

Preparation and characterization of end-reactive oligomers by thermal degradation of polyisobutylene

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The chemical structure of the non-volatile oligomers ($M_n = 2600-9000$) isolated from the polymer residues obtained by the thermal degradation of polyisobutylene at 300 and 320°C was determined by 400 MHz ^1H n.m.r. spectroscopy with regard to the reactive end groups. The functional groups formed in the degradation process are as follows: tert-butyl end group (t-Bu), isopropyl end group (i-Pr), terminal trisubstituted double bond (TTD), terminal vinylidene double bond (TVD), and non-terminal trisubstituted double bond (NTTD). The average number of TTD and TVD per molecule (f_t) is in a range from 1.46 to 1.64. This value suggests that 53-67 mol% of the non-volatile oligomers are telechelic oligomers having both TTD and/or TVD, and 39-29 mol% of the oligomers are macromonomer-like oligomers having a double bond at one chain end. Both t-Bu and i-Pr are produced by the intermolecular hydrogen abstraction of primary and tertiary terminal macroradicals, and the subsequent β scission of the resulting on-chain macroradicals at the skeletal C-C bond of the main chain yields TTD and TVD. The formation of telechelic oligomer is interpreted by a major contribution of the hydrogen abstraction of volatile radicals, in addition to a minor contribution of the hydrogen abstraction of terminal macroradicals. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

End-reactive polymers and oligomers are useful for the preparation of block copolymers and the chemical modification of some polymers. In the case of polyisobutylene, the cationic 'inifer' method was developed by Kennedy *et al.*¹⁻¹⁰, and the resulting end-reactive polymers having one or two tert-chloro groups could be converted to terminal-unsaturated polymers with isopropenyl group by dehydrochlorination^{1,2}. Thereby, a large number of terminal-functionalized polyisobutylenes as well as various block copolymers were prepared by successive reactions of chloro and isopropenyl end groups³⁻¹⁰. More recently, various polyisobutylene block copolymers were also prepared by living carbocationic polymerization using TiCl_4 ¹¹⁻¹⁸.

In recent years, the thermal degradation of polymers has been widely reinvestigated to prepare useful polymers, oligomers and monomers¹⁹. Moreover, some pyrolysis processes have been developed as a method for recovering carbonaceous compounds and fuel from waste polymers in view of the increasing crisis of the global environment²⁰.

In a previous paper²¹, we reported that almost all the non-volatile oligomers obtained by the thermal degradation of polyisobutylene are composed of telechelic oligomers having both terminal trisubstituted double

bond (TTD) and terminal vinylidene double bond (isopropenyl group, TVD). By the 100 MHz ^1H n.m.r. spectroscopy, signals of TTD and TVD could be clearly detected, but tert-butyl (t-Bu) and isopropyl (i-Pr) end groups²², which formed by the intermolecular hydrogen abstraction of primary (p) and tertiary (t) terminal macroradicals ($\text{R}_p\cdot$ and $\text{R}_t\cdot$) followed by β scission, were not detected. It is very interesting that only the telechelic oligomers were selectively produced.

In this paper, these partial structures of non-volatile oligomers are exactly redetermined by 400 MHz ^1H n.m.r. spectroscopy and a reasonable mechanism for their formation is discussed. These end-reactive oligomers are proved to be useful as macromers and telechelics.

EXPERIMENTAL

Sample, apparatus and procedure

The polyisobutylene sample and the experimental procedure were described in detail elsewhere²³. Molecular weight characteristics of the purified polyisobutylene are as follows: $M_n = 2.50 \times 10^5$ and $M_w/M_n = 2.50$. 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 cm³ of chloroform and the solution was reprecipitated by dropping in 50 cm³ of acetone to remove a small amount of the semi-volatile oligomers with a relatively low volatility. The reprecipitates were

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termed the non-volatile oligomers and analysed after vacuum drying under heating. As reported previously²³, the non-volatile oligomers thus obtained were almost completely separated from the semi-volatile oligomers.

Analysis

The 400 MHz ¹H 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-d₁. 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. Abe *et al.*²⁴ measured 400 MHz ¹H n.m.r. spectra of TTD, TVD and the tertiary chloro end group of isobutylene oligomers prepared by living cationic polymerization, and adopted a pulse angle of 45° and a pulse repetition time of 15 s. In this measurement 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.

To assign exactly signals of the spectrum, a mixture of isobutylene nonamers and that of their hydrogenates were prepared as model compounds from the volatile oligomers by preparative g.p.c. (Toyo Soda HLC-802 UR) using a stainless-steel column of TSK-GEL (G2000HG6 × 2).

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

The number average molecular weight (M_n) was calculated by the following equation²⁵ 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.

Hydrogenation of the non-volatile oligomers

The catalytic hydrogenation of the volatile and non-volatile oligomers was carried out in a 200 cm³ stainless-steel autoclave with a mechanical stirrer at 70 rev min⁻¹. The hydrogenation conditions were as follows: sample concentration, about 10% (w/v) in cyclohexane; catalyst, 10 wt% Pt (5%)–charcoal; hydrogen added, ~70 kg cm⁻³; temperature 50°C, time 5 h. The reaction mixture was filtered to remove catalyst. In the case of the volatile oligomers, the filtrate was concentrated by evaporation, and then dried under vacuum at room temperature. For the non-volatile oligomers, the filtrate was dropped in acetone and the precipitate was analysed after vacuum drying under heating.

RESULTS AND DISCUSSION

The yield of the polymer residues and the characteristics of the non-volatile oligomers obtained by the thermal degradation of polyisobutylene at 300 and 320°C for 30–180 min are listed in Table 1. The M_n values of the non-volatile oligomers range from 2600 to 9000. The M_w/M_n value remains approximately constant at ~2 at 300°C and decreases slightly to ~1.5 at 320°C. The composition and functionality of the non-volatile oligomers and the parameter α given in Table 1 are discussed later.

