Kinetic Study of Random Chain Scission by Viscometry

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Synopsis

Based on the Saito's model for random chain scission, a novel procedure is developed to determine the activation energy of polymer degradation process. Basically, this is a simple viscometric technique which yields reliable results. In fact, it is superior to the existing viscometry which has been widely used to study the kinetics of random scission. The present method is successfully applied to the thermal degradation of natural rubber, polycarbonate, and poly(tetramethylene oxide) in bulk.

INTRODUCTION

Thermal oxidative degradation of polymers can lead to chain scission and changes in molecular weights. Hence, the kinetics and mechanisms of these chemical processes may be investigated by a variety of molecular weight measurements including osmometry, light scattering, gel permeation chromatography (GPC), and dilute solution viscometry (DSV). Among them, the last two methods have recently been more widely applied. For example, the mechanisms of chain scission of poly(methyl methacrylate)[1] and some polyphosphazenes[2] were studied by GPC. Whereas, the DSV has been employed to examine the thermal degradation of polystyrene[3] and rubbers.[4]

In the present context, DSV is of particular interest because of its simplicity and reliability. This technique results in the intrinsic viscosity $[\eta]$, which is related to the viscosity-average molecular weight, $\bar{M}_v$, by the Mark-Houwink-Sakurada equation given by

$$[\eta] = K\bar{M}_v^a \tag{1}$$

where K and a are constants. However, the degree of degradation, $\bar{\alpha}$, defined as the number of chain scissions per initial number-average molecule is based on the number-average degree of polymerization, $\bar{P}_n$, namely[5]

$$\bar{\alpha} = \bar{P}_n^0 / \bar{P}_n^s - 1 \tag{2}$$

where $\bar{P}_n^0$ and $\bar{P}_n^s$ are the initial and resulting $\bar{P}_n$'s respectively. Despite this, eq. (1) is conventionally used to compute the parameter $\bar{\alpha}$ by assuming that the polymer is characterized by a particular molecular weight distribution insusceptible to chain scission.[3,4,6,7] This work offers a refined approach to derive an important kinetic parameter from the $[\eta]$ data of degraded polymers. It is not necessary to know the relationship between $[\eta]$ and $\bar{P}_n$ in the present calculations.

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THEORY

The kinetics of polymer degradation have been studied by various theoretical models.[8,9] For random chain scission, Inokuti has shown that the kth moment, μ_k, of the molecular weight distribution of a degraded polymer with degree of degradation $\overline{\alpha}$ is given by[10]

$$\mu_k(\overline{\alpha}) = \int_0^\infty J_k(p, \overline{\alpha}) m(p, 0)\, dp \tag{3}$$

where

$$J_k(p, \overline{\alpha}) = p^k \exp(-\overline{\alpha} p/\bar{P}_n^0) + 2(\overline{\alpha}/\bar{P}_n^0) I_k + (\overline{\alpha}/\bar{P}_n^0)^2 (pI_k + I_{1+k}) \tag{3a}$$

with

$$I_j = \int_0^p l^j \exp(-\overline{\alpha} l/\bar{P}_n^0)\, dl, \qquad j = k, 1 + k \tag{3b}$$

Here, p is the degree of polymerization and $m(p, o)$ designates the normalized initial molecular weight distribution function in the sense

$$\int_0^\infty pm(p, 0)\, dp = 1 \tag{4}$$

For a Schulz-Zimm distribution, we have

$$m(p, 0) = \frac{\gamma^{1+b}}{\Gamma(1 + b)} p^{b-1} \exp(-\gamma b) \tag{5}$$

where

$$\gamma = b/\bar{P}_n^0 = \left[\frac{\Gamma(1 + a + b)}{\Gamma(1 + b)}\right]^{1/a} \bigg/ \bar{P}_v^0 \tag{5a}$$

$$b = (D_0 - 1)^{-1} = (\bar{P}_w^0/\bar{P}_n^0 - 1)^{-1} \tag{5b}$$

with $\bar{P}_v^0$, $\bar{P}_w^0$ being the initial viscosity-average and initial weight-average degrees of polymerization respectively, D_0 being the initial polydispersity, and $\Gamma(x)$ being the Gamma function of x.

