# Recombination of Random Chain Scissions of Polyisobutylene in $\boldsymbol{n}$-Alkane Solutions* 

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#### Abstract

Random chain scission constants have been determined for the photolysis of polyisobutylene in $n$-alkane solutions. These rate constants are diffusion controlled since they are due to chain radicals escaping from medium cages. Plots of these rate constants $v s .1 / \eta$ (where $\eta$ is the solvent viscosity) and plots of the rate constants vs. $M_{n}^{-3 / 2}$ and $M_{n}^{-1 / 2}$, respectively, give straight lines. Discussion shows that the case of translational diffusion for $k_{\text {exp }}$ as a function of $1 / \eta$ and $1 / M_{n}^{1 / 2}$ is the one which gives the most reasonable results. About $10^{3}$ scissions are mended for each permanent chain scission undergone by the polymer. It is suggested that about $24 \AA$ separation of radicals (i.e., 4 times the radius of one solvent molecule) by translational diffusion are sufficient for effecting a permanent chain scission. A translation of ca. $370 \AA$, as required by the case where $k_{\text {exp }}$ is a function of $M_{n}^{-3 / 2}$, seems to be unrealistic.

KEY WORDS Random Chain Scission / Cage / Encounter Pair / Recombination / Segmental and Translational Diffusion / Photodegradation /


Mending of random chain scissions in polymer molecules has now been experimentally established. Newly produced polymer radicals are confined in medium cages where opportunity for collisions between them is large and only very few radicals can escape from cages leading to permanent chain scission. ${ }^{1}$ It is difficult to find suitable inert polymer solvent-solute systems where the only parameter which changes is the solvent viscosity. Such a system is polyisobutylene dissolved in $n$-alkanes. The photolysis of this system has been investigated here from the standpoint of medium cages or encounter pairs. The UV photolysis of polyisobutylene films was studied by Carstensen and Rånby. ${ }^{2}$

## EXPERIMENTAL

## Materials

Polyisobutylene (PIB, obtained from Polysciences Inc.) was fractionated and purified by addition of methanol to benzene solution. Three

[^0]fractions were isolated, thoroughly washed and dried in vacuum at $50^{\circ} \mathrm{C}$ for several days.

| Fraction | $[\eta]$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\mathrm{dlg}^{-1}$ |  | $M_{n}$ |
| $\mathrm{~g} \mathrm{~mol}^{-1}$ |  |  |  |
| A | 1.28 |  | 855000 |
| C | 1.35 |  | 940000 |
| D | 1.65 |  | 1345000 |

$[\eta]=6.10 \times 10^{-4} M_{n}^{0.56} \mathrm{dl} \mathrm{g}^{-1}$ for benzene solutions.
$n$-Alkanes were obtained from Aldrich Chemical Co. (all were of AR grade and redistilled).

## APPARATUS

The cylindrical quartz reaction vessel ( $c a$. 20 ml ) was thermostated at $30^{\circ} \mathrm{C} \pm 0.1^{\circ} \mathrm{C}$. The PIB solutions (ca. 0.2 to $0.3 \% \mathrm{w} / \mathrm{v}$ ) were irradiated under $\mathrm{N}_{2}$ by a water-cooled Hanovia 654A36 high pressure Quartz-Hg-lamp located in the water-bath. About $35 \%$ of the total radiated energy was in the range from $\lambda=300 \mathrm{~nm}$ to $\lambda=222 \mathrm{~nm}$. This energy is quite sufficient to rupture main chain $\mathrm{C}-\mathrm{C}$ links in PIB. ${ }^{2}$ Ubbelohde semimicroviscometers were used for intrinsic viscosity measurements. Solutions were
exposed to UV radiation after de-aeration with nitrogen and then kept under nitrogen. Aliquots were taken at various times. Solvent viscosities were also measured at $30^{\circ} \mathrm{C}$.

|  | $\eta / \mathrm{cP}$ |
| :--- | :--- |
| Octane | 0.474 |
| Decane | 0.714 |
| Dodecane | 1.215 |
| Tridecane | 1.500 |
| Pentadecane | 2.227 |
| Hexadecane | 2.676 |

