp. 5411-5420, 1996

0032-3861/96/$15.00+0.00
S0032-3861(96)00357-6

Effect of molecular weight on formation of non-volatile oligomers by thermal degradation of polyisobutylene and its kinetic analysis

Takashi Sawaguchi*, Tadashi Ikemura and Manabu Seno
Department of Industrial Chemistry, College of Science and Technology, Nihon University, Kandasurugadai, Chiyoda-ku, Tokyo 101, Japan
(Received 1 December 1995; revised 8 February 1996)

The formation of functional groups of non-volatile oligomers by the thermal degradation of polyisobutylene is characterized by a kinetic approach including intermolecular hydrogen abstraction of primary (p) and tertiary (t) terminal macroradicals ($R_p^\bullet$ and $R_t^\bullet$) and volatile small radicals ($S^\bullet$), followed by β-scission. By assuming in the kinetic analysis that the reaction occurs competitively under a steady state regarding the on-chain macroradicals, various composition ratios for the functional groups can be represented in terms of the rates of respective hydrogen abstraction. The ratio between the tert-butyl endgroup (t-Bu) and the isopropyl endgroup (i-Pr), which corresponds to that between the abstraction rates of $R_p^\bullet$ and $R_t^\bullet$, is expressed by the product of the rate constant ratio and the integrated macroradical concentration ratio ($[R_p^\bullet]/[R_t^\bullet]$). The observed value of the ratio [t-Bu]/[i-Pr] decreases with reaction time. This is induced by a decrease in the molecular weight (M) of the reaction medium. The molecular weight dependence (M^a) of [t-Bu]/[i-Pr] is expressed by that of $[R_p^\bullet]/[R_t^\bullet]$. The value of exponent a was determined to be about 1.2 and 0.7 at 300 and 320°C, respectively, from the analysis of data at various reaction times. These values are roughly consistent with average values (1.0 and 0.9) of the same power-law exponent for the volatile oligomers. These results support the hypothesis that the concentrations of the respective radicals decrease in different ways. Copyright © 1996 Elsevier Science Ltd.

(Keywords: thermal degradation; polyisobutylene; diffusion-controlled termination)

INTRODUCTION

Thermal degradation of main-chain-scission type polymers is a typical polymer reaction in the melt. One of the most remarkable features is a change in volume and molecular weight of the molten polymer matrix constituting the reaction medium. Although physical factors such as the volume and molecular weight of the matrix strongly affect the reaction[1,2], their effect is not yet well-understood. We have examined this effect via detailed structural and kinetic analyses of the products obtained upon thermal degradation of polyisobutylene. In previous papers[3-5] we showed that the main products in the volatile oligomers are four types of α-mono-olefin oligomers from dimers to dodecamers and that the formation of these olefins could be reasonably explained by a reaction model consisting of intramolecular hydrogen abstraction (back-biting) of primary (p) and tertiary (t) terminal macroradicals ($R_p^\bullet$ and $R_t^\bullet$) (see *Figure 1* for meanings of the symbols) and subsequent β-scission at the inner position of the main chain[2-7]. The effects of physical factors on the formation of the volatile oligomers were examined by a kinetic approach based on measurements of the composition ratios between respective α-monoolefins. The observed values of the ratios, which correspond to those between the abstraction rates of different types of hydrogen (CH_2 and CH_3) of a given macroradical, are constant independent of changes in the physical factors. On the other hand, the ratios between the abstraction rates of the same type of hydrogen (CH_2 or CH_3) of different macroradicals do not depend on the pressure in the reaction vessel and the volume of matrix, but depend on the molecular weight of the molten polymer[4]. These values clearly decrease as the reaction time increases[5] and the molecular weight decreases[4]. It can be deduced that the decrease in molecular weight of the polymer leads to a decreasing concentration ratio $[R_p^\bullet]/[R_t^\bullet]$. According to the proposed kinetics of the chain mechanism including diffusion-controlled termination, a marked reduction of the radical concentration ratio suggests that the rate of termination increases with decreasing molecular weight of the matrix and that the resulting decrease of kinetic chain length depresses the formation of $R_p^\bullet$ (ref. 4). Such a change in $[R_p^\bullet]/[R_t^\bullet]$ in the molten polymer matrix should be also realized for the formation of non-volatile products. We have clearly detected the presence of functional groups such as terminal trisubstituted double bonds (TTD) and terminal vinylidine double bonds (isopropenyl group, TVD), tert-butyl (t-Bu) and

---

* To whom correspondence should be addressed

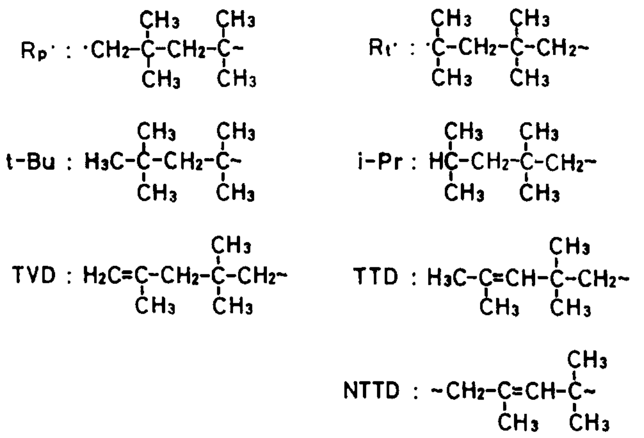


Figure 1 Abbreviations of terminal macroradicals ($R_p^{\bullet}$ and $R_t^{\bullet}$) and functional groups (t-Bu, i-Pr, TVD, TTD and NTTD)

isopropyl (i-Pr) endgroups in the non-volatile oligomers, which would be formed by intermolecular hydrogen abstraction of $R_p^{\bullet}$, $R_t^{\bullet}$ and volatile small radical ($S^{\bullet}$)[8] followed by β-scission[3-5,8,9] by 400 MHz ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy[8].

In this paper, the effect of molecular weight of the matrix polymer on the formation of non-volatile oligomers having these functional groups is examined by a kinetic approach, with measurements of the composition ratios between respective functional groups.

EXPERIMENTAL

Sample, apparatus and procedure

The polyisobutylene sample and the experimental procedure have been described in detail elsewhere[3], Molecular weight characteristics of the purified polyisobutylene are as follows: $M_n = 2.50 \times 10^5$ and $M_w/M_n = 2.50$. Six polyisobutylene samples having different molecular weights were prepared from the polymer residue obtained by thermal degradation of the original polyisobutylene[4], and their characteristics are shown in *Table 1*. The composition and functionality (f) of each of the endgroups and double bonds of the samples given in *Table 1* are described in a later section.

One gram of the sample was used for each degradation experiment at 300 or 320°C. After the degradation reaction the polymer residue in the reaction flask was dissolved in 10 cm^3 of chloroform and purified by reprecipitation in 50 cm^3 of acetone to remove a small amount of semi-volatile oligomers with a relatively low volatility. The reprecipitates were termed the non-volatile oligomers and analysed after vacuum drying under heating at 40°C. As reported previously[3], the non-volatile oligomers thus obtained were almost completely separated from the semi-volatile oligomers. The composition of the non-volatile and semi-volatile oligomers was determined from the difference between gel permeation chromatography (g.p.c.) curves of the polymer residue and the non-volatile oligomers. The volatilization, which represents the rate of formation of volatiles, was obtained from the following equation: 100 × (weight of sample − weight of polymer residues)/(weight of sample).