The viscosity-average degree of polymerization $\bar{P}_v^s$ at $\overline{\alpha}$ is given by

$$\bar{P}_v^s = [\mu_{1+a}(\overline{\alpha})]^{1/a} \tag{6}$$

Combining eqs. (3), (5), and (6) leads to

$$\frac{[\eta]_s}{[\eta]_0} = (1 + \bar{\alpha}/b)^{-(1+a+b)} + \frac{(\bar{\alpha}/b)}{(1 + a + b)} \times \left\{ \int_0^\infty x^{b-1} \exp(-x)\, dx \left[(2 - x\bar{\alpha}/b) \int_0^x y^{1+a} \exp(-y/b)\, dy - (\bar{\alpha}/b) \int_0^x y^{2+a} \exp(-\bar{\alpha}y/b)\, dy \right] \right\} \quad (7)$$

where $[\eta]_s$ and $[\eta]_o$ are the intrinsic viscosities at $\bar{\alpha}$ and $\bar{\alpha} = 0$ respectively. Unfortunately, the definite integrals in eq. (7) can only be estimated by means of numerical integration which is tedious and subject to numerous algorithm errors. However, for minor chain scission, eq. (7) is converted to

$$\frac{[\eta]_s}{[\eta]_0} = (1 + \bar{\alpha}/b)^{-(1+a+b)} + \frac{(\bar{\alpha}/b)}{(1 + a + b)} \sum_{i=0} \frac{(-\bar{\alpha}/b)^i \Gamma(1 + a + b + i)}{i!(2 + a + i)} \times \left[2 + \frac{(1 + a + b + i)(2 + a + b + i)}{(3 + a + i)} \left(\frac{\bar{\alpha}}{b} \right) \right], \quad \bar{\alpha}/b < 1 \quad (8)$$

Certainly, eq. (8) is more practical than eq. (7) in computing the ratio $[\eta]_s/[\eta]_o$.

In view of the complexity of the foregoing solutions, we resort to a closed expression given by

$$\frac{[\eta]_s}{[\eta]_0} = \left(\frac{1}{1 + \bar{\alpha}} \right)^a F(b, b_s) \quad (9)$$

where

$$F(b, b_s) = \left(\frac{b}{b_s} \right)^a \frac{\Gamma(1 + b)\Gamma(1 + a + b_s)}{\Gamma(1 + b_s)\Gamma(1 + a + b)} \quad (9a)$$

This equation was developed by Kotliar[11] by assuming that both the initial and resulting molecular weight distributions are of the Schulz-Zimm type but with different width parameters respectively denoted by b and b_s. It can be shown[10]

$$b_s = \{2(1 + \bar{\alpha}^{-1})[1 + \bar{\alpha}^{-1}((1 + \bar{\alpha}/b)^{-b} - 1)] - 1\}^{-1} \quad (10)$$

Eq. (10) exhibits a unique feature of random chain scission, which causes any initial molecular weight distribution to approach the most probable one (i.e., $b_s = 1$).

Figure 1 shows the monotonic decrease of $[\eta]_s/[\eta]_0$, predicted by eqs. (9) and (10), with increasing $\bar{\alpha}$ over a practical range of D_0 varying from 1 to 10. However, the corresponding function F is more interesting in that it does not follow the foregoing decaying pattern with increasing $\bar{\alpha}$ for $D_0 < 2$, as illustrated

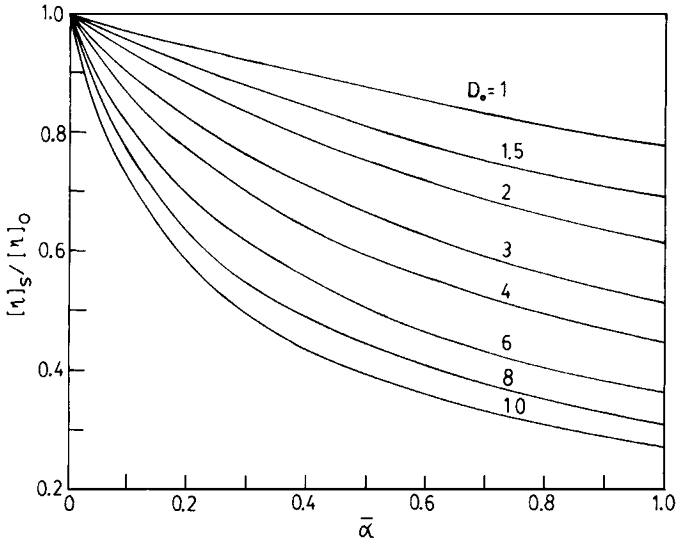

Fig. 1. Variation of $[\eta]_s/[\eta]_0$ with $\overline{\alpha}$ for various values of D_0 at $a = 0.70$.

in Figure 2. In addition, it is demonstrated that the initial most probable distribution ($D_0 = 2$) is virtually preserved during random chain scission. Hence, one may take advantage of this peculiar situation, which renders $F(1, 1) = 1$, to facilitate the thermal degradation studies. In general, the function F may be represented by an empirical relation

$$F(b, b_s) = A(1 + \overline{\alpha})^n, \quad \overline{\alpha} > 0 \tag{11}$$

where A and n are constants for low degree of degradation. Some values of these constants are displayed in Table I. Combining eqs. (9) and (11) yields

$$[\eta]_s/[\eta]_0 = A(1 + \overline{\alpha})^{n-a}, \quad \overline{\alpha} > 0 \tag{12}$$

for low conversion.