## RESULTS

Scission rate constants were determined for PIB Fraction D in the $n$-alkane solvents. The MarkHouwink constants $K$ and ' $a$ ' were obtained for all solvents by means of the three fractions $\left(30^{\circ} \mathrm{C}\right)$ :

|  | $a$ | $10^{5} \mathrm{~K} / \mathrm{dlg}^{-1}$ |
| :--- | :---: | :---: |
| Octane | 0.76 | 7.86 |
| Decane | 0.84 | 2.57 |
| Dodecane | 0.84 | 2.63 |
| Tridecane | 0.72 | 13.4 |
| Pentadecane | 0.73 | 11.3 |
| Hexadecane | 0.84 | 2.07 |

The theoretical average number $\bar{s}$ of chain scissions in each original chain was obtained by computer for $\bar{s}=0.1$ to $\bar{s}=10$ in $\bar{s}=0.01$ increments for each ' $a$ ' value from an equation by Durup. ${ }^{4}$ However the experimental $\bar{s}$ values were all smaller than $\bar{s}=1.0$. The degree of degradation $\alpha$ was derived from

$$
\begin{equation*}
\alpha=\frac{\bar{s}}{D P_{0}-1} \cong \frac{\bar{s}}{D P_{0}}=\frac{1}{\overline{D P_{n, t}}}-\frac{1}{D P_{0}}=k_{\exp } t \tag{1}
\end{equation*}
$$

as $\frac{D P_{0}}{\overline{D P}_{n, t}}=\bar{s}+1$
$\alpha$ plotted $v s . t$ gives in all cases good straight lines ( $\overline{D P}_{n, t}=$ number average chainlength at $t$ ). Random chain scission rate constants were obtained from the slopes.*

[^1]|  | $1 / \eta$ |  |
| :--- | :---: | :---: |
|  |  | $10^{9} k_{\text {exp }}$ |
|  | $\mathrm{cP}^{-1}$ |  |
| Octane | 2.11 |  |
| $\mathrm{~s}^{-1}$ |  |  |
| Decane | 1.40 |  |
| Dodecane | 0.82 |  |
| Tridecane | $0.6 \pm 0.3$ |  |
| Pentadecane |  | $1.1 \pm 0.0$ |
| Hexadecane | 0.45 |  |
|  | 0.37 | $0.1 \pm 0.0$ |
|  |  | $\sim 0$ |

$\pm$ values are standard deviations.

The rate constants are a function of the light intensity $l_{\text {abs }}$ absorbed and the chain scission quantum yield $\phi_{\mathrm{s}}$, i.e., $k_{\text {exp }}=\phi_{\mathrm{s}} f(l)_{\mathrm{abs}} /[n] \quad\left(\mathrm{s}^{-1}\right)$ where $[n]$ is the concentration of main chain links in the system at $t$. Figure 1 shows the experimental rate


Figure 1. Experimental chain scission rate constants ( $k_{\text {exp }}$ ) of fraction D in $n$-alkanes as a function of reciprocal solvent viscosity $(\eta \mathrm{cP})\left(30^{\circ} \mathrm{C}\right)$.
constants plotted vs. $1 / \eta_{\text {solv }}$. A good straight line is obtained. Fractions A, C and D were photolysed in octane, tridecane and hexadecane, respectively, at
$30^{\circ} \mathrm{C}$. The rate constants are given below.

|  | $10^{9} k_{\text {exp }}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $\mathrm{s}^{-1}$ |  |  |
|  | A | C | D |
| Octane | $19.8 \pm 0.5$ | $14.1 \pm 0.6$ | $4.6 \pm 0.3$ |
| Tridecane | $1.3 \pm 0.0$ | $0.8 \pm 0.0$ | $0.7 \pm 0.0$ |
| Hexadecane | $0.3 \pm 0.0$ | $0.3 \pm 0.0$ | $\sim 0$ |

Figure 2 shows $k_{\exp }$ vs. $M_{n}^{-3 / 2}$; good straight lines are obtained.


Figure 2. $k_{\text {exp }} v s .1 / M_{n}^{-3 / 2}$ in octane ( $O$ ), tridecane ( $\square$ ), and hexadecane $(\triangle)\left(30^{\circ} \mathrm{C}\right)$.

## DISCUSSION

Two different types of diffusion processes, or both simultaneously, may be involved in the escape of radicals from cages: (1) segmental diffusion or (2) translational diffusion. In the first instance, the diffusion is a function of $1 / \eta_{\text {solv }}$ and practically
independent of the chainlength or molecular weight of the solute; in the second one, it will be a function of $1 / \eta_{\text {solv }}$ and also the chainlength. If both diffusion processes are operative simultaneously, they will behave like parallel processes and the fastest will be rate determining.