Analysis

The 400 MHz ^{1}H n.m.r. spectra were measured with a Jeol JNM-GX400 spectrometer operating at 399.65 MHz and room temperature with an internal lock. Sample concentrations were approximately 10% (w/v) in chloroform-d$_1$. Tetramethylsilane (TMS) was used as an internal standard and 5 mm diameter sample tubes were used. Spectral widths were 4.5 kHz, and 65 536 data points were accumulated in a JEC 32 computer. In the quantitative measurements[8], a pulse width of 90° (approximately 11.7 μs) and a pulse repetition time of 37.281 s were adopted. A typical measurement was performed for about 10–45 h. The signal intensities in the spectra were measured by a weighing method. The composition of the functional groups was determined from the intensities of signals of the methyl protons[8].

The molecular weight distribution (M_w/M_n) was measured by an analytical g.p.c. (Toyo Soda HLC-802 UR) using a stainless steel column of TSK-GEL (2× HMG6 + H4000HG8 + H2000HG8). The data were calibrated with polystyrene standards.

The number-average molecular weight (M_n) was calculated by the following equation[10] from the limiting viscosity number measured at 30°C in toluene: $[\eta] = 3.71 \times 10^{-4} P^{0.75}$, where $[\eta]$ is the limiting viscosity number (l g^{-1}) and P is the number-average degree of polymerization determined by the osmotic pressure method.

RESULTS AND DISCUSSION

Functional groups and reaction model

The volatilization and characteristics of the non-volatile oligomers obtained by thermal degradation of polyisobutylene at 300 and 320°C for 30 to 300 min are listed in *Table 2*. The increase in volatilization means a decrease in the polymer residue constituting the reaction medium as the reaction proceeds. The M_n values of the non-volatile oligomers decrease to 5500 at 300°C for 300 min and to 2600 at 320°C for 180 min. M_w/M_n maintains a constant value of about 2 at 300°C but decreases markedly to ~ 1.5 at 320°C for 180 min.

In a preceding paper[8], the chemical structures of the non-volatile oligomers were determined by 400 MHz ^{1}H n.m.r. spectroscopy and the resulting functional groups such as t-Bu, i-Pr, TVD, TTD and non-terminal trisubstituted double bond (NTTD) were clearly detected. The composition of each of the endgroups and double bonds of the non-volatile oligomers was determined from the intensity of the signal of corresponding methyl protons and the results are listed in *Table 2*[8]. The functionality of the functional group of interest, defined as an average number of the functional group per molecule, is calculated by the following equation, assuming all the non-volatile oligomers are linear:

$$f = \frac{2 \times [\text{signal intensity of the functional group of interest}]}{[\text{signal intensity of all endgroups (i-Pr + t-Bu + TTD + TVD)}]}$$

The functionalities f_t and f_{tn} in *Table 2* represent average numbers of the terminal double bonds and the total double bonds per molecule, respectively.

The original polyisobutylene ($M_{n0} = 2.5 \times 10^5$), which is prepared by cationic polymerization, is a linear polymer having a saturated endgroup and a terminal double bond[11]; it is deduced from the cationic mechanism that the former is t-Bu and the latter is TTD or TVD. Changes in the values of M_n and M_w/M_n (*Table 2*) suggest that the scission reaction of the main chain occurs at a random

Table 1 Characteristics of molecular weight and chemical structure of polyisobutylene samples having different molecular weights (M_{n0})

M_{n0}[a]		Composition[c] (mol%)					Functionality[i]							$\frac{[\text{t-Bu}]}{[\text{i-Pr}]}$	$\frac{[\text{TTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]+[\text{NTTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]}{[\text{NTTD}]}$
$\times 10^{-3}$	M_w/M_n[b]	[i-Pr][d]	[t-Bu][e]	[TTD][f]	[TVD][g]	[NTTD][h]	$f_{\text{i-Pr}}$	$f_{\text{t-Bu}}$	f_{TTD}	f_{TVD}	f_{NTTD}	f_t[j]	f_{tn}[k]				
250	2.50																
64.8[l]	2.43																
49.9[l]	2.35																
7.09[l]	1.64	1.00	15.43	50.84	20.44	12.29	0.023	0.352	1.16	0.466	0.280	1.63	1.91	15.4	2.49	3.09	4.14
3.62[l]	1.35	2.82	19.89	45.97	12.87	18.46	0.069	0.488	1.13	0.316	0.453	1.44	1.90	7.05	3.57	5.01	2.49
2.32[l]	1.36	5.00	30.23	34.77	13.88	16.13	0.119	0.721	0.83	0.331	0.385	1.16	1.54	6.05	2.51	3.67	2.16
2.00[l]	1.28	4.56	24.79	45.57	13.13	13.94	0.104	0.563	1.04	0.298	0.317	1.33	1.65	5.44	3.47	4.53	3.27

[a] Determined by measurements of limiting viscosity number

[b] Heterogeneity index of molecular weight distribution determined by g.p.c. measurements

[c] 100 × [each CH_3 peak intensity/total CH_3 peak intensity (i-Pr + t-Bu + TTD + TVD + NTTD)]

[d] Iso-propyl; $(CH_3)_2CH\sim$

[e] Tert-butyl; $(CH_3)_3C\sim$

[f] Terminal trisubstituted double bond; $(CH_3)_2C{=}CH\sim$

[g] Terminal vinylidene double bond; $CH_2{=}C(CH_3)\sim$

[h] Non-terminal trisubstituted double bond; $\sim(CH_3)C{=}CH\sim$

[i] Average number of each functional group per molecule; $f = 2 \times$ [each functional group peak intensity]/[total terminal peak intensity (i-Pr + t-Bu + TTD + TVD)]

[j] Average number of terminal double bonds per molecule; $f_t = 2 \times ([\text{TTD}] + [\text{TVD}])/([\text{i-Pr}] + [\text{t-Bu}] + [\text{TTD}] + [\text{TVD}])$

[k] Average number of total double bonds per molecule; $f_{tn} = 2 \times ([\text{TTD}] + [\text{TVD}] + [\text{NTTD}])/([\text{i-Pr}] + [\text{t-Bu}] + [\text{TTD}] + [\text{TVD}])$

[l] Oligomer samples prepared by thermal degradation of polyisobutylene ($M_{n0} = 2.50 \times 10^5$)

Table 2 Volatilization, and the composition and functionality of respective endgroups and double bonds of the non-volatile oligomers by thermal degradation of polyisobutylene ($M_{n0} = 2.5 \times 10^5$)