Table 1 Yield of polymer residues, and the composition and functionality of respective end groups, double bonds of the non-volatile oligomers, value of parameter α by thermal degradation of polyisobutylene

Temp. (°C)	Time (min)	Yield ^a (wt%)	M_n^b ($\times 10^{-3}$)	M_w/M_n^c	Composition ^d (mol%)					Functionality ^f						α^m		
					[i-Pr] ^e	[t-Bu] ^f	[TTD] ^g	[TVD] ^h	[NTTD] ⁱ	f_{i-Pr}	f_{t-Bu}	f_{TTD}	f_{TVD}	f_{NTTD}	f_t^k		f_{in}^l	
300	0	0.0	250	2.50														
	120	88.5	8.97	2.24	1.04	16.01	52.90	20.13	9.92	0.023	0.355	1.17	0.447	0.220	1.62	1.84	3.9	
	180	83.5	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	3.2	
300	76.4	5.52	2.11	2.01	17.90	52.73	15.97	11.39	0.045	0.404	1.19	0.360	0.257	1.55	1.81	3.0		
320	0	0.0	250	2.50														
	30	85.9	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	4.4	
	60	78.1	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	3.3	
	90	52.2	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	3.8	
	120	40.4	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	2.5	
320	180	31.8	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	2.3	

^a $100 \times (\text{residue weight})/(\text{sample weight})$

^b By intrinsic viscosity measurements

^c Heterogeneity index of molecular weight distribution determined by g.p.c. measurements

^d $100 \times [\text{each CH}_3 \text{ peak intensity}/\text{total CH}_3 \text{ peak intensity (i-Pr + t-Bu + TTD + TVD + NTTD)}]$

^e Iso-propyl; $(\text{CH}_3)_2\text{CH}\sim$

^f Tert-butyl; $(\text{CH}_3)_3\text{C}\sim$

^g Terminal trisubstituted double bond; $(\text{CH}_3)_2\text{C}=\text{CH}\sim$

^h Terminal vinylidene double bond; $\text{CH}_2=\text{C}(\text{CH}_3)\sim$

ⁱ Non-terminal trisubstituted double bond; $\sim(\text{CH}_3)\text{C}=\text{CH}\sim$

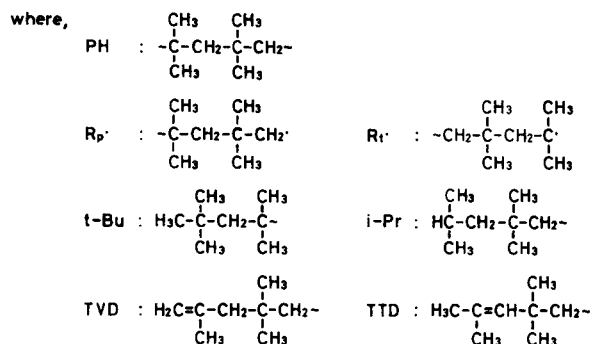
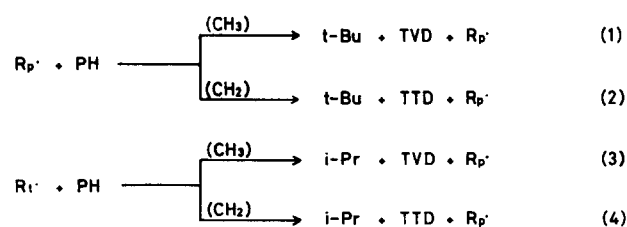
^j Average number of each functional group per molecule; $f = 2 \times [\text{each functional group peak intensity}]/\text{total terminal peak intensity (i-Pr + t-Bu + TTD + TVD)}$

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

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

^m Calculated from [TTD]

The chemical structures of the non-volatile oligomers are determined by the type of intermolecular hydrogen abstractions of $R_p\cdot$ and $R_t\cdot$ (see *Scheme 1* for the meanings of the symbols) and the subsequent β scission of the resulting on-chain macroradicals^{21,22}. These elementary reactions are summarized in *Scheme 1*. As shown in equations (1) and (2), the hydrogen abstraction of $R_p\cdot$ yields t-Bu and two types of on-chain macroradicals, depending on the position (CH₃ and CH₂) of hydrogen abstraction, and the β scission of the latter gives TVD and TTD. On the other hand, the hydrogen abstraction of $R_t\cdot$ produces i-Pr (equations (3) and (4)), and TVD and TTD are formed by the subsequent β scission. TVD and TTD given by equations (3) and (4) are the same as those formed by equations (1) and (2), respectively. Thus, only two types of on-chain macroradicals are formed depending on the two positions of intermolecular hydrogen abstraction (equations (1) and (3), and equations (2) and (4)), while the four types of on-chain macroradicals result from the back-bitings of $R_p\cdot$ and $R_t\cdot$ (refs 22, 23). Only TVD and TTD were identified by 100 MHz ¹H n.m.r. spectroscopy, but t-Bu and i-Pr



Scheme 1 Intermolecular hydrogen abstractions followed by β scissions of $R_p\cdot$ and $R_t\cdot$.

