Distribution of double bonds in thermally degraded polyisobutylene

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The distribution of double bonds in thermally degraded polyisobutylene was determined quantitatively by using pulsed Fourier transform ^1H n.m.r. spectroscopic analysis. The double bonds in the degraded polymer did not exist in the interior but at the terminal positions of the polymer chain. These olefins were of the terminal trisubstituted and terminal vinylidene types. The content of the former was much greater than that of the latter. This shows that radical chain transfer predominantly occurs at the methylene hydrogen rather than at the methyl groups of the polymer chain. The average number of double bonds per molecule, *f*, was greater than 1 and tended to be near 2. Thereby most of the degraded polyisobutylene was shown to have two terminal unsaturations per molecule.

Keywords Thermal degradation; double bond; polyisobutylene; pulsed Fourier transform ^1H nuclear magnetic resonance; telechelics; reactive oligomer

INTRODUCTION

The mechanism of thermal degradation of polymers is an interesting subject not only because of fundamental interest in the polymeric reaction but also with regard to heat resistance, characteristics of polymer processing such as extrusion or injection moulding, and the effective utilization of plastic wastes. Recently the thermal degradation of polymers has been widely reinvestigated to synthesize new compounds, polymers, oligomers and monomers[1], and is very interesting as an important unit reaction in synthetic chemistry.

The thermal degradation of polyisobutylene (PIB) is similar to that of polystyrene (PS), which has been studied in relatively great detail[2,3]. The volatiles consist of oligomers having a number of carbons in the range of about C_1 to about C_{28} and the monomer content is over 10%[4,5]. It has been shown from the results of structural analysis of the volatiles that the formation of mainly volatiles is caused via intramolecular chain transfer (back-biting) of macroradicals[6,7]. It has also been reported from the changes in the rate of volatilization, as well as from determination of the molecular weight and the molecular weight distribution, that the kinetic chain length (*KCL*) is relatively long[8] and is about 30 (also about 30 for PS)[9]. In all cases the degradation has been discussed with respect to a radical chain mechanism and the changes in chemical structure of the products should correspond to this mechanism. However, the changes in chemical structure of the thermally degraded polymer have not been analysed, in contrast to that of the volatiles. The authors wish to determine here the chemical structure of the thermally degraded polymer from this point of view. Since the double bonds in the thermally degraded polymer are considered to be formed mainly via radical chain transfer followed by β-scission during propagation, and via the bimolecular termination of both the macroradicals, determination of the distribution of double bonds is of significance for the whole degradation.

The purpose of this study is to determine the double bond distribution by pulsed Fourier transform n.m.r. spectroscopy, and then to discuss the mechanism of thermal degradation. In this paper, qualitative and quantitative analyses of the double bonds in the thermally degraded polymer are also examined in greater detail as given below.

EXPERIMENTAL

Polyisobutylene

The polyisobutylene used was a commercial 'Vistanex L-80' grade, and was purified by dissolving in hot xylene under nitrogen and precipitating with acetone. The precipitate was washed with methyl alcohol several times, and was then dried under vacuum.

Apparatus and procedure for thermal degradation

The flow diagram of the apparatus for thermal degradation is shown in *Figure 1*. The apparatus was made of Pyrex glass. The degradation experiments were done using the following procedure. One gram of sample was placed in a flask and the air in the apparatus was replaced by nitrogen, which was reported to contain 0.0007% by volume of oxygen and to be over 99.999% purity, at a pressure of 4 mmHg. The flask was contacted with the metal bath maintained at a specified temperature and was then immediately immersed in the bath, when the sample attained a temperature of ~200°C. The reaction temperature was measured by an alumel–chromel thermocouple installed at the bottom of the flask and was controlled to ±2°C during the experiment. The volatiles were recovered by a liquid fraction trap cooled by a dry ice–methyl alcohol bath. After the reaction the thermally degraded polymer in the flask was dissolved in xylene and