The cage effect can be treated following Smoluchowski, ${ }^{5}$ i.e., a diffusion controlled reaction results whose rate constant for escape from cages is given by,

$$
\begin{equation*}
\left.k_{\mathrm{ab}}=4 \pi R_{\mathrm{ab}} D_{\mathrm{ab}} \mathrm{~cm}^{3} \text { (molecule) }\right)^{-1} \mathrm{~s}^{-1} \tag{2}
\end{equation*}
$$

Here, $R_{\mathrm{ab}}$ is the distance between the centers of the small molecular weight reactants ' $a$ ' and ' $b$ ' and $D_{\mathrm{ab}}$ is the diffusion constant of " $a$ " relative to " $b$ ". $k_{\mathrm{ab}}$ is the diffusion controlled rate constant for escape. Equation 2 has to be suitably adapted to polymer molecules.

The mean displacement of a segment by Brownian movement during time $t$ is, according to Einstein, ${ }^{6}$

$$
\begin{equation*}
\bar{R}_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}^{2}=6 D_{\mathrm{x} . \mathrm{y}, \mathrm{segm}} t=6\left(D_{\mathrm{x}}+D_{\mathrm{y}}\right)_{\mathrm{segm}} t \tag{3}
\end{equation*}
$$

Here $\bar{R}_{\mathrm{x}, \mathrm{y}}$ is the average cage radius equal to the length of the radical chainend-segment. $D_{x, y, s e g m}$ is the diffusion coefficient of the end-segment $x$ (or $y$ ) with respect to y (or x ). $t$ represents the average lifetime of a segment pair in a cage. If one radical reaches the cage boundary during time $t$, a permanent scission results. $t$ is related to a firstorder diffusion process out of a cage, and hence,

$$
\begin{equation*}
k_{2 . \operatorname{segm}}=1 / t_{\mathrm{av}} \tag{4}
\end{equation*}
$$

Inserting $t_{\mathrm{av}}$ into eq 3 gives the diffusion controlled rate constant of escape or permanent chain scission rate constant with respect to the cage concentration (see eq 11a).

$$
\begin{equation*}
k_{2, \text { segm }}=\frac{6 D_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}}{\bar{R}_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}^{2}} \tag{5}
\end{equation*}
$$

However, the movement of the chain segment is not unhindered; it needs an energy of activation for rotation around $\mathrm{C}-\mathrm{C}$ bonds. Hence eq 5 becomes,

$$
\begin{align*}
D_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}^{\prime} & =D_{\mathrm{x}, \mathrm{y}, \mathrm{o}, \mathrm{segm}} \exp -(1 / R T)\left(E_{\mathrm{D}}+E_{\mathrm{h}}\right) \\
& =D_{\mathrm{x}, \mathrm{y}, \mathrm{segm}} \exp -E_{\mathrm{h}} / R T \tag{6}
\end{align*}
$$

where $D_{x, y, 0, \text { segm }}$ is the pre-exponential factor in the Arrhenius equation for the diffusion coefficient. $E_{\mathrm{D}}$ and $E_{\mathrm{h}}$ are the energies of activation for the diffusion coefficient and rotation, respectively. The
"free" diffusion coefficient is given by the StokesEinstein relation,

$$
\begin{equation*}
D_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}=\frac{k_{\mathrm{B}} T}{{ }^{\prime} a^{\prime} \eta \pi \bar{r}_{\mathrm{segm}}} \tag{7}
\end{equation*}
$$

$k_{\mathrm{B}}$ is Boltzmann's constant, ' $a$ ' is a constant usually equal to 6 for large molecules, $\bar{r}_{\text {segm }}$ is the average radius of the segment-cage (equal to the average length of the segment radical); $\eta$ is the solvent viscosity (in many cases equal to the local viscosity in the cage). Therefore, eq 5 (considering also eq 6 ) becomes,

$$
\begin{equation*}
k_{2, \mathrm{segm}}=\frac{k_{\mathrm{B}} T \mathrm{e}^{-E_{\mathrm{h}} / R T}}{\eta \pi \bar{r}_{\mathrm{segm}} \bar{R}_{\mathrm{x}, \mathrm{y}, \mathrm{segm}}^{2}} \tag{8}
\end{equation*}
$$

Hence the experimental chain scission rate constant, equal to the constant of escape by diffusion, should be proportional to $1 / \eta_{\text {solv }}$ and practically independent of $M_{n}$ and the chainlength.