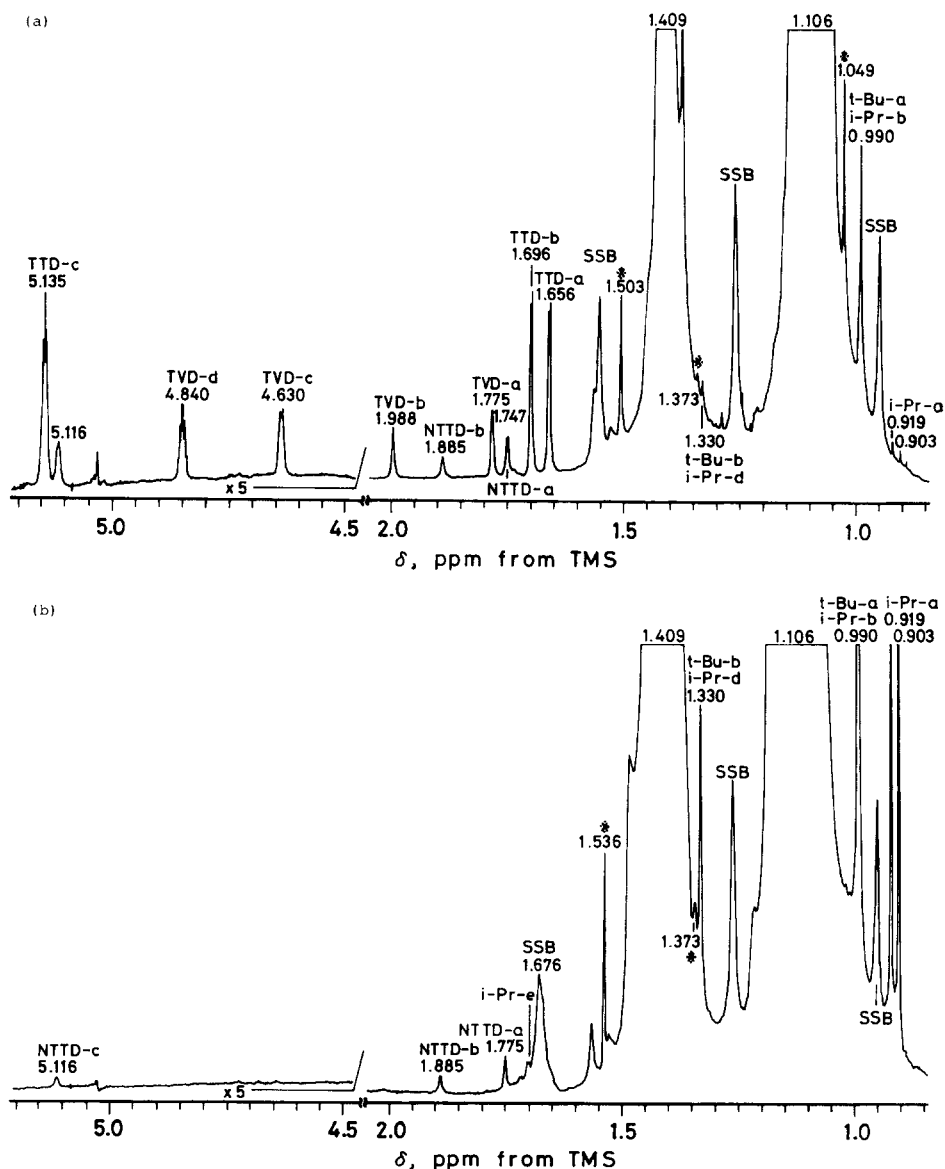


Figure 1 400 MHz ¹H n.m.r. spectra of the non-volatile oligomers (a) before and (b) after hydrogenation

could not be detected as reported before²¹ and, therefore, details of the intermolecular hydrogen abstraction of the macroradicals could not be made clear. An objective of this report is to detect these two saturated end groups of the non-volatile oligomers and to characterize the mechanism of thermodegradation of polyisobutylene.

The 400 MHz ¹H n.m.r. spectra of the non-volatile oligomers ($M_n = 7.09 \times 10^3$) prepared by the reaction at 320°C for 30 min and their hydrogenates are shown in Figures 1a and 1b, respectively. Most of the main components of the volatile oligomers consist of four types of the terminal mono-olefins made of a combination of two types of the saturated end groups (t-Bu and i-Pr) and two types of the terminal double bonds (TTD and TVD)²³. To assign these n.m.r. signals, a mixture of isobutylene nonamers containing only a small amount of decamers and that of their hydrogenates were prepared as the model compounds. The 400 MHz ¹H n.m.r. spectra of the nonamers before and after hydrogenation are

shown in Figures 2a and 2b, respectively. These signals of the spectra could be precisely assigned with reference to the well-defined n.m.r. signals of various isobutylene oligomers^{23,24,26-28} and polymers²¹. The characteristic n.m.r. signals assigned to the partial structures of the non-volatile oligomers are summarized in Table 2. Besides TTD and TVD²¹, non-terminal trisubstituted double bond (NTTD) as well as both t-Bu and i-Pr were first detected in this experiment. Almost all the signals identified in Figures 2a and 2b were also detected in the spectra in Figures 1a and 1b. The peaks marked with an asterisk in the figures are considered to be assigned to protons of the partial structures shown above, but are not yet identified. A signal assigned to i-Pr-c could not be detected in Figures 1a and 1b, because of its relatively small concentration with an increase in molecular weight. In summary, concerning the signals assigned to i-Pr, t-Bu and NTTD, the peaks at 0.903 and 0.919 ppm are assigned to protons of two methyl groups (i-Pr-a) of