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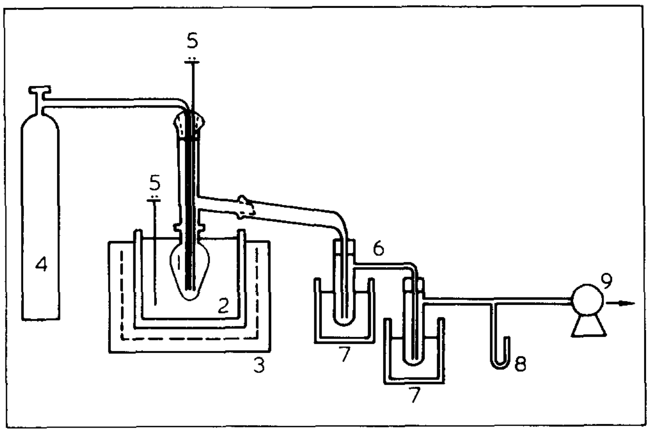


Figure 1 Flow diagram of the apparatus used for thermal degradation: 1, flask; 2, metal bath; 3, electric furnace; 4, N_2 gas; 5, thermocouple; 6, liquid fraction trap; 7, dry ice–methyl alcohol bath; 8, mercury manometer; 9, vacuum pump

was then reprecipitated with acetone. The reprecipitate was used as the sample for analysis after vacuum drying. The volatiles were dissolved in acetone.

ANALYSIS

^1H n.m.r. spectra were measured using a Jeol JNM-FX100 spectrometer operating at 99.6 MHz and room temperature, with an internal lock. Sample concentrations were approximately 13% (w/v) in a 1:2 (by volume) mixture of carbon tetrachloride (E. Merk, Uvasol, 99.7% purity) and chloroform-d_1 (E. Merk, Uvasol, 99.95% deuteration); 5 mm sample tubes were used. Tetramethyl silane (TMS) was used as an internal standard for chemical shifts. 1,1,1,2-Tetrachloroethane (Tokyo Chemical Industry, Co., Ltd, 99.9% purity) was used as an internal standard for quantitative analysis. The sample tubes were de-aerated by several freeze–pump–thaw cycles of a vacuum system and were then sealed with a Teflon cap, after nitrogen gas was admitted into the evacuated tube. Spectral widths were 1 kHz, excluding the overflowing spectral region except for the chemical shift range of about 3–6 ppm, with 8192 data points acquired on a JEC 980 computer. The pulse widths were 8 μs (a 45° pulse) with pulse repetition of 10 s and 2000–10 000 scans.

The intensity of the peak in ^1H n.m.r. spectra was measured by a spectral integration curve (integration method) and by cutting out and weighing each band area in a Xerox copy of the expanded spectrum (weighing method).

The number average molecular weight, $\bar{M}_n$, was calculated by the following equation after measuring the intrinsic viscosity at 30°C in toluene, as per Sakaguchi *et al.*[10]:

$$[\eta]=3.71\times10^{-4}P^{0.75} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity ($l\,g^{-1}$), and P is the number average degree of polymerization determined by the osmotic pressure method. Solution viscosities were measured using an Ostwald viscometer, and $[\eta]$ was determined from the four-point measurement by extrapolation.

The concentration of the double bonds in the thermally degraded polymer was determined using the iodine–mercury acetate–trichloroacetic acid method (an improved Wijis method) which was applied earlier to the thermal degradation products of atactic polypropylene by Ogata *et al.*[11]

For a qualitative analysis of the double bonds in the thermally degraded polymer, the isobutylene oligomers were prepared as olefinic model compounds from the pyrolysis products, as explained elsewhere[12], using preparative gel permeation chromatography (g.p.c.) This employed a Toyo Soda HLC-802 UR high-speed liquid chromatograph equipped with differential refractometer and u.v. detector, and with a stainless-steel column containing TSK-GEL (G3000HG6 + G2000HG6) of Toyo Soda Manufacturing Co. Ltd. The molecular weight (M^+) of the isolated pentamers was determined by GC-Mass spectrometer (Shimadzu LKB 9000) equipped with a data processor (Shimadzu MSPAK 300B).