Temp. (°C)	Time (min)	C^a (wt%)	$M_n{}^b$ $\times 10^{-3}$	$M_w/M_n{}^c$	Composition^d (mol%)					Functionality^j						
					[i-Pr]^e	[t-Bu]^f	[TTD]^g	[TVD]^h	[NTTD]^i	$f_{\text{i-Pr}}$	$f_{\text{t-Bu}}$	f_{TTD}	f_{TVD}	f_{NTTD}	$f_t{}^k$	$f_{tn}{}^l$
300	0	0.0	250	2.50												
	30	6.3	15.0	2.17	0.53	15.37	51.09	23.36	9.65	0.012	0.340	1.13	0.517	0.214	1.65	1.86
	60	6.9	13.0	2.14	0.61	16.00	51.51	23.33	9.95	0.013	0.354	1.14	0.494	0.220	1.63	1.85
	120	11.5	8.97	2.12	1.04	16.01	52.90	20.13	9.92	0.023	0.355	1.17	0.447	0.220	1.62	1.84
	140	12.6	8.47	2.15	1.12	15.32	52.35	21.18	10.03	0.025	0.341	1.16	0.471	0.223	1.63	1.86
	180	16.0	7.02	2.11	1.41	17.90	51.62	18.72	10.35	0.031	0.399	1.15	0.418	0.231	1.57	1.80
	300	23.6	5.52	2.10	2.01	17.90	52.73	15.97	11.39	0.045	0.404	1.19	0.360	0.257	1.55	1.81
320	0	0.0	250	2.50												
	15	7.0	13.3	2.35	0.70	15.57	51.79	22.38	9.56	0.015	0.344	1.15	0.495	0.211	1.64	1.85
	30	14.1	6.69	2.08	0.92	14.88	50.82	20.44	12.94	0.021	0.342	1.17	0.470	0.297	1.64	1.93
	60	21.9	5.26	1.94	1.54	17.34	51.53	18.50	11.08	0.035	0.390	1.16	0.416	0.249	1.58	1.82
	90	47.8	3.30	1.61	1.74	15.53	55.65	13.18	13.91	0.040	0.361	1.29	0.306	0.323	1.60	1.92
	120	59.6	2.90	1.56	2.40	19.72	53.46	10.43	14.00	0.056	0.467	1.24	0.243	0.326	1.49	1.81
	180	68.2	2.60	1.48	3.04	20.03	54.25	8.49	14.19	0.071	0.467	1.26	0.198	0.331	1.46	1.79

[a] Volatilization

[b] Determined by measurements of limiting viscosity number

[c] Determined by g.p.c. measurements

[d] 100 × [each CH_3 peak intensity/total CH_3 signal intensity (i-Pr + t-Bu + TTD + TVD + NTTD)]

[e] Iso-propyl; $(CH_3)_2CH \sim$

[f] Tert-butyl; $(CH_3)_3C \sim$

[g] Terminal trisubstituted double bond; $(CH_3)_2C{=}CH \sim$

[h] Terminal vinylidene double bond; $CH_2{=}C(CH_3) \sim$

[i] Non-terminal trisubstituted double bond; $\sim (CH_3)C{=}CH \sim$

[j] Average number of each functional group per molecule; $f = 2 \times$ [each functional group peak intensity]/[total terminal peak intensity (i-Pr + t-Bu + TTD + TVD)]

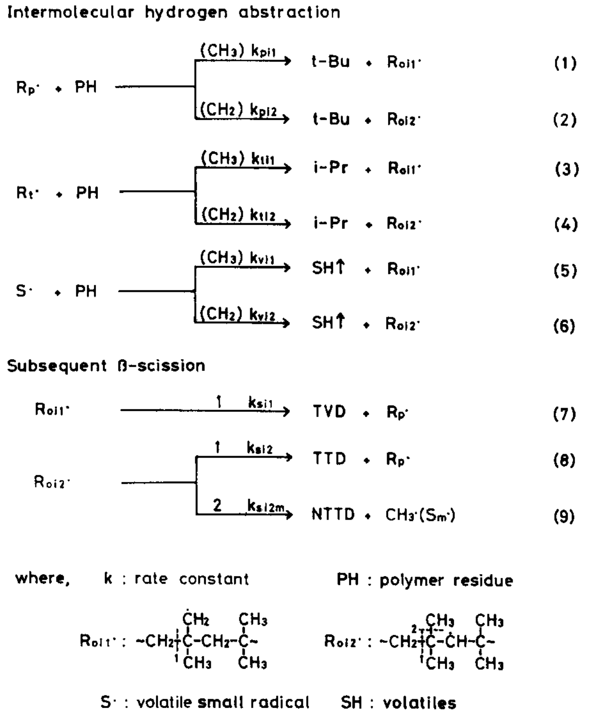
[k] Average number of terminal double bonds per molecule; $f_r = 2 \times ([\text{TTD}] + [\text{TVD}])/([\text{i-Pr}] + [\text{t-Bu}] + [\text{TTD}] + [\text{TVD}])$

[l] Average number of total double bonds per molecule; $f_{tn} = 2 \times ([\text{TTD}] + [\text{TVD}] + [\text{NTTD}])/([\text{i-Pr}] + [\text{t-Bu}] + [\text{TTD}] + [\text{TVD}])$

position in the polymer. The average number of scissions, which is estimated by $(M_{n0}/M_n) - 1$, ranges from about 16 to 124 for the non-volatile oligomers. Thereby, more than 94% of the endgroups of these oligomers would be newly formed by the thermal degradation.

As shown in *Table 2*, at both temperatures the functionalities of t-Bu and i-Pr increase markedly, while those of TTD and NTTD increase slightly and that of TVD decreases, as the degradation proceeds. In particular, the f_t value is greater than 1 and decreases with degradation time at both temperatures. This result can be interpreted by the intermolecular hydrogen abstraction of $S^\bullet$ (ref. 8), in addition to those of $R_p^\bullet$ and $R_t^\bullet$ (refs 6 and 9), and subsequent β-scission.

Reasonable elementary reactions[8] for the formation of these functional groups are proposed as shown in *Scheme 1*. In equations (1) to (6), the intermolecular hydrogen abstraction of radicals gives two types of on-chain macroradical ($R_{oi1}^\bullet$ and $R_{oi2}^\bullet$), depending on the position (CH_3 or CH_2) of hydrogen abstraction, rather than the on-radical type. The hydrogen abstraction of $R_p^\bullet$ [equations (1) and (2)], $R_t^\bullet$ [equations (3) and (4)] and $S^\bullet$ [equations (5) and (6)] yields t-Bu, i-Pr and SH (volatiles), respectively. The β-scission of $R_{oi1}^\bullet$ occurs only at the main chain (position 1) and exclusively results in the formation of TVD and $R_p^\bullet$ [equation (7)]. On the other hand, the β-scission of $R_{oi2}^\bullet$ produces TTD and $R_p^\bullet$ [equation (8)], or NTTD and methyl radical [equation (9)], depending on the position of scission 1 (main chain) or 2 (side methyl group). Thus, only two types of on-chain macroradical are formed depending on position (CH_3 and CH_2) from the intermolecular hydrogen abstraction of various radicals, while four types of on-chain macroradical result from the back-biting of $R_p^\bullet$ and $R_t^\bullet$ (refs 3–5).