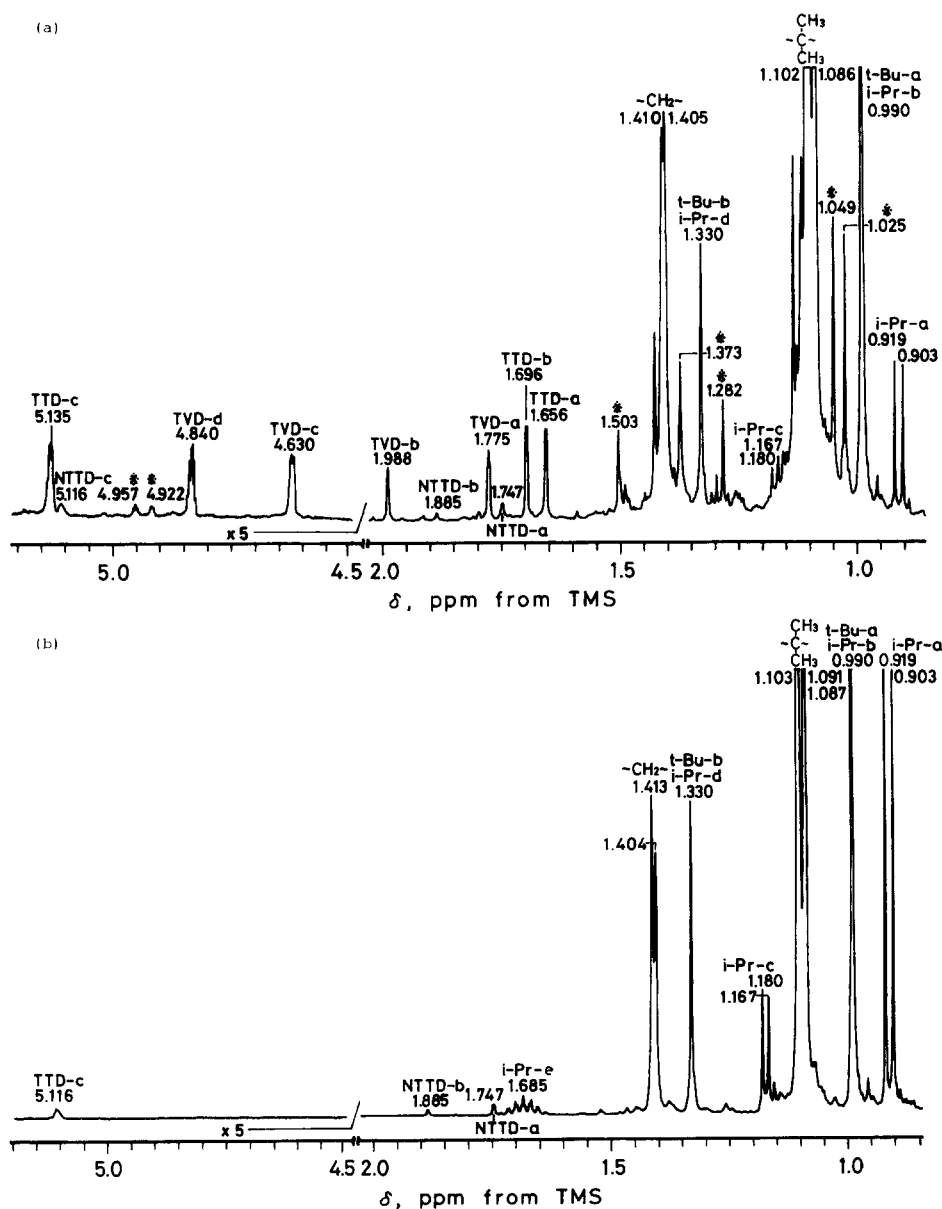


Figure 2 400 MHz ¹H n.m.r. spectra of a mixture of isobutylene nonamers prepared from the volatile oligomers (a) before and (b) after hydrogenation

Table 2 Summary of characteristic ^1H n.m.r. signals assigned to partial structures of isobutylene nonamers and non-volatile oligomers

Partial structures	Observed δ values (ppm from TMS) ^a	
$\begin{array}{c} \text{}^a\text{H}_3\text{C} \quad \text{}^c\text{H} \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{C}=\text{C}-\text{C}-\text{CH}_2-\text{C}\sim \\ \quad \quad \quad \\ \text{}^b\text{H}_3\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	a: 1.656 (d) c: 5.135 (m)	b: 1.696 (d)
$\begin{array}{c} \text{CH}_3 \quad \text{}^c\text{H} \quad \text{CH}_3 \\ \quad \quad \\ \sim\text{C}-\text{}^b\text{H}_2\text{C}-\text{C}=\text{C}-\text{C}\sim \\ \quad \quad \\ \text{CH}_3 \quad \text{}^a\text{H}_3\text{C} \quad \text{CH}_3 \end{array}$	a: 1.747 c: 5.116 (m)	b: 1.885
$\begin{array}{c} \text{}^d\text{H} \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{C}=\text{C}-\text{}^b\text{H}_2\text{C}-\text{C}-\text{CH}_2-\text{C}\sim \\ \quad \quad \quad \\ \text{}^c\text{H} \quad \text{C}^a\text{H}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	a: 1.775 c: 4.630 (m)	b: 1.988 d: 4.840 (m)
$\begin{array}{c} \text{}^a\text{H}_3\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{}^a\text{H}_3\text{C}-\text{C}-\text{}^b\text{H}_2\text{C}-\text{C}-\text{CH}_2-\text{C}\sim \\ \quad \quad \\ \text{}^a\text{H}_3\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	a: 0.990	b: 1.330
$\begin{array}{c} \text{}^a\text{H}_3\text{C} \quad \text{}^b\text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \quad \\ \text{}^c\text{H}-\text{C}-\text{}^e\text{H}_2\text{C}-\text{C}-\text{}^d\text{H}_2\text{C}-\text{C}\sim \\ \quad \quad \\ \text{}^a\text{H}_3\text{C} \quad \text{}^b\text{H}_3\text{C} \quad \text{CH}_3 \end{array}$	a(d): 0.903, 0.919 c(d): 1.167, 1.180 e: 1.685 (m)	b: 0.990 d: 1.330

^a Characters in parentheses represent multiplicity of signal of interest and underlined signals are observed in the spectra of the non-volatile oligomers

i-Pr, and a peak at 0.990 ppm is assigned to protons of two methyl groups (i-Pr-b) bonded to β -carbon from i-Pr and protons of three methyl groups (t-Bu-a). The signals of methine proton (i-Pr-e) and methylene protons (i-Pr-c) adjacent to the methine carbon appear around 1.77 ppm (multiplet) and at 1.167 and 1.180 ppm (doublet), respectively. The signals of protons of signs a, c and e of i-Pr are coupled with each other. Moreover, a peak at 1.330 ppm is assigned to protons of t-Bu-b and i-Pr-d. The signal of methylene proton of i-Pr-e was detected around 1.685 ppm in the spectrum of the hydrogenated nonamers (Figure 2b). The intensities of the peaks at 1.747, 5.116 and 1.885 ppm have a relative ratio of 3:1:2 and decrease markedly by hydrogenation, while the intensity of peak of t-Bu-a is unchanged before and after hydrogenation and, therefore, these peaks are assigned to methyl protons (NTTD-a) bonded to NTTD, an olefinic proton (NTTD-c) and methylene protons (NTTD-b) adjacent to NTTD, respectively. For the non-terminal vinylidene double bond (NTVD) structure deduced from the mechanism described later, the protons of two methylene groups bonded to NTVD and the two magnetically equivalent olefinic protons should appear as sharp singlet signals around 2.00 and 4.77 ppm, respectively, as suggested by Francis and Archer²⁶, but these signals were not detected.