RESULTS AND DISCUSSION

A summary of the results obtained by thermal degradation at 320°C is given in *Table 1*. The expanded ^1H n.m.r. spectrum of the thermally degraded polymer is given in *Figure 2*. The three multiplet signals around 4.64, 4.84 and 5.14 ppm can be seen. The signal at 4.28 ppm is assigned to the two protons in 1,1,1,2-tetrachloroethane used as an internal standard for quantitative analysis.

The double bonds in the thermally degraded polymer are formed by propagation and termination, and removed by end-initiation. The distribution of double bonds is considered to be mainly dependent upon the propagation step because of the long *KCL*[8]. In the case of the propagation step, the double bonds are formed via intermolecular radical transfer followed by β-scission. The four chemical structures estimated from the position of β-scission are as follows:

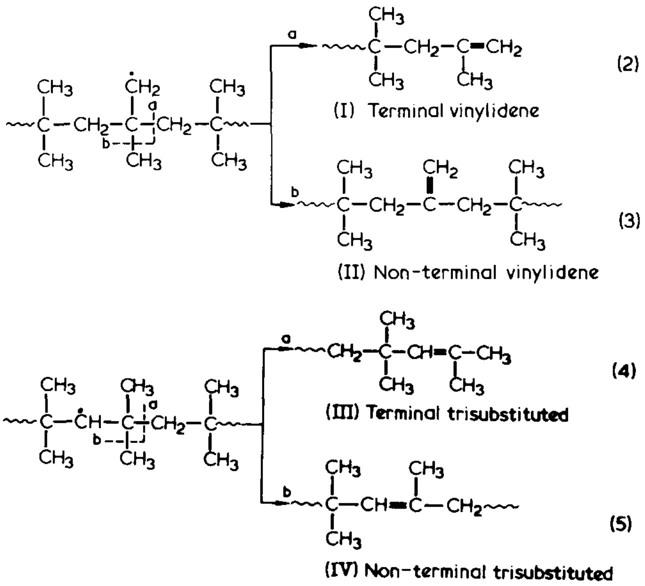


Table 1 Results of degradation of polyisobutylene at 320°C

Time (min)	Volatilization (%)	$\bar{M}_n$
15	14.6	6400
30	24.9	4500
60	35.9	3700
120	60.2	2400

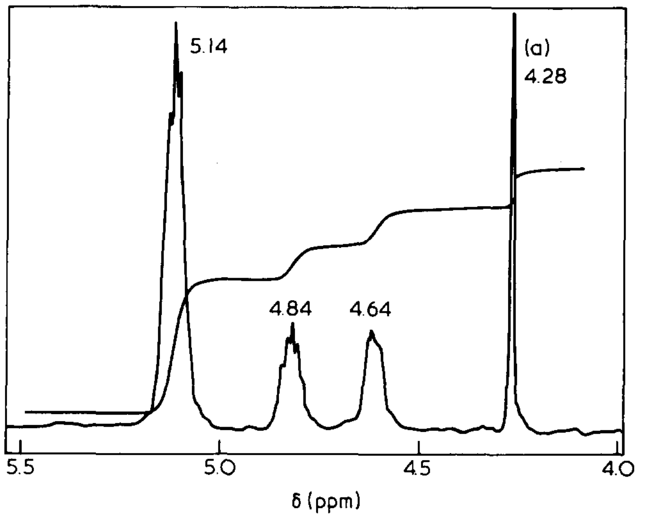


Figure 2 Expanded ^{1}H n.m.r. spectrum of the thermally degraded polyisobutylene: peak (a) is 1,1,1,2-tetrachloroethane used as internal standard