Scheme 1 Reaction scheme of intermolecular hydrogen abstractions followed by β-scissions of $R_p^\bullet$, $R_t^\bullet$ and $S^\bullet$

The concentration [P] of polymer in the molten polymer matrix is expressed[12,13] by ρ/M, where ρ and M are the density and molecular weight of the polymer, respectively. The density can be set to be almost constant during the degradation, because the specific volume (v_{sp}) of polyisobutylene having molecular weight ranging from 3540 to 115 000 at 217°C is nearly constant, as given by the equation[14]: $v_{sp} = 1.225 + 32/M$. Under these conditions, the concentrations (mol cm^{-3}) of the respective functional groups are expressed as follows:

$$[\text{t-Bu}] = [\text{P}]f_{\text{t-Bu}} = \rho f_{\text{t-Bu}}/M \tag{10}$$

$$[\text{i-Pr}] = [\text{P}]f_{\text{i-Pr}} = \rho f_{\text{i-Pr}}/M \tag{11}$$

$$[\text{TTD}] = [\text{P}]f_{\text{TTD}} = \rho f_{\text{TTD}}/M \tag{12}$$

$$[\text{TVD}] = [\text{P}]f_{\text{TVD}} = \rho f_{\text{TVD}}/M \tag{13}$$

$$[\text{NTTD}] = [\text{P}]f_{\text{NTTD}} = \rho f_{\text{NTTD}}/M \tag{14}$$

Assuming 0.75 g cm^{-3} for the value of ρ $(1/v_{sp})$, the molar concentrations given by equations (10) to (14) can be calculated from the observed values of functionality and M_n (*Table 2*). The results are shown in *Figure 2*, where the concentration of each functional group is plotted against time. The concentrations [t-Bu], [i-Pr], [TTD] and [NTTD] increase with increasing time owing to the decrease of M_n and the increase of the respective functionalities at both temperatures. However, at 320°C, a curve of [TVD] has a maximum value at about 90 min owing to a marked decrease in the f_{TVD} value. As it is considered as described above, a molecule of the original polyisobutylene ($M_{n0} = 2.5 \times 10^5$) has a t-Bu and a terminal double bond of TTD or TVD with a ratio of 1/1 (ref. 11); thus the initial concentrations $[\text{P}]_0$ and $[\text{t-Bu}]_0$ are 2.91×10^{-6}, $[\text{TTD}]_0$ and $[\text{TVD}]_0$ are 1.46×10^{-6}, and $[\text{i-Pr}]_0 = [\text{NTTD}]_0 = 0$. In thermal degradation, the end initiation[2] at thermally labile bonds at the β-position from the terminal double bond (such as TVD and TTD) is important in addition to the random initiation by scission of the skeletal C–C bond[3–5]. However, in the depropagation step, elementary reactions to form TVD and TTD occur more frequently than the initiation from TVD and TTD, owing to a relatively large kinetic chain length[2]. Consequently, it can be deduced that the concentration changes of

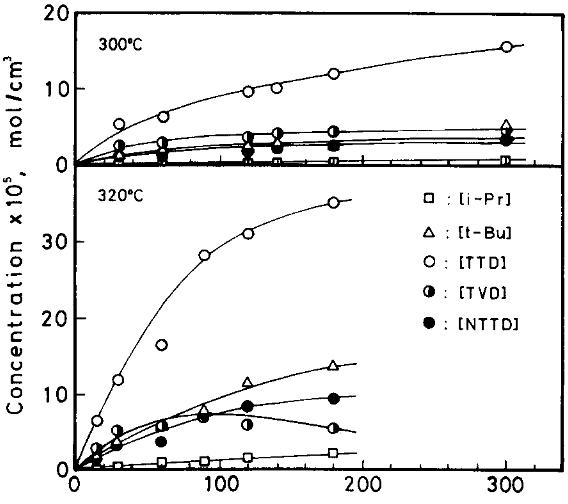


Figure 2 Time course of concentration of respective functional groups of the non-volatile oligomers

functional groups (*Figure 2*) depend mainly on the elementary reactions in the depropagation step (*Scheme 1*) rather than on the initial concentration as well as the initiation and termination reactions.

Kinetic analysis

According to the reaction model shown in *Scheme 1*, the rates of formation of the respective functional groups of the non-volatile oligomers are given as follows:

$$\frac{d[\text{t-Bu}]}{dt} = (k_{pi1} + k_{pi2})[R_p^\bullet][P] = (k_{pi1} + k_{pi2})[R_p^\bullet][N] \qquad (15)$$

$$\frac{d[\text{i-Pr}]}{dt} = (k_{ti1} + k_{ti2})[R_t^\bullet][P] = (k_{ti1} + k_{ti2})[R_t^\bullet][N] \qquad (16)$$

$$\frac{d[\text{TVD}]}{dt} = k_{si1}[R_{oi1}^\bullet] \qquad (17)$$

$$\frac{d[\text{TTD}]}{dt} = k_{si2}[R_{oi2}^\bullet] \qquad (18)$$

$$\frac{d[\text{NTTD}]}{dt} = k_{si2m}[R_{oi2}^\bullet] \qquad (19)$$

where [N] is the concentration of monomer units in the polymer, which is used instead of [P][4], and is equal to ρ/m, where m is the molecular weight of monomer. As given in equations (15) and (16), the formation rates of t-Bu and i-Pr are represented by the intermolecular hydrogen abstraction rates of $R_p^\bullet$ and $R_t^\bullet$, respectively. Assuming that the reactions of equations (1) to (9) occur competitively under a steady state, where the concentrations of the on-chain macroradicals ($R_{oi1}^\bullet$ and $R_{oi2}^\bullet$) are kept low and constant, $[R_{oi1}^\bullet]$ and $[R_{oi2}^\bullet]$ are written as follows:

$$[R_{oi1}^\bullet] = \frac{1}{k_{si1}}(k_{pi1}[R_p^\bullet] + k_{ti1}[R_t^\bullet] + k_{vi1}[S^\bullet])[N] \qquad (20)$$

$$[R_{oi2}^\bullet] = \frac{1}{(k_{si2} + k_{si2m})}(k_{pi2}[R_p^\bullet] + k_{ti2}[R_t^\bullet] + k_{vi2}[S^\bullet])[N] \qquad (21)$$

When equations (17)–(19) are substituted into equations (20) and (21), the formation rate of each double bond can be also represented by a sum of the rate of intermolecular hydrogen abstraction for respective radicals as follows:

$$\frac{d[\text{TVD}]}{dt} = (k_{pi1}[R_p^\bullet] + k_{ti1}[R_t^\bullet] + k_{vi1}[S^\bullet])[N] \qquad (22)$$

$$\frac{d[\text{TTD}]}{dt} = \frac{k_{si2}}{(k_{si2} + k_{si2m})} \times (k_{pi2}[R_p^\bullet] + k_{ti2}[R_t^\bullet] + k_{vi2}[S^\bullet])[N] \qquad (23)$$

$$\frac{d[\text{NTTD}]}{dt} = \frac{k_{si2m}}{(k_{si2} + k_{si2m})} \times (k_{pi2}[R_p^\bullet] + k_{ti2}[R_t^\bullet] + k_{vi2}[S^\bullet])[N] \qquad (24)$$