The composition of these functional groups was determined from the intensities of signals corresponding to the methyl protons (i-Pr-a, i-Pr-b, t-Bu-a, TTD-a, TTD-b, TVD-a and NTTD-a). The signal intensity per methyl group of TTD, TVD and NTTD should be three times larger than that per olefinic proton (TTD-c, TVD-c

or TVD-d, and NTTD-c). This relationship between the relative intensities was checked and the data satisfying this relationship were adopted as the intensity per methyl group. The composition and functionality (f) of each of the end groups and double bonds of the non-volatile oligomers are given in Table 1. The functionality of the functional group of interest is defined as the average number of this functional group per molecule, and calculated by the following equation, assuming all the non-volatile oligomers are linear:

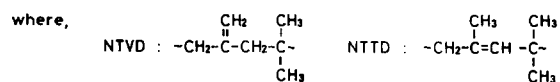
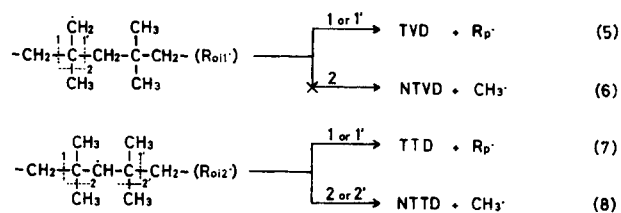
$$f = \frac{2 \times [\text{signal intensity of the functional group of interest}]}{[\text{signal intensity of all end groups (i-Pr + t-Bu + TTD + TVD)}]}$$

The functionalities f_t and f_{in} in Table 1 represent average numbers of the terminal double bonds and the total double bonds per molecule, respectively.

According to the products catalogue and a comment by Exxon Chemical Co. Ltd²⁹, the sample of polyisobutylene, which is prepared by cationic polymerization, is a linear polymer having a saturated end group and a terminal double bond; it is deduced from the cationic mechanism that the former is t-Bu and the latter is TTD or TVD. The values of M_n and M_w/M_n (Table 1) suggest that the scission reaction of the main chain occurs at a random position on the polymer. The average number of scissions, which is estimated by $(M_{n0}/M_n) - 1$, is from 24 to 124 for the non-volatile oligomers. Thereby, over 96% of the end groups of these oligomers are formed by the scission reactions; that is, most of the functional groups of the non-volatile oligomers are newly produced by the intermolecular hydrogen abstractions and the subsequent β scissions of both the macroradicals (equations (1)–(4)). The hydrogen abstractions of $R_p\cdot$ and $R_t\cdot$ yield t-Bu and i-Pr, respectively, and the β scissions at the skeletal C–C bond of the main chain produce TVD and TTD, depending on the types (CH_3 and CH_2) of abstracted hydrogens.

A reasonable mechanism for the formation of NTTD is shown in Scheme 2. The terminal functional groups formed depend on the position of β scission of the on-chain macroradicals ($R_{011}\cdot$ and $R_{012}\cdot$). The scission at the side methyl group (equations (6) and (8)) gives NTVD and NTTD, while the scission at the skeletal C–C bond (equations (5) and (7)) affords TVD and TTD. The present experiment shows that NTVD is not produced but NTTD is produced. This result suggests that the reactivity for β scissions is related to the segmental rotational motion of the reacting radical.

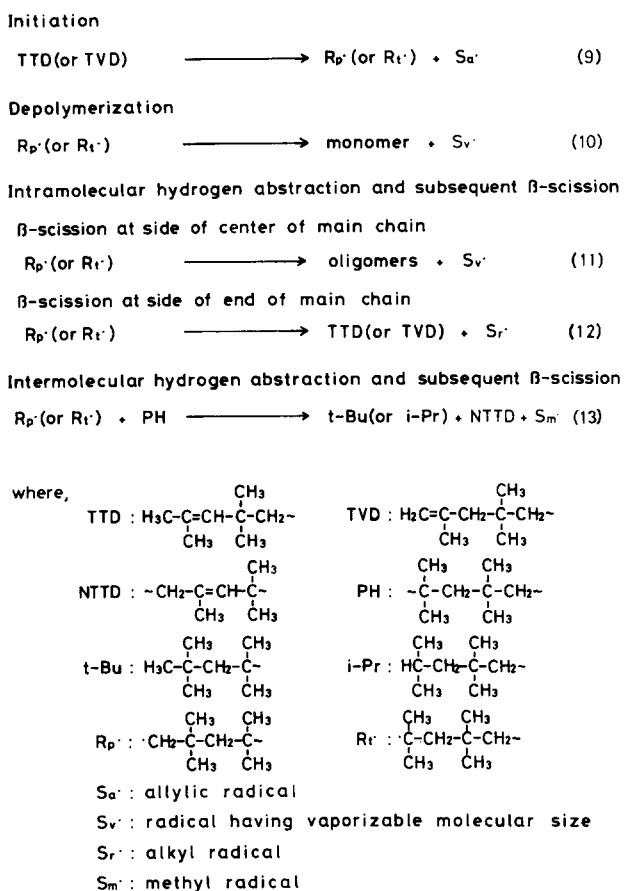
As shown in Table 1, the functionalities of the t-Bu and

**Scheme 2** β Scissions of the on-chain macroradicals ($R_{011}\cdot$ and $R_{012}\cdot$), leading to the non-terminal double bonds

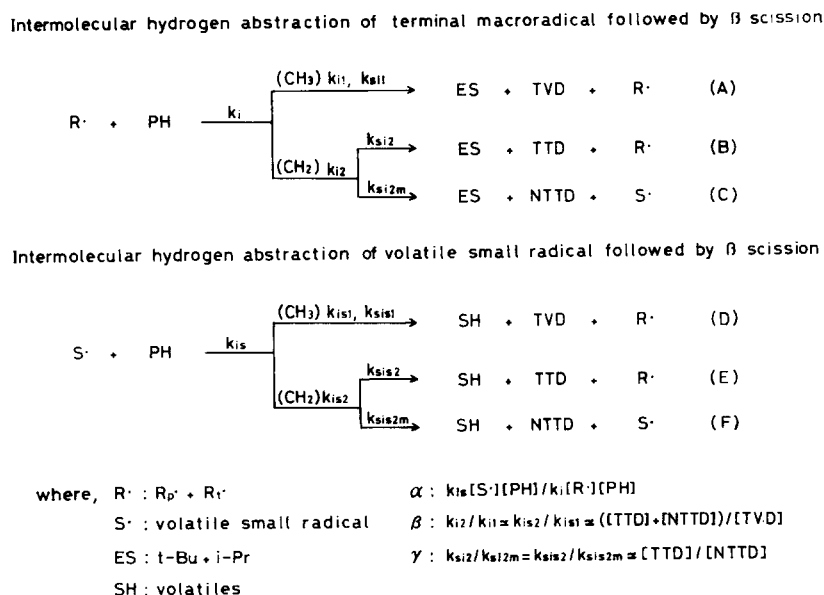
i-Pr increase, and in particular that of TVD decreases as the degradation proceeds at both temperatures. It is noteworthy that the f_t value decreases from 1.64 to 1.46 with the degradation time at 320°C. If the structural changes of the non-volatile oligomers occur only by the intermolecular hydrogen abstractions of $R_p\cdot$ and $R_t\cdot$ and the subsequent β scission, the f_t value tends statistically towards 1, because both the saturated and the unsaturated