The simplified-assumption is made for translational diffusion that during the initial stages of the scission reaction, the chains are on the average cut into halves.

Here, once again,

$$
\begin{equation*}
\bar{R}_{x, y, \text { trans }}^{2}=6 D_{x, y, \text { trans }} t \tag{9}
\end{equation*}
$$

$\bar{R}_{\mathrm{x}, \mathrm{y}}$ is the average radius of the cage approximately equal to the radius of gyration $R_{\mathrm{G}}$ of the original chains. This radius of gyration is proportional to $M_{n}{ }^{1 / 2}$, (this is strictly true for 0 solvents). Similarly as for the segmental case one obtains,

$$
\begin{equation*}
k_{2, \text { trans }}=\frac{1}{t_{\mathrm{av}}} \text { or } k_{2, \text { trans }}=\frac{6 D_{\mathrm{x}, \mathrm{y}, \text { trans }}}{\bar{R}_{\mathrm{x}, \mathrm{y}, \text { trans }}^{2}} \tag{10}
\end{equation*}
$$

Again, the Stokes-Einstein relation gives,

$$
\begin{align*}
k_{2, \text { trans }} & =\frac{k_{\mathrm{B}} T}{\eta \pi \bar{r}_{\text {trans }} \bar{R}_{\mathrm{x}, \mathrm{y}, \text { trans }}^{2}} \\
& =\frac{k_{\mathrm{B}} T}{\eta \pi R_{\mathrm{G}}^{3}}=\frac{k_{\mathrm{B}} T}{\eta \pi C^{\prime} M_{n}^{3 / 2}} \tag{11}
\end{align*}
$$

$C^{\prime}$ is a proportionality constant; in this case $k_{2 . \text { trans }}$ should be proportional to $1 / \eta$ and $M_{n}{ }^{-3 / 2}$.

The rate of permanent chain scission is,

$$
\begin{equation*}
-\frac{\mathrm{d}[n]}{\mathrm{d} t}=k_{2(\text { (rans or segm) }}\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right] \tag{11a}
\end{equation*}
$$

where $[\rangle]$ stands for cage concentration. Further,

$$
\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]_{\text {Steady State }}=\frac{k_{1}[n]}{k_{-1}+k_{2}}
$$

$k_{-1}$ is the rate constant for recombination and $k_{1}$, the constant for producing radical pairs in cages. if $k_{-1} \gg k_{2}$, then the rate of permanent chain scission becomes,

$$
\begin{equation*}
-\frac{\mathrm{d}[n]}{\mathrm{d} t}=k_{2} \frac{k_{1}}{k_{-1}}[n]_{0}=k_{1} k_{2}[n]_{0}=k_{\exp }[n]_{0} \tag{12}
\end{equation*}
$$

Here, $[n]$ is the concentration of main chain links left intact at $t ;[n]_{0}$, the concentration at $t=0$ (in our case $[n] \cong[n]_{0}$ ). Hence, the experimental rate constant $k_{\text {exp }}=k_{2} K_{1} \cdot k_{\text {exp }}$ is either proportional to $1 / \eta$ and independent of $M_{n}$ (segmental diffusion) or proportional to $1 / \eta$ and $M_{n}^{-3 / 2}$. In the present instance, the second alternative, i.e., translational diffusion, seems to be realized.

It is also possible in principle, that the present case is due to simultaneous segmental and translational diffusion. However, this is not realized because $k_{\text {exp }}$ vs. $1 / \eta$ and $k_{\text {exp }}$ vs. $1 / M_{n}^{3 / 2}$ must have smaller slopes than Figures 1 and 2 indicate.