Accordingly, the molar concentrations of the functional groups formed for a given time interval (t) are obtained by integration of equations (15), (16), (22), (23) and (24) as follows:

$$[\text{t-Bu}] = (k_{pi1} + k_{pi2})[\mathbf{R_p^\bullet}][N] + [\text{t-Bu}]_0 \qquad (25)$$

$$[\text{i-Pr}] = (k_{ti1} + k_{ti2})[\mathbf{R_t^\bullet}][N] + [\text{i-Pr}]_0 \qquad (26)$$

$$[\text{TVD}] = (k_{pi1}[\mathbf{R_p^\bullet}] + k_{ti1}[\mathbf{R_t^\bullet}] + k_{vi1}[\mathbf{S^\bullet}])[N] + [\text{TVD}]_0 \qquad (27)$$

$$[\text{TTD}] = \frac{k_{si2}}{(k_{si2} + k_{si2m})}(k_{pi2}[\mathbf{R_p^\bullet}] + k_{ti2}[\mathbf{R_t^\bullet}] + k_{vi2}[\mathbf{S^\bullet}])[N] + [\text{TTD}]_0 \qquad (28)$$

$$[\text{NTTD}] = \frac{k_{si2m}}{(k_{si2} + k_{si2m})}(k_{pi2}[\mathbf{R_p^\bullet}] + k_{ti2}[\mathbf{R_t^\bullet}] + k_{vi2}[\mathbf{S^\bullet}])[N] + [\text{NTTD}]_0 \qquad (29)$$

where $[\mathbf{R_p^\bullet}] = \int[R_p^\bullet]dt$, $[\mathbf{R_t^\bullet}] = \int[R_t^\bullet]dt$ and $[\mathbf{S^\bullet}] = \int[S^\bullet]dt$. Thus, the molar concentrations given by equations (25) to (29) correspond to those given by equations (10) to (14). In this study, the mechainsm for formation of these functional groups is examined by analysing the observed values of concentration ratios between respective functional groups, based on the kinetic equations of the corresponding ratios shown in *Table 3*. That is to say, the ratio [t-Bu]/[i-Pr] is expressed by a product of the ratio of the rate constants (sum) and the macroradical concentration ratio ($[\mathbf{R_p^\bullet}]/[\mathbf{R_t^\bullet}]$). Thus, a change in the observed value of the composition ratio reflects that of the macroradical concentrations during degradation. On the other hand, in relation to the double bond distribution, the ratio ([TTD] + [NTTD])/[TVD] corresponds to that between the abstraction rates (sum) of different types of hydrogen (CH_2 and CH_3) of $R_p^\bullet$, $R_t^\bullet$ and $S^\bullet$. The ratio [TTD]/[NTTD] is given only by the rate constant ratio of competitive β-scission at different positions of $R_{oi2}^\bullet$. This ratio should remain unchanged during degradation.

The composition ratios calculated from the experimental data (*Table 2*) for various reaction times at 300 and 320°C are listed in *Table 4*. As shown in this table, the value of [t-Bu]/[i-Pr] clearly decreases with reaction time at both temperatures. This tendency holds for the corresponding composition ratio in the volatile oligomers[5]. The decrease in the ratio [t-Bu]/[i-Pr] with time evidently results from the decrease in the macroradical concentration ratio as the degradation proceeds. This result suggests that this degradation proceeds under an unsteady state regarding terminal macroradical concentration. The same situation is deduced also from the result on the composition ratio of terminal monoolefins in the volatile oligomers[4,5].

Table 3 Kinetic equations for composition ratio between functional groups of the non-volatile oligomers

Composition ratio	Kinetic equation
$\frac{[\text{t-Bu}]}{[\text{i-Pr}]}$	$\frac{(k_{pi1} + k_{pi2})[\mathbf{R_p^\bullet}]}{(k_{ti1} + k_{ti2})[\mathbf{R_t^\bullet}]}$
$\frac{[\text{TTD}] + [\text{NTTD}]}{[\text{TVD}]}$	$\frac{(k_{pi2}[\mathbf{R_p^\bullet}] + k_{ti2}[\mathbf{R_t^\bullet}] + k_{vi2}[\mathbf{S^\bullet}])}{(k_{pi1}[\mathbf{R_p^\bullet}] + k_{ti1}[\mathbf{R_t^\bullet}] + k_{vi1}[\mathbf{S^\bullet}])}$
$\frac{[\text{TTD}]}{[\text{NTTD}]}$	$\frac{k_{si2}}{k_{si2m}}$

Table 4 Changes in composition ratios between functional groups of the non-volatile oligomers by thermal degradation of polyisobutylene ($M_{n0} = 2.5 \times 10^5$)

Temp. (°C)	Time (min)	$\frac{[\text{t-Bu}]}{[\text{i-Pr}]}$	$\frac{[\text{TTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]+[\text{NTTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]}{[\text{NTTD}]}$	$\frac{[\text{TTD}]}{[\text{TTD}]+[\text{NTTD}]}$
300	0					
	30	29.0	2.19	2.60	5.29	0.84
	60	26.2	2.31	2.75	5.18	0.84
	120	15.4	2.63	3.12	5.33	0.84
	140	13.7	2.47	2.90	5.22	0.84
	180	12.7	2.76	3.31	4.99	0.83
	300	8.91	3.30	4.02	4.63	0.82
320	0					
	15	22.2	2.31	2.74	5.42	0.84
	30	16.2	2.49	3.12	3.93	0.80
	60	11.3	2.79	3.38	4.65	0.82
	90	8.93	4.22	5.28	4.00	0.80
	120	8.22	5.13	6.46	3.82	0.79
	180	6.59	6.39	8.06	3.82	0.79

On the other hand, the value of ([TTD] + [TVD])/[TVD] increases gradually at 300°C and markedly at 320°C with increasing time, in contrast to the result[5] that the corresponding composition ratios for the volatile oligomers are nearly constant with reaction time. This tendency for the non-volatile oligomers is mainly due to the decreasing [TVD] during the degradation and it is deduced from the corresponding kinetic expression given in *Table 3* that the ratios between the abstraction rates of the same type of hydrogen (CH_2 or CH_3) of different radicals differ from one another. The ratio [TTD]/[NTTD], which corresponds to the rate constant ratio between the β-scission rates of $R^{\bullet}_{oi2}$, decreases gradually with reaction time at both temperatures. This result suggests that the reactivity for β-scission is related to the segmental rotational motion of the reacting radical.

Effect of molecular weight

It is of interest whether the value of [t-Bu]/[i-Pr] related to intermolecular hydrogen abstraction followed by β-scission of $R^{\bullet}_p$ and $R^{\bullet}_t$ is dependent on the molecular weight of the molten polymer matrix. In our previous paper[4] we showed that both the pressure and volume of the matrix did not affect the back-biting of $R^{\bullet}_p$ and $R^{\bullet}_t$, but that these elementary reactions depend strongly on the molecular weight of the matrix. In this study, the effects of pressure, volume and molecular weight on the composition ratios for respective functional groups of the non-volatile oligomers were examined.