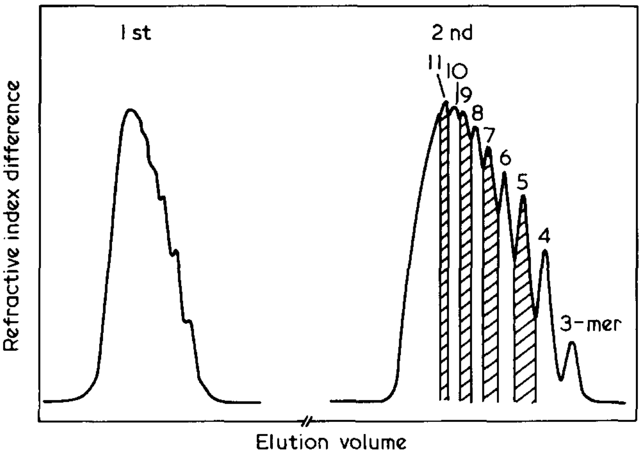


Figure 3 Recycle gel permeation chromatogram of the isobutylene oligomers

If the double bonds are formed by a disproportionation termation, which is a minor contribution for the whole degradation, the structures I and III are to be expected.

The ^{1}H n.m.r. spectrum of isobutylene oligomers (trimers and tetramers) having the partial structures I, II, III and IV have been measured by Francis *et al.*[13] and Manatt *et al.*[14] in carbon tetrachloride solution. According to their results, the two non-equivalent olefinic protons of structure I show absorption in the 4.55–4.63 and 4.73–4.80 ppm regions, respectively, and with equal intensities. The signal of the two equivalent olefinic protons of structure II appears in the 4.73–4.80 ppm region. The olefinic proton of structure III shows an absorption in the 5.08–5.10 ppm region. The absorption of the olefinic proton of structure IV appears at 5.12 ppm and is observed slightly downfield compared to that of structure III. Manatt *et al.*[14] and Paskas *et al.*[15] have determined by ^{1}H n.m.r. spectroscopy the double bonds in polyisobutylene having a relatively lower weight ($\bar{M}_n = 500$–3600). The absorptions of olefinic protons of structure I appear at 4.68 and 4.87 ppm[14], or at 4.62 and 4.82 ppm[15]. The olefinic proton of structure III shows an absorption at 5.21 ppm[14], or at 5.12 ppm[15]. Thus the chemical shift corresponding to these structures is dependent upon the conditions of measurement as well as the $\bar{M}_n$ of the sample. Paskas *et al.*[15] have recognized a sharp absorption at 4.77 ppm and have assigned it to a structure similar to structure II. We have isolated isobutylene oligomers (5, 7, 9 and 11 monomer units) from the liquid products obtained by thermal degradation of PIB, using preparative g.p.c. The chromatogram is shown in *Figure 3*. The expanded ^{1}H n.m.r. spectrum of the region for olefinic protons of the pentamer fraction is shown in *Figure 4*. These oligomers consist mainly of the terminal mono-olefins having partial structures I and III, as is previously known[6,7]. As shown in *Figure 4*, two signals of equal intensities around 4.64 and 4.85 ppm are assigned to structure I, and a signal around 5.14 ppm is assigned to structure III. The chemical shift was not dependent upon the number of monomer units. From the results mentioned above, in *Figure 2* a signal around 5.14 ppm is assigned to a terminal trisubstituted olefinic proton (structure III) and two signals of equal intensities around 4.64 and 4.84 ppm are assigned to terminal olefinic protons (structure I). As a result, it becomes clear that the double bonds in the thermally degraded polymer do not consist of structures II and IV, but are likely to have structures I and III, and the β-scission of primary and secondary macroradicals in the above equation occurs exclusively at the position a of the C–C bond in the polymer chain.