end groups are formed through elementary reactions. In such a situation, the f_t value is considered to be kept at a constant value of around 1 during the degradation, because the f_t value is expected to be independent of the concentration of macroradicals, although the concentration of $R_p\cdot$ decreases as reactions proceed³⁰. However, the observed value of f_t changes from 1.64 to 1.46; this result could not be interpreted only on the basis of equations (1)–(4). An f_t value greater than 1 was also found for the non-volatile oligomers formed by the thermal degradation of isotactic polypropylene³¹. In order to resolve this problem, our attention is directed to the volatile radicals ($S\cdot$), which have not been taken into consideration hitherto. The volatile radicals disappear by vaporization from the reaction field without further reactions with the molten polymer. Recently, it was noted that the intermolecular hydrogen abstraction of $S\cdot$ from polymer molecules plays an important role in the total reactions^{32–35}. In the case of polyisobutylene³⁶, it is indicated that the rate of volatilization of the volatile products decreases as the degradation proceeds and that the kinetic chain length decreases owing to a change in the rate ratio between the disappearance (a quasi-termination) by vaporization and the intermolecular hydrogen abstraction of $S\cdot$. Elementary reactions leading to the formation of $S\cdot$ are shown in *Scheme 3*. Equation (9) represents the formation of an allylic radical by the end initiation of a molecule having a terminal double bond. In equations (10) and (11) the volatile radicals are formed by depolymerization and back-biting followed by β scission^{22,23}, respectively. In equation (12), an alkyl radical is formed by β scission at the end of the main chain. Equation (13) represents the formation of a methyl radical together with NTTD.

A statistical reaction model which traces a change of the f_t value is given in *Scheme 4*. This is composed of the intermolecular hydrogen abstractions of terminal macroradicals (equations (A)–(C)) and volatile radicals (equations (D)–(F)), and the subsequent β scissions of the on-chain macroradicals. The hydrogen abstraction in equations (A)–(C) produces a saturated end group (ES) of the non-volatile oligomers, and the subsequent β



Scheme 3 Possible reaction scheme for the formation of volatile radicals ($S\cdot$) during degradation



Scheme 4 A reaction model for statistical analysis on the saturated and unsaturated end groups of the non-volatile oligomers

Table 3 Statistical weight and molar ratio of end groups derived from the model

Eq.	Rate	Statistical weight	Molar ratio			
			[ES]	[TVD]	[TTD]	[NTTD]
A	$\frac{(k_{i1})k_i[R\cdot][PH]}{(k_{i1} + k_{i2})}$	$\frac{1}{(1 + \beta)}$	$\frac{1}{(1 + \beta)}$	$\frac{1}{(1 + \beta)}$	0	0
B	$\frac{(k_{si2})(k_{i2})k_i[R\cdot][PH]}{(k_{si2} + k_{si2m})(k_{i1} + k_{i2})}$	$\frac{\beta\gamma}{(1 + \beta)(1 + \gamma)}$	$\frac{\beta\gamma}{(1 + \beta)(1 + \gamma)}$	0	$\frac{\beta\gamma}{(1 + \beta)(1 + \gamma)}$	0
C	$\frac{(k_{si2m})(k_{i2})k_i[R\cdot][PH]}{(k_{si2} + k_{si2m})(k_{i1} + k_{i2})}$	$\frac{\beta}{(1 + \beta)(1 + \gamma)}$	$\frac{\beta}{(1 + \beta)(1 + \gamma)}$	0	0	$\frac{\beta}{(1 + \beta)(1 + \gamma)}$
D	$\frac{(k_{is1})k_{is}[S\cdot][PH]}{(k_{si1} + k_{si2})}$	$\frac{\alpha}{(1 + \beta)}$	0	$\frac{\alpha}{(1 + \beta)}$	0	0
E	$\frac{(k_{sis2})(k_{is2})k_{is}[S\cdot][PH]}{(k_{sis2} + k_{sis2m})(k_{is1} + k_{is2})}$	$\frac{\alpha\beta\gamma}{(1 + \beta)(1 + \gamma)}$	0	0	$\frac{\alpha\beta\gamma}{(1 + \beta)(1 + \gamma)}$	0
F	$\frac{(k_{sis2m})(k_{is2})k_{is}[S\cdot][PH]}{(k_{sis2} + k_{sis2m})(k_{is1} + k_{is2})}$	$\frac{\alpha\beta}{(1 + \beta)(1 + \gamma)}$	0	0	0	$\frac{\alpha\beta}{(1 + \beta)(1 + \gamma)}$
A, B, C, D, E, F			1	$\frac{(1 + \alpha)}{(1 + \beta)}$	$\frac{(1 + \alpha)\beta\gamma}{(1 + \beta)(1 + \gamma)}$	$\frac{(1 + \alpha)\beta}{(1 + \beta)(1 + \gamma)}$

Table 4 Molar ratios and functionality products by thermal degradation of polyisobutylene estimated from the model