The original polyisobutylene was degraded under pressure ranging from 0.1 to 168 mmHg at 320°C for 45 min[4]. With the increase of pressure, the composition of volatiles tends to decrease and those of the semi-volatile and non-volatile oligomers increase slightly. However, M_n of the non-volatile oligomer is almost unchanged with pressure. *Figure 3* shows plots of the composition ratios [t-Bu]/[i-Pr], ([TTD] + [NTTD])/[TVD] and [TTD]/[NTTD] against pressure. A marked dependence on pressure is not found for any composition ratio. The effect of the volume of matrix was examined at 300°C for 120 min and at 320°C for 45 min by varying the initial sample weight in a range from 0.4 to 1.0 g (ref. 4). *Figure 4* shows plots of the composition ratios for respective functional groups against the initial sample weight. At both temperatures, the composition ratios as well as the volatilization and M_n of the non-volatile oligomers[4] are not affected by the initial sample weight.

Thus, it was revealed that both the pressure and volume of the matrix do not affect the relative rates of intermolecular hydrogen abstraction followed by β-scission, as well as those of back-biting followed by β-scission[4]. As described in the Experimental, the reacting molten polymer in the reaction vessel was vigorously stirred with bubbles of N_2 introduced, so that the molten polymer was well dispersed in the vessel during degradation. This could be the main reason why the volume of highly viscous sample scarcely affects the degradation.

The effect of the molecular weight of the matrix polymer was investigated by varying the initial molecular weight (M_{n0}) of the polyisobutylene sample. Six samples

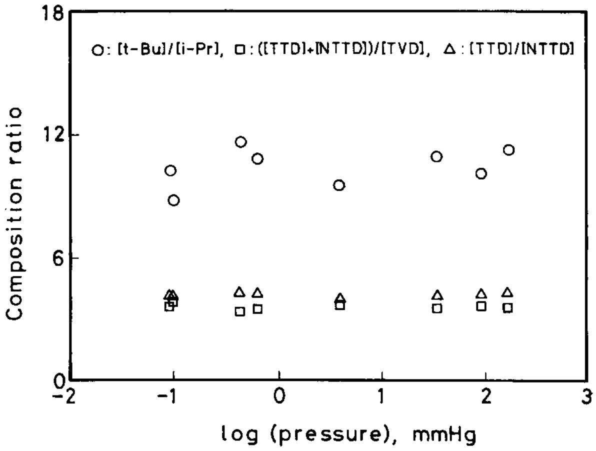


Figure 3 Plots of the composition ratios between respective functional groups of the non-volatile oligomers *versus* pressure at 320°C

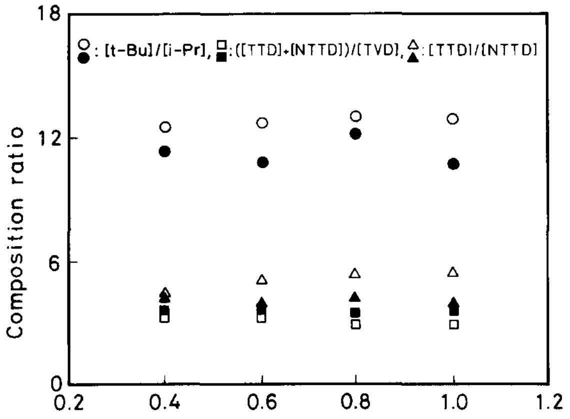


Figure 4 Plots of the composition ratios between respective functional groups of the non-volatile oligomers *versus* initial sample weight at 300°C (○□△) and 320°C (●■▲)

(*Table 1*) prepared by thermal degradation of the original polyisobutylene ($M_{n0} = 2.5 \times 10^5$) at 320°C have t-Bu, i-Pr, TTD, TVD and NTTD as functional groups. The compositions and the ratios of these functional groups are similar to those of the corresponding non-volatile oligomers at 320°C shown in *Tables 2* and *4*. The results of thermal degradation of these samples at 300°C for 90 min and at 320°C for 45 min are given in *Tables 5* and *6*, respectively. The volatilization rate increases with decreasing M_{n0}, probably because of an increase in the rate of end initiation[2,4]. *Figures 5* and *6* show plots of the composition ratios *versus* M_n of the non-volatile oligomers obtained from the data on various initial molecular weights (*Table 6*) and reaction times (*Table 4*). The relationships between ratios and M_n obtained from data for various initial molecular weights agree roughly with those estimated from the change with reaction time, except for the ratio ([TTD] + [NTTD])/[TVD] in the case of M_n lower than 3000. In the case of samples with relatively lower molecular weights, the sample has a high initial concentration of the functional groups (*Table 1*), so that the concentrations of the respective functional groups formed by reactions (1) to (9) should be evaluated by the following equations:

$$[\text{t-Bu}] - [\text{t-Bu}]_0 = (k_{\mathrm{pi1}} + k_{\mathrm{pi2}})[\mathbf{R}_{\mathrm{p}}^\bullet][\mathrm{N}] \tag{30}$$

$$[\text{i-Pr}] - [\text{i-Pr}]_0 = (t_{\mathrm{ti1}} + k_{\mathrm{ti2}})[\mathbf{R}_{\mathrm{t}}^\bullet][\mathrm{N}] \tag{31}$$

$$[\mathrm{TVD}] - [\mathrm{TVD}]_0 = (k_{\mathrm{pi1}}[\mathbf{R}_{\mathrm{p}}^\bullet] + k_{\mathrm{ti1}}[\mathbf{R}_{\mathrm{t}}^\bullet] + k_{\mathrm{vi1}}[\mathrm{S}^\bullet])[\mathrm{N}] \tag{32}$$

$$[\mathrm{TTD}] - [\mathrm{TTD}]_0 = \frac{k_{\mathrm{si2}}}{(k_{\mathrm{si2}} + k_{\mathrm{si2m}})} \times (k_{\mathrm{pi2}}[\mathbf{R}_{\mathrm{p}}^\bullet] + k_{\mathrm{ti2}}[\mathbf{R}_{\mathrm{t}}^\bullet] + k_{\mathrm{vi2}}[\mathrm{S}^\bullet])[\mathrm{N}] \tag{33}$$

$$[\mathrm{NTTD}] - [\mathrm{NTTD}]_0 = \frac{k_{\mathrm{si2m}}}{(k_{\mathrm{si2}} + k_{\mathrm{si2m}})} \times (k_{\mathrm{pi2}}[\mathbf{R}_{\mathrm{p}}^\bullet] + k_{\mathrm{ti2}}[\mathbf{R}_{\mathrm{t}}^\bullet] + k_{\mathrm{vi2}}[\mathrm{S}^\bullet])[\mathrm{N}] \tag{34}$$

In the present study, this problem cannot be discussed in detail. We will report results obtained on the thermal degradation of polyisobutylene ($M_{n0} = 7.09 \times 10^3$) with a different initial distribution of functional groups, prepared by hydrogenation, in the near future.