Table I also contains the index ϵ defined by[10]

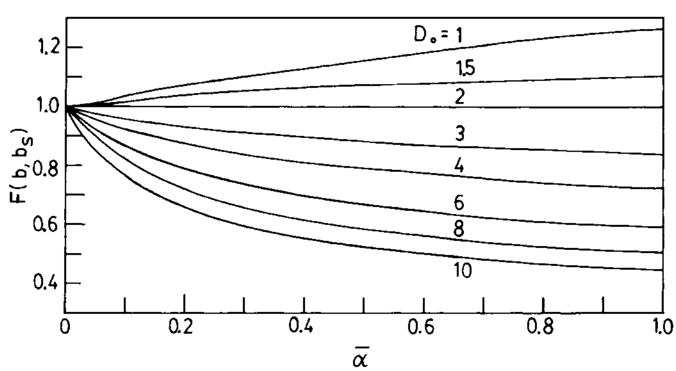

Fig. 2. Variation of $F(b, b_s)$ with $\overline{\alpha}$ for various values of D_0 at $a = 0.70$.

TABLE I
Values of Empirical Constants A and n for Low Degree of Degradation and a = 0.7

No.	D_0	A	n	$[\eta]_s/[\eta]_0$	$\bar{\alpha}$	ϵ
1	1.0[a]	1.003	0.348	≥ 0.78	≤ 1.0	≤ 1.15
2	1.5	1.004	0.157	≥ 0.69	≤ 1.0	≤ 1.02
3	2.0	1.000	0.000	> 0	> 0	1.00
4	3.0	0.991	−0.294	≥ 0.63	≤ 0.6	< 1.01
5	4.0	0.981	−0.560	≥ 0.60	≤ 0.5	≤ 1.02
6	6.0	0.977	−1.165	≥ 0.65	≤ 0.25	≤ 1.04
7	8.0	0.976	−1.719	≥ 0.63	≤ 0.20	≤ 1.06
8	10.0	0.961	−2.293	≥ 0.64	≤ 0.15	≤ 1.07

[a] Based on $b = 10^4$.

$$\epsilon = [2(1 + b_s^{-1}) - 1]/C' \tag{13}$$

where

$$C' = \bar{P}_z^s/\bar{P}_n^s = \frac{3(1+\bar{\alpha})\{1 + (1+\bar{\alpha}/b)^{-(1+b)} + 2/\bar{\alpha}[1 - (1+\bar{\alpha}/b)^{-b}]\}}{\bar{\alpha} - 1 + (1+\bar{\alpha}/b)^{-b}} \tag{13a}$$

with $\bar{P}_z^s$ being the resulting z-average degree of polymerization. This parameter is introduced to monitor the extent of deviation between eqs. (7) and (9). For perfect agreement, the ϵ is unity. Clearly, Table I shows that the Kotliar's approximation is valid for $D_0 \leq 10$ if $\bar{\alpha}$ is sufficiently low. On the other hand, one obtains

$$\lim_{\alpha \to \infty} \epsilon = 1 \tag{14}$$

indicating that eq. (9) is equally true for very large numbers of scissions. Hence when $\bar{\alpha}$ approaches infinity, eq. (9) becomes

$$\frac{[\eta]_s}{[\eta]_0} = \left(\frac{1}{1+\bar{\alpha}}\right)^a F_\infty \tag{15}$$

where

$$F_\infty = F(b, 1) = \frac{b^a \Gamma(1+b)\Gamma(2+a)}{\Gamma(1+a+b)} \tag{15a}$$

which is independent of $\bar{\alpha}$.

Table II compares the numerical results on $[\eta]_s/[\eta]_0$ obtained by various approaches. The average deviation between the predictions of eqs. (8) and (9), σ_s, defined in Table II, is found to be less than 0.01 except for a broad molecular weight distribution of $D_0 = 10$ which registers $\sigma_s = 0.0142$. Also Table II exhibits the good agreement between eqs. (9) and (12) in terms of σ_a detailed therein.

TABLE II
Comparison of Different Approaches in Predicting the $[\eta]_s/[\eta]_0$ of Degraded Polymers

No.	D_0	$\sigma_s{}^a \times 10^3$	$\sigma_a{}^b \times 10^3$
1	1.0[c]	7.6	3.9
2	1.5	1.3	2.8
3	2.0	0.3	0.0
4	3.0	0.9	4.5
5	4.0	4.5	7.7
6	6.0	6.0	6.2
7	8.0	2.4	8.3
8	10.0	14.2	7.9

[a] σ_s = root-mean square of the differences between the predictions of eqs. (8) and (9) for a set of m data = $[\sum_{i=1}^{m} (\Delta_i)^2/m]^{1/2}$, where $\Delta = R_s - R_k$, with R_s and R_k being the ratios $[\eta]_s/[\eta]_o$ obtained by eqs. (8) and (9) respectively.