Eq.	Molar ratio			Functionality	
	[ES-ES]	[ES-EU]	[EU-EU]	f_t	f_n
A, B, C, D, E, F	1	$\frac{2(1 + \alpha)(1 + \beta\gamma + \gamma)}{(1 + \beta)(1 + \gamma)}$	$\frac{((1 + \alpha)(1 + \beta\gamma + \gamma))^2}{((1 + \beta)(1 + \gamma))^2}$	$\frac{2(1 + \alpha)(1 + \beta\gamma + \gamma)}{(1 + \beta)(1 + \gamma) + (1 + \alpha)(1 + \beta\gamma + \gamma)}$	$\frac{2(1 + \alpha)(1 + \beta)(1 + \gamma)}{(1 + \beta)(1 + \gamma) + (1 + \alpha)(1 + \beta\gamma + \gamma)}$

scission (equations (A) and (B)) produces an unsaturated end group [EU : TVD + TTD]. On the other hand, in equations (D)–(F), volatile oligomers SH formed from the hydrogen abstraction of S· disappear by vaporization from the reaction residue and only unsaturated groups are produced as the non-volatile oligomers. Although the component SH has not yet been quantitatively analysed, isobutylene monomer, 2,4-dimethyl-2-pentene and methane have been detected²². The saturated compounds²³ in the volatile oligomers would be saturated isobutylene oligomers produced from hydrogen abstraction of S_r· (equation (12)). The semi-volatile oligomers²³ which were fractionated from the polymer residues may be related to S_v· formed in equations (10) and (11). Thus, the formation ratio of respective functional groups of the non-volatile oligomers is expressed by the rate ratio of the hydrogen abstractions of radicals. The α value is defined as a statistical weight for analysis of statistical probability of formation of functional groups by the following equation:

$$\alpha = \frac{\text{rate of intermolecular hydrogen abstraction of } S\cdot}{\Sigma(\text{rate of intermolecular hydrogen abstractions of } R\cdot)}$$

Moreover, two other parameters, β and γ , of statistical weight are defined by the ratio of kinetic parameters as follows:

$$\beta = \frac{k_{i2}}{k_{i1}} \cong \frac{k_{is2}}{k_{is1}} \cong \frac{[\text{TTD}] + [\text{NTTD}]}{[\text{TVD}]}$$

$$\gamma = \frac{k_{si2}}{k_{si2m}} = \frac{k_{sis2}}{k_{sis2m}} \cong \frac{[\text{TTD}]}{[\text{NTTD}]}$$

Table 5 Values of parameters β and γ on thermal degradation of polyisobutylene

Temp. (°C)	Time (min)	β	γ
300	120	3.12	5.33
	180	3.31	4.99
	300	4.02	4.63
320	30	3.12	3.93
	60	3.38	4.65
	90	5.28	4.00
	120	6.46	3.82
	180	8.06	3.82

The molar ratios of respective end groups and components of the non-volatile oligomers and the f_t value are given in terms of α , β and γ as represented in Tables 3 and 4. ES-ES, ES-EU and EU-EU represent components having two ES, one ES and one EU, and two EU, respectively. In the hydrogen abstractions shown by equations (A) and (B) (at $\alpha = 0$), the f_t value as well as both the ES and EU values are found to be 1.0, independent of the radical concentration. In this case, the molar fraction of the components ES-ES, ES-EU and EU-EU should be a ratio of 1:2:1. On the other hand, in the hydrogen abstraction by equations (D) and (E) (at $\alpha = \infty$), no ES end is formed and all of the non-volatile oligomers consist of only the component EU-EU; the f_t value is 2.0.

The present result described above suggests competitive occurrence of the reactions in equations (A)–(F).

The values of statistical weights β and γ are related to the ratios $([TTD] + [NTTD])/[TVD]$ and $[TTD]/[NTTD]$, respectively. The estimated values of β and γ are listed in Table 5. At both temperatures, the values of β increase with time, while γ decreases somewhat. Thus, these

values are not kept constant during the degradation. The compositions of end groups and components and the functionality calculated from the model with the assigned values of α , β and γ are listed in Table 6. In this model, the composition [ES] is dependent only on the α value.

Table 6 Compositions and functionality of products by thermal degradation of polyisobutylene estimated from the model with various assigned values of statistical weights

Statistical weight			Composition (mol%)				Composition (mol%)			Functionality	
α	β	γ	[ES]	[TVD]	[TTD]	[NTTD]	[ES-ES]	[ES-EU]	[EU-EU]	f_i	f_{in}
2.0	3.0	3.8	25.0	18.8	44.5	11.7	8.0	40.6	51.4	1.43	1.70
2.0	3.0	5.4	25.0	18.7	47.5	8.8	7.5	39.8	52.7	1.45	1.65
2.0	3.3	4.7	25.0	17.4	47.5	10.1	7.7	40.2	52.1	1.44	1.67
2.0	8.0	3.8	25.0	8.3	52.8	13.9	8.4	41.2	50.4	1.42	1.74
2.0	8.0	5.4	25.0	8.3	56.3	10.4	7.8	40.2	52.0	1.44	1.67
5.0	3.0	3.8	14.3	21.4	50.9	13.4	2.7	27.6	69.7	1.67	1.98
5.0	3.0	5.4	14.3	21.4	54.2	10.1	2.5	26.7	70.8	1.68	1.91
5.0	3.3	4.7	14.3	19.9	54.3	11.5	2.6	27.1	70.3	1.68	1.94
5.0	8.0	3.8	14.3	9.5	60.3	15.9	2.9	28.2	68.9	1.66	2.04
5.0	8.0	5.4	14.3	9.5	64.3	11.9	2.6	27.2	70.2	1.68	1.95

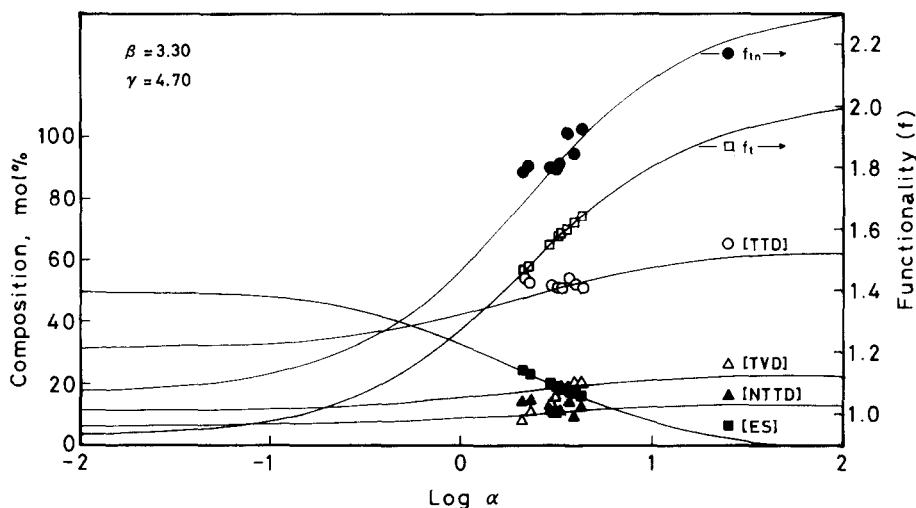


Figure 3 Changes in composition of respective end groups and f_i and f_{in} values with the α value