The changes in the ratios between the concentrations of the respective functional groups of the non-volatile oligomers during degradation depend clearly on the molecular weight of matrix polymer rather than on the pressure and volume. In particular, the value of [t-Bu]/[i-Pr] decreases evidently with decreasing molecular weight during degradation. This suggests that the decrease in molecular weight leads to a decreasing concentration ratio of $[\mathbf{R}_{\mathrm{p}}^\bullet]/[\mathbf{R}_{\mathrm{t}}^\bullet]$.

Molecular weight dependence

As described in the previous paper[4], the molecular weight dependence of the terminal macroradical concentration ratio ($[\mathbf{R}_{\mathrm{p}}^\bullet]/[\mathbf{R}_{\mathrm{t}}^\bullet]$) can be estimated from that of the composition ratio $[\mathrm{TVD}]_{\mathrm{p}}/[\mathrm{TVD}]_{\mathrm{t}}$ or $[\mathrm{TTD}]_{\mathrm{p}}/[\mathrm{TTD}]_{\mathrm{t}}$ as follows:

$$\frac{[\mathbf{R}_{\mathrm{p}}^\bullet]}{[\mathbf{R}_{\mathrm{t}}^\bullet]} \propto \frac{[\mathrm{TVD}]_{\mathrm{p}}}{[\mathrm{TVD}]_{\mathrm{t}}} \propto \frac{[\mathrm{TTD}]_{\mathrm{p}}}{[\mathrm{TTD}]_{\mathrm{t}}} \propto M_n{}^a \tag{35}$$

This relationship was verified with a relatively high correlation (>0.92) for every oligomer from trimers to heptamers. The value of exponent *a* was determined to be ~ 1.04 and 0.88 at 300 and 320°C, respectively, on an average from the results at various reaction times[4]. Similarly, the molecular weight dependence of $[\mathbf{R}_{\mathrm{p}}^\bullet]/[\mathbf{R}_{\mathrm{t}}^\bullet]$ could be also obtained from the composition ratio [t-Bu]/[i-Pr], which shows a molecular weight dependence as follows:

$$\frac{[\mathbf{R}_{\mathrm{p}}^\bullet]}{[\mathbf{R}_{\mathrm{t}}^\bullet]} \propto \frac{[\text{t-Bu}]}{[\text{i-Pr}]} \propto M_n{}^a \tag{36}$$

The double logarithmic plot of equation (36) was checked by the least-squares method, and the value of *a* was obtained from the data at various reaction times (*Table 4*). At 300 and 320°C, the relationships (36) are verified with relatively high correlation (>0.97) to afford the value of exponent *a* to be 1.18 at 300°C and 0.72 at 320°C. These results are nearly consistent with those obtained for the volatile oligomers at the same temperatures.

The non-volatile oligomers were isolated from the molten polymer (polymer residues) constituting the reaction medium after the degradation. On the other hand, the volatile oligomers formed in the molten polymer phase were transferred from the polymer phase to the gaseous phase accompanied by N_2 gas introduced into the polymer phase, and recovered in a fraction trap chilled with liquid N_2. Despite such a difference in conditions, the same molecular weight dependence of $[\mathbf{R}_{\mathrm{p}}^\bullet]/[\mathbf{R}_{\mathrm{t}}^\bullet]$ is obtained for the non-volatile and the volatile oligomers. This fact indicates that the similar behaviours of the decrease in the ratio $[\mathrm{R}_{\mathrm{p}}^\bullet]/[\mathrm{R}_{\mathrm{t}}^\bullet]$ during degradation are observed by two different methods of structural and kinetic analyses of the two different products formed either via intramolecular hydrogen abstraction (back-biting) followed by β-scission or intermolecular hydrogen abstraction followed by β-scission, respectively. This result clearly supports the assumption on the kinetics of our proposed chain mechanism including self-diffusion-controlled termination[4], in which the termination rate increases with the decrease in molecular weight of the matrix

Table 5 Changes in volatilization and composition and functionality of respective functional group of the non-volatile oligomers by thermal degradation of polyisobutylenes having different initial molecular weights (M_{n0})

Temp. (°C)	Time (min)	M_{n0}[a] ×10^{-3}	C[b] (wt%)	M_n[a] ×10^{-3}	M_w/M_n[c]	Composition[d] (mol%) [i-Pr][e]	[t-Bu][f]	[TTD][g]	[TVD][h]	[NTTD][i]	Functionality[j] $f_{i\text{-Pr}}$	$f_{t\text{-Bu}}$	f_{TTD}	f_{TUD}	f_{NTTD}	f_t[k]	f_{tn}[l]
300	90	250	8.7	9.45	2.13	1.30	17.92	49.88	20.72	10.18	0.029	0.399	1.11	0.461	0.227	1.57	1.80
	90	64.8	6.2	10.1	2.29	1.18	17.29	50.34	21.22	9.97	0.026	0.384	1.12	0.471	0.221	1.59	1.81
	90	49.9	9.3	8.48	2.09	1.57	17.65	50.18	20.69	9.91	0.035	0.392	1.11	0.459	0.220	1.57	1.79
	90	7.09	19.1	3.30	1.81	3.34	18.39	48.87	17.74	11.66	0.076	0.416	1.11	0.402	0.264	1.51	1.77
	90	7.09	22.1	3.68	1.89	3.76	19.67	48.60	16.55	11.41	0.085	0.444	1.10	0.374	0.258	1.47	1.73
	90	3.62	32.8	3.03	1.62	5.10	20.98	46.39	13.58	13.95	0.119	0.488	1.08	0.316	0.324	1.40	1.72
	90	2.30	38.7	1.93	1.40	9.54	25.45	38.21	13.26	13.54	0.221	0.589	0.88	0.307	0.313	1.19	1.50
320	45	250	21.5	5.52	1.83	1.42	16.65	51.13	18.92	11.89	0.032	0.378	1.16	0.429	0.270	1.59	1.86
	45	64.8	19.6	4.48	2.08	2.14	19.40	49.52	17.82	11.12	0.048	0.437	1.11	0.401	0.250	1.52	1.77
	45	49.9	23.1	4.02	2.04	2.67	19.96	49.75	17.03	10.59	0.060	0.446	1.11	0.381	0.237	1.49	1.73
	45	7.09	31.0	2.92	1.83	3.70	18.98	49.83	15.61	11.88	0.084	0.431	1.13	0.354	0.270	1.49	1.75
	45	3.62	42.4	2.17	1.60	4.84	19.69	47.64	13.26	14.57	0.113	0.461	1.12	0.310	0.341	1.43	1.77
	45	2.00	40.7	1.93	1.45	7.18	24.14	43.17	11.79	13.71	0.166	0.560	1.00	0.273	0.318	1.27	1.59

[a] Determined by measurements of limiting viscosity number

[b] Volatilization

[c] Determined by g.p.c. measurements

[d] 100 × [each CH_3 peak intensity/total CH_3 peak intensity (i-Pr + t-Bu + TTD + TVD + NTTD)]