The concentrations of terminal trisubstituted olefins (U_{tri}) or terminal vinylidene olefins (U_{vin}) per unit weight of thermally degraded polymer (mol g^{-1}) are determined by ^{1}H n.m.r. spectroscopy using the following equation[15]:

$$U_{tri} \text{ or } U_{vin} = \frac{W_{in}}{M_{in}} n \frac{I_s}{I_{in}} \frac{1}{W_s} \qquad (6)$$

where M_{in} is molecular weight (167.85) of 1,1,1,2-tetrachloroethane used as an internal standard; W_{in} is weight of 1,1,1,2-tetrachloroethane in the sample tube (g); I_{in} is the signal intensity of protons (around 4.28 ppm) of 1,1,1,2-tetrachloroethane; I_s is the signal intensity of olefinic protons (around 5.14 ppm) of terminal trisubstituted double bond or olefinic protons (around 4.64 and 4.84 ppm; $I_s = (I_{4.64} + + I_{4.84})/2$) of vinylidene double

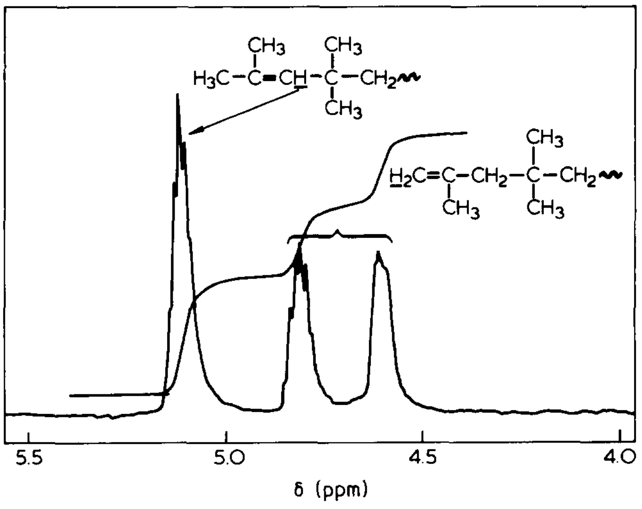


Figure 4 Expanded ^{1}H n.m.r. spectrum of the isobutylene pentamers fraction

bond; and n is the number of protons per molecule of 1,1,1,2-tetrachloroethane (i.e. $n=2$).

The concentration of double bonds per unit weight of the thermally degraded polymer (mol g^{-1}) was determined by the iodine number method using the following equation:

$$U=\frac{\text{iodine no.}}{126.91}\times 10^{-2} \tag{7}$$

Here U is the sum of U_{tri} and U_{vin} (mol g^{-1}). The results of quantitative analysis of the double bond in the thermally degraded polymer are shown in *Table 2*. The extreme right column in this table gives an average number of double bonds per molecule of the thermally degraded polymer.

For the quantitative analysis with ^{1}H n.m.r., a comparison between the weighing method and the integration method is given in *Figure 5*. The values obtained by the weighing method are slightly smaller than those by the integration method, but both values show good agreement within 10%. However, since the differences in the values of the two methods become large for a smaller signal-to-noise ratio (S/N ratio), by obtaining an S/N ratio as large as possible data within 10% variation were adopted as the U values from the n.m.r. method. A comparison of the values obtained by the n.m.r. method with those by the iodine number method is shown in *Figure 6*. The figure clearly shows that the values from the n.m.r. method are in fair agreement with those from the iodine number method. Accordingly, it is apparent that the double bonds in the thermally degraded PIB by pulsed Fourier transform ^{1}H n.m.r. spectroscopy could be obtained with good accuracy. As shown in *Table 2*, the content of terminal trisubstituted olefin is 2–4 times that of terminal vinylidene olefin and the concentration of the former increases slightly with reaction time. The value of f is greater than 1 and tends to be near 2, that is, most of the thermally degraded polymer has 2 terminal unsaturations per molecule.

Although, strictly speaking, the scission of allylic position in end-initiation and disproportionation termination should be checked for the distribution of double bonds in the thermally degraded polymer, the double bonds are considered to be mainly formed via intermolecular radical transfer followed by β-scission because of the points mentioned above. In this case the intermolecular transfer of macroradical occurs at the methylene hydrogen of the polymer chain or at the methyl groups, as is represented by the following equation.