Thus, it appears that only translational diffusion out of cages is operative, i.e.,

$$
\begin{equation*}
-\left(\frac{\mathrm{d}[n]}{\mathrm{d} t}\right)_{\substack{\text { permanent } \\ \text { scission }}}=\frac{k_{1} k_{2, \text { trans }}[n]_{0}}{k_{-1}+k_{2, \text { trans }}}=k_{\text {exp }}[n]_{0} \tag{13}
\end{equation*}
$$

Figures 1 and 2 show straight lines, hence $k_{-1} \gg k_{2 . \text {.rans }}$ and

$$
\begin{equation*}
-\frac{\mathrm{d}[n]}{\mathrm{d} t}=\frac{k_{1} k_{\mathrm{B}} T[n]_{0}}{k_{-1} \eta \pi C^{\prime} M_{n}^{3 / 2}}=k_{\exp }[n]_{0} \tag{14}
\end{equation*}
$$

Further $r_{0} / M_{n}{ }^{1 / 2}=0.78 \AA$ and $r_{0}{ }^{2}=6 R_{\mathrm{G}}{ }^{2}$ (strictly for a $\theta$ solvent $)^{2}$; for fraction $\mathrm{D}: M_{n}=1.35 \times 10^{6}$, $R_{\mathrm{G}} \cong 3.7 \times 10^{-6} \mathrm{~cm}$, and $C^{3}=C^{\prime}=3.25 \times 10^{-26}$.

Figures 1 and 2 show that $k_{\text {exp }}$ becomes zero at finite values of $1 / \eta_{\mathrm{f}}$ and $1 / M_{n, \mathrm{f}}^{3 / 2}$, respectively. The empirical equations for $k_{\text {exp }}$ are given by ( $K_{1}=k_{1} / k_{-1}$ ),

$$
\begin{aligned}
M_{n} & =\mathrm{const}
\end{aligned} \quad k_{\exp }=K_{1} \frac{k_{\mathrm{B}} T}{\pi C^{\prime} M_{n}^{3 / 2}}\left(\frac{1}{\eta}-\frac{1}{\eta_{\mathrm{f}}}\right)
$$

or

$$
\begin{align*}
k_{\exp }= & K_{1} \frac{k_{\mathrm{B}} T}{\pi C^{\prime}}\left[\frac{1}{M_{n}^{3 / 2}}\left(\frac{1}{\eta}-\frac{1}{\eta_{\mathrm{f}}}\right)\right. \\
& \left.+\frac{1}{\eta}\left(\frac{1}{M_{n}^{3 / 2}}-\frac{1}{M_{n, \mathrm{f}}^{3 / 2}}\right)\right] \frac{1}{2} \tag{15}
\end{align*}
$$

Differentiation yields

$$
\begin{aligned}
& M_{n}=\text { const } \\
& \qquad \begin{aligned}
\eta= & \frac{\mathrm{d} k_{\text {exp }}}{\mathrm{d}(1 / \eta)}=K_{1}\left[\frac{k_{\mathrm{B}} T}{\pi C^{\prime}}\left(\frac{2}{M_{n}^{3 / 2}}-\frac{1}{M_{n, \mathrm{f}}^{3 / 2}}\right)\right] \frac{1}{2} \\
& \frac{\mathrm{~d} k_{\text {exp }}}{\mathrm{d}\left(1 / M_{n}^{3 / 2}\right)}=K_{1}\left[\frac{k_{\mathrm{B}} T}{\pi C^{\prime}}\left(\frac{2}{\eta}-\frac{1}{\eta_{\mathrm{f}}}\right)\right] \frac{1}{2}
\end{aligned}
\end{aligned}
$$

For Fraction D ( $M_{n}=$ const), Figure 1 gives,

$$
\begin{gathered}
\text { Slope }=2.70 \times 10^{-11}=K_{1} \times 1.67 \times 10^{2}\left(\mathrm{~s}^{-1} \mathrm{P}\right) \\
\therefore \quad K_{1}=1.60 \times 10^{-13}
\end{gathered}
$$

For Fraction A, C, D in octane ( $\eta=$ const), Figure 2 yields,

$$
\begin{gathered}
\text { Slope }=22.73=K_{1} \times 1.39 \times 10^{14} \mathrm{~s}^{-1} \\
\therefore \quad K_{1}=1.64 \times 10^{-13}
\end{gathered}
$$

Further

$$
K_{1}=\frac{k_{1}}{k_{-1}}=\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right] /[n]_{0}
$$

where $[n]_{0}=4 \times 10^{-2} \mathrm{M}$.
Hence

$$
\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]=6.5 \times 10^{-13} \mathrm{M}
$$