[e] Iso-propyl; $(CH_3)_2CH\sim$

[f] Tert-butyl; $(CH_3)_3C\sim$

[g] Terminal trisubstituted double bond; $(CH_3)_2C{=}CH\sim$

[h] Terminal vinylidene double bond; $CH_2{=}C(CH_3)\sim$

[i] Non-terminal trisubstituted double bond; $\sim(CH_3)C{=}CH\sim$

[j] Average number of each functional group per molecule; $f = 2 \times$ [each functional group peak intensity]/total terminal peak intensity (i-Pr + t-Bu + TTD + TVD)

[k] Average number of terminal double bonds per molecule; $f_t = 2 \times ([TTD] + [TVD])/([i\text{-}Pr] + [t\text{-}Bu] + [TTD] + [TVD])$

[l] Average number of total double bonds per molecule; $f_{tn} = 2 \times ([TTD] + [TVD] + [NTTD])/([i\text{-}Pr] + [t\text{-}Bu] + [TTD] + [TVD])$

Table 6 Changes in composition ratios between functional groups of the non-volatile oligomers by thermal degradation of polyisobutylenes with different initial molecular weights (M_{n0})

Temp. (°C)	Time (min)	M_{n0} $\times 10^{-3}$	$\frac{[\text{t-Bu}]}{[\text{i-Pr}]}$	$\frac{[\text{TTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]+[\text{NTTD}]}{[\text{TVD}]}$	$\frac{[\text{TTD}]}{[\text{NTTD}]}$
300	90	250	13.8	2.41	2.90	4.90
	90	64.8	14.7	2.37	2.84	5.05
	90	49.9	11.2	2.43	2.90	5.06
	90	7.09	5.51	2.75	3.41	4.19
	90	7.09	5.23	2.94	3.63	4.26
	90	3.62	4.11	3.42	4.44	3.33
	90	2.30	2.67	2.88	3.90	2.82
320	45	250	11.7	2.70	3.30	4.30
	45	64.8	9.07	2.78	3.40	4.45
	45	49.9	7.48	2.92	3.54	4.70
	45	7.09	5.13	3.19	3.95	4.19
	45	3.62	4.07	3.59	4.69	3.27
	45	2.00	3.36	3.66	4.82	3.15

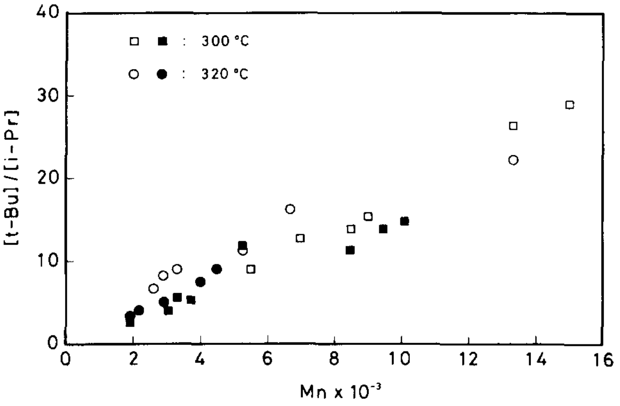


Figure 5 Plots of the composition ratios between respective functional groups of the non-volatile oligomers *versus* M_n of the non-volatile oligomers in the cases of various initial molecular weights (■●) and reaction times (□○)

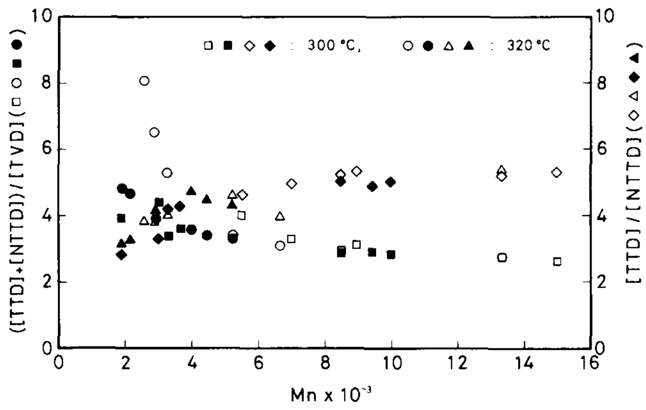


Figure 6 Plots of the composition ratios between respective functional groups of the non-volatile oligomers *versus* M_n of the non-volatile oligomers in the cases of various initial molecular weights (■◆●▲) and reaction times (□◇○△)

and a resulting decrease of kinetic chain length depresses the formation of the primary terminal macroradical ($R_p^{\bullet}$) in the depropagation step.

On the basis of these results, we could formulate a model of the whole degradation process of polyisobutylene including the self-diffusion-controlled termination mechanism, and the result of a computer simulation will be reported in a subsequent paper.

CONCLUSIONS

The formation of functional groups in non-volatile oligomers upon the thermal degradation of polyisobutylene is analysed by a kinetic approach to elucidate the effect of molecular weight of the matrix on the intermolecular hydrogen abstraction followed by β-scission. The results show a decrease in the radical concentration with decreasing molecular weight during the degradation, which is consistent with the result obtained for the volatile oligomers[4]. The decrease of radical concentration results from a large depression of kinetic chain length owing to the increase in the rate of self-diffusion-controlled bimolecular termination[4].

REFERENCES

1 Mita, I. and Horie, K. 'Degradation of and Stabilization of Polymers—1' (Ed. H. H. G. Jellinek), Elsevier, New York, 1983, p. 235
2 Mita, I. 'Aspects of Degradation and Stabilization of Polymers' (Ed. H. H. G. Jellinek), Elsevier, New York, 1978, p. 247
3 Sawaguchi, T., Tekesue, T., Ikemura, T. and Seno, M. *Macromol. Chem. Phys.* 1995, **196**, 4139
4 Sawaguchi, T. and Seno, M. *Polym. J.* 1996, **28**, 392
5 Sawaguchi, T., Ikemura, T. and Seno, M. *Macromol. Chem. Phys.* 1996, **197**, 215
6 Tsuchiya, Y. and Sumi, K. *J. Polym. Sci., Part A-1* 1969, **7**, 813
7 Kiran, E. and Gillham, K. J. *J. Appl. Polym. Sci.* 1976, **20**, 2045
8 Sawaguchi, T. and Seno, M. *Polymer* 1996, **37**, 3697
9 Kuroki, T., Sawaguchi, T., Suzuki, K., Ide, S. and Ikemura, T. *Polymer* 1983, **24**, 428
10 Sakaguchi, Y. and Sakurada, I. *Koubunsi Kagaku* 1948, **5**, 242
11 Exxon Chemical Co. Ltd, VISTANEX Polyisobutrylene—its Properties and Applications', Exxon Corporation, Houston, 1993
12 Cameron, G. G. *Makromol. Chem.* 1978, **100**, 255
13 Cameron, G. G., Meyer, J. M. and McWalter, I. T. *Macromolecules* 1978, **11**, 696
14 Fox, T. G. and Flory, P. J. *J. Phys. Colloid Chem.* 1951, **55**, 221