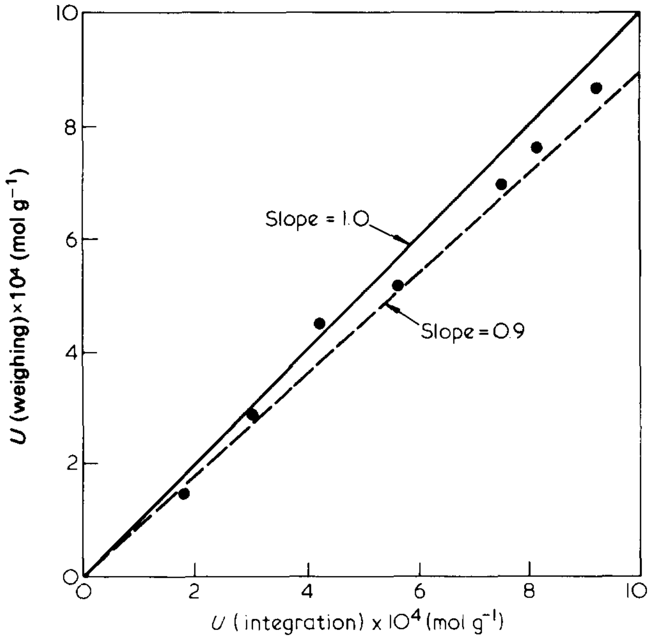


Figure 5 Comparison of the integration method with the weighing method with n.m.r. measurements

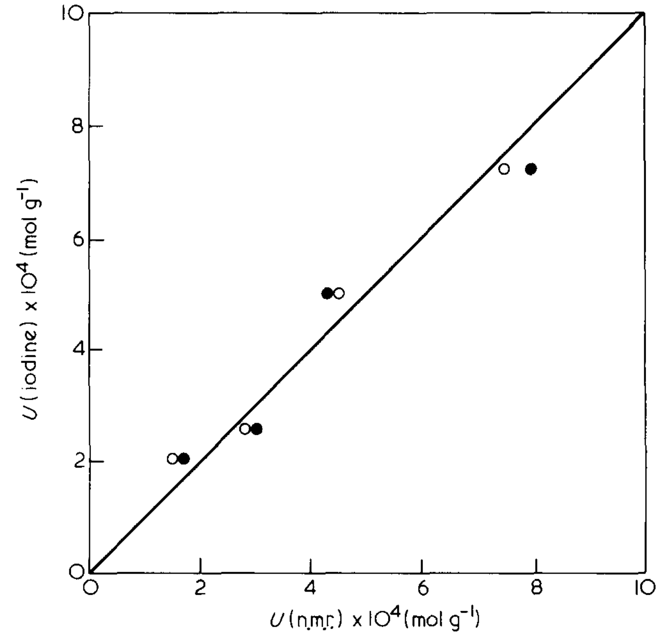
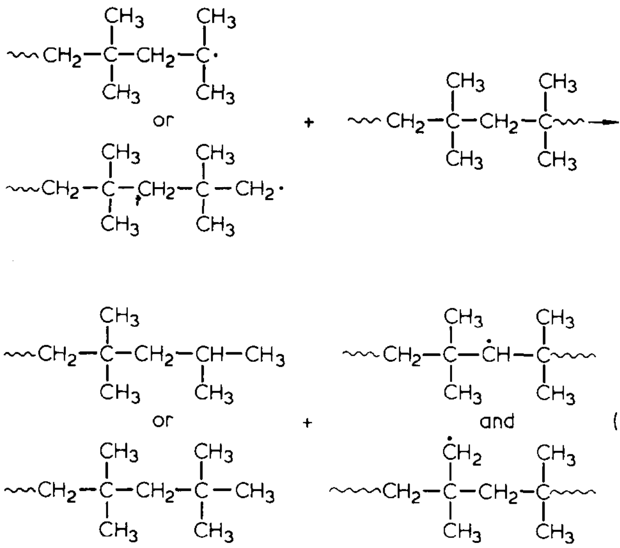