$k_{2 . \text { trans }}=5.53 \times 10^{4} \mathrm{~s}^{-1}$ is obtained from eq 11 ; eq 10 gives $D_{\text {x.y.trans }}=1.26 \times 10^{-7} \mathrm{~cm}^{2} \mathrm{~s}^{-1} ; k_{-1 \text {.trans }}$ can also be calculated from eq 10 for the above value of $D_{\text {x.y.trans }}$ assuming that one solvent molecule (i.e., one octane molecule) lies, on the average, between the radical chainends, i.e., ca. $12 \AA$ (see North ${ }^{7}$ ). Hence $R_{\mathrm{G}}=r=6 \times 10^{-8} \mathrm{~cm}$ in eq 10 yielding $k_{-1}=2.1 \times 10^{8} \mathrm{~s}^{-1}$. As $K_{1}=k_{1} / k_{-1}$ one also obtains $k_{1}=3.5 \times 10^{-5} \mathrm{~s}^{-1}$. If $f$ is the fraction of geminate pairs recombining in cages and $(1-f)$, the fraction which escapes, i.e., which leads to permanent chain scission, then

$$
\begin{equation*}
\frac{f}{1-f}=\frac{k_{-1}\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]}{k_{2}\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]}=3.8 \times 10^{3} \tag{16}
\end{equation*}
$$

Hence $3.8 \times 10^{3}$ main $\mathrm{C}-\mathrm{C}$ link scissions are mended
for each permanent (i.e., experimentally measured) chain scission.

Horie and Mita ${ }^{8}$ (see also Mahabadi and O'Driscoll $^{9}$ ) reported encounter-reactions between polystyrene chains having benzil and anthrazene end-groups. In this way, encounters by quenching can be studied. Their quenching rate constants $k_{-1}$ for benzene solutions were found to be $k_{-1}=10^{8}$ to $10^{9} 1 \mathrm{~m}^{-1} \mathrm{~s}^{-1}$. Our value $k_{-1}=2.1 \times 10^{8} \mathrm{~s}^{-1}$ can be converted to a second order rate constant,

$$
k_{-1}=4 \pi D_{\mathrm{x}, \mathrm{y}, \text { trans }} r_{\text {octane }} N_{\text {Avogadro }} / 10^{3} \mathrm{~lm}^{-1} \mathrm{~s}^{-1}
$$

Inserting the respective values of $D_{\mathrm{x}, \mathrm{y}, \text { trans }}$ and $r_{\text {octane }}$ given above leads to $k_{-1}=5.75 \times 10^{7} 1 \mathrm{~m}^{-1} \mathrm{~s}^{-1}$ ( $r=6 \times 10^{-8} \mathrm{~cm}$ ).

It appears unrealistic that for a permanent chain scission to occur, the two radical chain-ends have to diffuse by translation a distance of several hundred $\AA$ ingstroms apart ( $R_{\mathrm{G}}=370 \AA$ for $k_{2 \text {.trans }}$ ). It is more reasonable that a separation of about 4 octane molecules ( $4 r=24 \AA$ ) is a sufficient distance for effecting permanent chain scission. In such a case,

$$
\begin{equation*}
k_{2, \text { trans }}^{\prime}=\frac{k_{\mathrm{B}} T}{\eta \pi R_{\mathrm{G}} r_{\mathrm{oct}}^{2}}=\frac{k_{\mathrm{B}} T}{\eta \pi C M_{n}^{1 / 2}(4 r)_{\mathrm{oct}}^{2}} \tag{17}
\end{equation*}
$$

Figure 3 shows that $k_{\text {exp }}$ vs. $1 / M_{n}^{1 / 2}$ also gives a straight line, whose equation is,


Figure 3. $k_{\text {exp }}$ vs. $1 / M_{n}^{1 / 2}$ in octane ( O ) and tridecane (©) $\left(30^{\circ} \mathrm{C}\right)$.

$$
k_{\exp }=K_{1} \frac{k_{\mathrm{B}} T}{\pi C(4 r)^{2}}\left(\frac{2}{\eta}-\frac{1}{\eta_{\mathrm{f}}}\right) \frac{1}{2}
$$