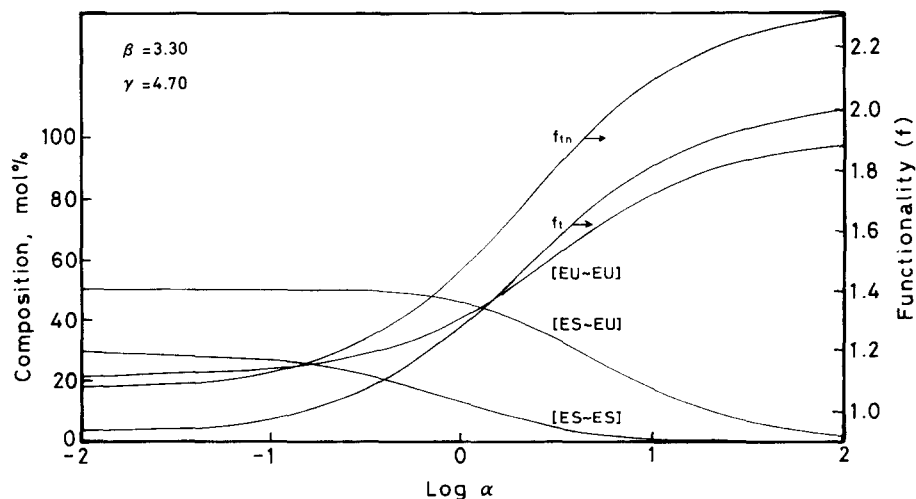


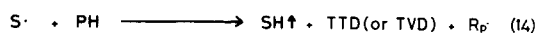
Figure 4 Changes in composition of respective components and the f_i and f_{in} values with the α value

With an increasing β value, the composition [TVD] decreases and the compositions [TTD] and [NTTD] increase. [TTD] increases and [NTTD] decreases as the γ value increases. However, the composition of each component and the functionality are markedly dependent not on the β and γ values but on the α value.

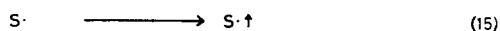
Changes in composition of the end groups and of the components with the α value are shown in Figures 3 and 4, where the values of β and γ are set at 3.3 and 4.7, respectively. In Figure 3 the observed values of respective functional groups are plotted by using the f_i value as reference. As shown above, the f_i values are calculated from compositions of the saturated end groups (ES: i-Pr + t-Bu) and the unsaturated end groups (EU: TTD + TVD). The observed values of [ES] and [EU] are consistent with the estimated values, but [TTD] and [NTTD] increase and [TVD] decreases with a decrease in the f_i value, in contrast with the trend of curves shown in Figure 3. This discrepancy is a result of a marked increase in the β value observed (Table 6).

In this statistical analysis, the α value can also be calculated from the composition of the end groups. Therefore, the observed values of [TTD] given in Table 1 show that the α value decreases from 4.4 to 2.3 as the degradation proceeds. The component EU-EU, a telechelic oligomer having two reactive end groups, constitutes 67–53 mol% of the non-volatile oligomers, while the component EU-ES, a macromonomer-like oligomer having one reactive end group, constitutes 29–39 mol%. This decrease of the α value with time would be caused by a decrease in the radical concentration ratio ($[S\cdot]/\Sigma[R\cdot]$); this is interesting in connection with the effect of the physical factors on the elementary reactions^{23,30}. As shown in Scheme 5, if the hydrogen abstraction (equation (14)) and the disappearance by vaporization (equation (15)) of $S\cdot$ occur competitively, the decrease in the volume and molecular weight of the molten polymer during degradation (Table 1) would result in a decrease in the α value. This is considered to be evidence for a decrease in the rate of volatilization with time³⁶. Thus, the thermal degradation of polyisobutylene is mainly controlled by the elementary reactions of $S\cdot$ as well as $R_p\cdot$ and $R_t\cdot$ which are produced during the degradation, and the concentrations of these radicals change with time. Moreover, the rates of change in concentration of the respective radicals are expected to differ markedly from each other, as suggested from the result that the concentration ratio ($[R_p\cdot]/[R_t\cdot]$) decreases as the reactions proceed³⁰. To elucidate a reasonable mechanism for the total reactions, further information is needed on a kinetic analysis for structural changes of the non-volatile oligomers, and studies for this purpose are now in progress.

Intermolecular hydrogen abstraction and subsequent β -scission



Vaporization without the abstraction in the polymer residue



where, $S\cdot$: volatile small radicals

SH : volatiles

Scheme 5 Competitive reaction scheme for disappearance of $S\cdot$

In conclusion, the functional groups of the non-volatile oligomers are produced via the intermolecular hydrogen abstractions of $R_p\cdot$ and $R_t\cdot$ and the subsequent β scissions of resulting on-chain macroradicals. The presence of NTTD and the absence of NTVD are clearly demonstrated. The f_i value changes from 1.64 to 1.46. If the functional groups are formed by the intermolecular hydrogen abstractions of $R_p\cdot$ and $R_t\cdot$ and the subsequent β scissions, the f_i value is calculated to be 1. The observed values of f_i could be reasonably explained by taking into consideration the intermolecular hydrogen abstractions of $S\cdot$ in addition to $R_p\cdot$ and $R_t\cdot$. The decrease in the α value with progress of the degradation is due to a decrease of the $[S\cdot]/\Sigma[R\cdot]$ ratio, which is caused by a decrease in physical factors such as volume and molecular weight of the molten polymer matrix. Statistical analysis of the observed f_i value shows that 53–67 mol% of the non-volatile oligomers is telechelic oligomer having both TTD and/or TVD, and 39–29 mol% of the oligomers is macromonomer-like end-reactive oligomer having TTD or TVD only at one chain end.

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