Figure 6 Comparison of the n.m.r. method with the iodine number method for the measurement of unsaturations: ○, weighing method; ●, integration method

Table 2 Distribution of double bonds in thermally degraded polyisobutylene by different methods

	Unsaturation x 10^4 (mol g^{-1})									
Time	n.m.r. (weighing)			n.m.r. (integration)			Iodine no.	n.m.r. (weighing)	n.m.r. (integration)	Iodine no.
(min)	U_{tri}	U_{vin}	U	U_{tri}	U_{vin}	U	U	f^a	f^a	f^a
15	1.10	0.40	1.50	1.24	0.49	1.73	1.85	0.96	1.11	1.18
30	2.14	0.69	2.83	2.20	0.77	2.97	3.07	1.27	1.34	1.38
60	3.59	0.92	4.51	3.46	0.82	4.28	4.68	1.67	1.58	1.73
120	6.55	1.01	7.56	6.96	1.14	8.10	7.63	1.81	1.94	1.83

^{a} Average number of double bonds per molecule



(8)

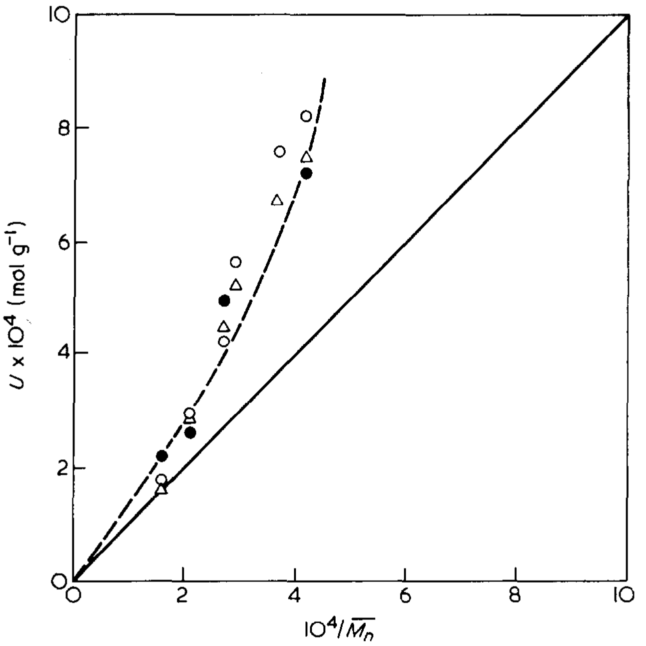


Figure 7 Plot of U vs. $1/\bar{M}_n$: △, weighing method; ○, integration method; ●, iodine number method

The distribution of double bonds shown in *Table 2* suggests that these intermolecular radical transfers occur predominantly at the methylene hydrogen rather than at the methyl groups of the polymer chain. This should be noted, in contrast to the fact that the intramolecular radical transfer (back-biting)[6,7], by which most of the volatiles are formed, occurs predominantly at the methyl groups rather than at the methylene hydrogen because of a steric hindrance. If the degradations proceed exclusively with these intermolecular radical transfers (equation (8)) followed by β-scission, the value of f should tend towards 1 because of a minor contribution of end-initiation and disproportionation termination for the formation of double bonds in the thermally degraded polymer. The plot of U vs. $1/\bar{M}_n$ is shown in *Figure 7*. When the degradations mostly obey equation (8), the value of U varies with $1/\bar{M}_n$ along the solid line in this figure. The value of U obtained in these experiments gradually deviated from this solid line. This tendency shows that the distribution of double bonds in the thermally degraded polymer cannot be interpreted with these mechanisms.

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