In this case, the respective values are:
Slope (Figure 3; $\eta$ =const., A, C, D in Octane $)=6.93 \times 10^{-5} \mathrm{~s}^{-1} ; \quad K_{1}{ }^{\prime}=5.48 \times 10^{-15}(\eta=$ const and also for $M_{n}=$ const); $k_{2, \text { trans }}^{\prime}=1.3 \times 10^{7} \mathrm{~s}^{-1}$ ( $r_{\text {oct }}=6 \AA$; eq 11); $k_{-1, \text { trans }}^{\prime}=2.1 \times 10^{8} \mathrm{~s}^{-1}\left(r_{\text {oct }}=6 \AA\right)$; $k_{1}{ }^{\prime}=1.2 \times 10^{-8} \mathrm{~s}^{-1} ; \quad D_{\mathrm{x}, \mathrm{y} \text {,trans }}^{\prime}=1.26 \times 10^{-7} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$ (eq 10); $\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]=2.1 \times 10^{-14} \mathrm{ml}^{-1}$; finally $f /(1-f) \cong 16$. This latter value is much too small. Hence, this second case is also not satisfactory.

The results for segmental diffusion are also of interest in order to see whether the molecular weight dependence and also $f /(1-f)$ are of reasonable magnitudes. A segment length or cage radius of $24 \AA$ and an energy of activation for rotation $E_{\mathrm{h}}=2000 \mathrm{cal}$ were taken (see eq 8 ). Results were obtained as follows: $k_{1 . \text { segm }}=7.5 \times 10^{6} \mathrm{~s}^{-1}$; Figures 2 and 3 were ignored. Slope (Figure 1 ) $=2.7 \times 10^{-11} \mathrm{~s}$ $\mathrm{P}^{-1}, \quad K_{1 . \mathrm{segm}}=7.61 \times 10^{-16} ; \quad D_{\text {x.y.segm }}=7.2 \times 10^{-8}$ $\mathrm{cm}^{2} \mathrm{~s}^{-1} ; k_{-1, \mathrm{segm}}=8.8 \times 10^{8} \mathrm{~s}^{-1}(r=7 \AA) ; k_{1, \mathrm{segm}}=$ $6.7 \times 10^{-6} \mathrm{~s}^{-1} ;\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]_{\mathrm{segm}}=2.8 \times 10^{-15} \mathrm{ml}^{-1}$; $f /(1-f) \cong 12$. Here again, the last value is too small.

The experimental change of $k_{\text {exp }}$ with $M_{n}$ found in our work is much larger than expected from the calculations by Horie and Mita. ${ }^{10} k_{\text {exp }}$ decreases for our experiments about four times (i.e., $19.8 \times 10^{-9}$ $\mathrm{s}^{-1}$ to $4.6 \times 10^{-9} \mathrm{~s}^{-1}$ ) within a range of molecular weights from $0.86 \times 10^{6}$ to $1.35 \times 10^{6}$. Segmental diffusion does not appear to be verified.

Only the translational case 2 (i.e., $k_{\text {exp }} \sim f\left(M_{n}^{-1 / 2}\right)$ will be discussed below, since the other two are not satisfactory. Case 2 is also not satisfactory as far as the value of $f^{\prime} /(1-f)$ is concerned. However, there are two possibilities for overcoming this difficulty.

The rate constant $k_{-1, \text { rans }}^{\prime}$ for mending chain scissions can be discussed in terms of collisions in the cage. The average life-time of an encounter of small-molecular-weight radicals is about $10^{-8}$ to $10^{-10} \mathrm{~s}$ in liquids of normal viscosity. ${ }^{7}$ The collision frequency of a geminate pair is about $10^{12} \mathrm{~s}^{-1}$. Hence, a radical in a cage undergoes $10^{2}$ to $10^{4}$ collisions $\mathrm{s}^{-1}$. This number of collisions will be more than enough to effect combination. If the radicals are polymeric, then fewer collisions will take place per second by translational diffusion. However, the chance of recombination will still be
very large. Hence, disappearance of cages will proceed with a half-life of about $10^{-10}$ to $10^{-12} \mathrm{~s}$ or $k_{-1}=7 \times 10^{9}$ to $7 \times 10^{11} \mathrm{~s}^{-1}$ (i.e., the average distance between the radical chain-ends calculated from eq 11 for these $k_{-1}$ values lies in the range from $r=1.1 \times 10^{-8} \mathrm{~cm}$ to $1.1 \times 10^{-9} \mathrm{~cm}$. Thus $f /(1-f)$ values are in the range from $5.4 \times 10^{2}$ to $5.4 \times 10^{4}$, and are reasonable. Moreover, the cage radius (i.e., $24 \AA$ ) is also reasonable.

The second possibility for overcoming these difficulties consists in formulating a transition state before the cage formation, as North pointed out, ${ }^{7}$ i.e.,

$$
\begin{aligned}
P \stackrel{k_{1}^{\prime}}{k_{-1}^{\prime}}\left(R_{\mathrm{x}} R_{\mathrm{y}}\right) & \stackrel{k_{1}}{\text { Transition state }} \\
& \xrightarrow{\stackrel{k_{2}}{\rightleftharpoons}}\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle \\
& \xrightarrow{k_{2}} \text { Products }
\end{aligned}
$$

The following reasonable values for the rate constants were chosen: $k_{1} \sim 10^{7} \mathrm{~s}^{-1} ; k_{-1}=10^{8} \mathrm{~s}^{-1}$; $k_{1}{ }^{\prime} \sim 10^{-5} \mathrm{~s}^{-1} ; k_{-1}^{\prime}=10^{9} \mathrm{~s}^{-1} ; k_{2} \sim 10^{7} \mathrm{~s}^{-1}$. The. above scheme leads to,

$$
\begin{aligned}
& k_{\exp }=k_{2} K_{1}{ }^{\prime} K_{1}=k_{2}\left(\frac{k_{1}{ }^{\prime}}{k_{-1}^{\prime}} \frac{k_{1}}{k_{-1}}\right) \cong 10^{-8} \mathrm{~s}^{-1} \\
& \frac{f}{1-f}=\frac{k_{-1}^{\prime}}{k_{2}^{\prime}} \frac{\left[\left(R_{\mathrm{xy}}\right)\right]}{\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]} \cong \frac{10^{9}}{10^{7}} \frac{10^{8}}{10^{7}} \cong 10^{3}
\end{aligned}
$$

$\left[\left(R_{\mathrm{x}, \mathrm{y}}\right)\right]$ and $\left[\left\langle R_{\mathrm{x}} \cdots R_{\mathrm{y}}\right\rangle\right]$ are steady state values.
This is also a reasonable result. Thus, it may be concluded that the translational case with a functional relationship of $k_{\text {exp }} \sim f\left(1 / M_{n}{ }^{1 / 2}\right)$ leads to reasonable results as far as cage radius and the number of mended chain scissions for each permanent scission are concerned. However, there is still much speculative material in these evaluations and far more research is needed, especially for the rate of cage-consumption or combination of geminate pairs.

Schnabel et al. ${ }^{11}$ obtained half-lives by light scattering after irradiation with electrons of the system PIB- $n$-alkanes. These half-lives were assigned to disentanglement of scissioned chains by diffusion. Their $t_{1 / 2}$ vs. $\eta$ plots or rate constants $v s$. $1 / \eta$ give straight lines. The half-lives are of the order of $30 \mu$ s for octane solutions (the molecular weight is of the same magnitude as in our case). Our $t_{1 / 2}$ values ( $k_{2 \text {.trans }}$ ) amount to $12.5 \mu \mathrm{~s}$ and $0.05 \mu \mathrm{~s}$ for cage radii of $R_{\mathrm{G}}=3.7 \times 10^{-6} \mathrm{~cm}$ and $\bar{r}=2.4 \times 10^{-7}$ cm , respectively. We believe that our values belong
to translational diffusion of chain radicals out of cages as they are functions of molecular weight; further, the $n$-alkanes are good solvents.

Not only the viscosity changes if a good solvent is replaced by a poor one, but also the conformation and degree of aggregation or entanglement are simultaneously altered. This will decrease the random chain scission rate since the geminate pair will have an increased life-time in the cage; i.e., the degree of degradation will decrease for equal times and more scissions will be mended. Our method measures only permanent chain scissions and the disentanglement process as such does not enter the picture directly but only indirectly, slowing down the diffusion process. Disentanglement will not play a significant role for segmental diffusion in dilute solutions. Translational diffusion will be more affected by entanglement depending also on the magnitude of the cage radius. Solvent power will have the greatest influence on escape from cages.

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[^0]:    * Presented at the Joint ACS/JCS Meeting of The American Chemical Society and The Chemical Society of Japan, Honolulu, April 1979.

[^1]:    * Heptane, in spite of repeated purification, gave abnormal results $1 / \eta=2.72\left(\mathrm{cP}^{-1}\right) ; 10^{+9} k_{\text {exp }}=4.1 \pm 0.1$ $\left(\mathrm{s}^{-1}\right)$; the reason for this is quite obscure.