[b] Analogously $\sigma_a = [\sum_{i=1}^{m} (\Delta_i')^2/m]^{1/2}$, where $\Delta' = R_a - R_k$ with R_a being the $[\eta]_s/[\eta]_o$ given by eq. (12).

[c] Based on $b = 10^4$.

To further compare eqs. (8) with (12), we refer to the sum of σ_s and σ_a. The maximum average deviation of $(\sigma_s + \sigma_a)$ displayed in Table II is noted to be 0.0221 for the case of $D_0 = 10$. Since eq. (12) holds for $[\eta]_s/[\eta]_0 \geq 0.64$ (Table I) for this particular system, the maximum error in $[\eta]_s/[\eta]_0$ introduced by the foregoing approximations would be $\sim$ 3.5%. The experimental uncertainty in $[\eta]_s/[\eta]_0$ is of the order of $\sim$ 4% or higher.[12] This justifies the utility of the proposed approximate analytical functions for the ensuing analysis.

If the random scission occurs at chain linkages whose rate of disappearance follows a first order kinetics,[7] one obtains

$$\overline{\alpha} = \bar{P}_n^0[1 - \exp(-kt)] \tag{16}$$

where k is the rate constant, and t is the degradation time. For relatively short t, eq. (16) is simplified to

$$\overline{\alpha} = \bar{P}_n^0 kt \tag{17}$$

Equations (16) and (17) are to be applied in conjunction with eqs. (15) and (12) respectively.

EXPERIMENTAL

Fresh natural rubber (NR) latex was coagulated by formic acid. The coagulated NR was thoroughly rinsed with water and dried in air at ambient temperature. In order to modify the molecular weight distribution close to the Schulz-Zimm type, the NR sample was slightly premasticated into thin sheet.

Intrinsic viscosity measurements were performed on dilute NR solutions using toluene as solvent at 30.0 ± 0.1°C. An Ubbelohde dilution viscometer was employed. The kinetic energy and shear corrections were negligible. Intrinsic viscosities were determined by the extrapolation method based on Huggins equation and the single-point determination. For the latter, we have first established the relation[14]

$$k_H = 0.32 + 0.31/[\eta] \tag{18}$$

where k_H is the Huggins coefficient. Combining eq. (18) with the Huggins equation[13] leads to

$$[\eta] = \frac{-(1 + 0.31C) + [(1 + 0.31C)^2 + 1.28(\eta_r - 1)]^{1/2}}{0.64C} \tag{19}$$

where C is the concentration of NR solution in g/dL and η_r is the relative viscosity. The $[\eta]$ of the initial NR sample was found to be 5.47 dL/g, corresponding to $\bar{M}_v = 9.8 \times 10^5$ based on a = 0.70 and $K = 3.5 \times 10^{-4}$ dL/g.[15]

The thermal oxidative degradation of NR was carried out in an oven at 100.0, 120.0, 140.0, and 160.0°C in the presence of air. Every measure was taken to ensure the equilibrium oxygen content in the NR film. The samples were quenched with water at ambient temperature after aging for the designated periods of time, t.

Least-squares analyses were performed for all linear relationships.

RESULTS AND DISCUSSION

It has been shown that the random chain scission of NR obeys a pseudo-zeroth order kinetics during the initial oxidative degration stage.[3,16] Hence, we have

$$[\mathrm{NR}] - [\mathrm{NR}]_0 = k't \tag{20}$$

where [NR], $[\mathrm{NR}]_0$ are respectively the concentrations of NR (mol/Uvol) at time t and $t = 0$, and k' is the rate constant. It is noted that eqs. (17) and (20) are indeed equivalent if the zeroth and first order rate constants are correlated by $k' = \rho k/M_r$, where ρ is the density (g/mL) of NR and M_r is the molecular weight of its repeat unit. Hence, eq. (17) is applicable to this system.

Substituting eqs. (17)–(12) yields

$$[\eta]_s = A[\eta]_0(1 + \bar{P}_n^0 kt)^{n-a}, \quad t > 0 \tag{21}$$

Eq. (21) implies that the product kt is only dependent on the degradation temperature, T, at a constant $[\eta]_s$. The values of the foregoing t, hereafter designated by t_s, may be readily interpolated from the $[\eta]_s - t$ plots at various temperatures as demonstrated in Figure 3(A). Figure 3(B) exhibits the Arrhenius plots for the NR by plotting ln t_s^{-1} against T^{-1} at the three levels of chain scissions indicated by the $[\eta]_s$ values. The straight lines are discernibly parallel, with slopes giving the average activation energy, E_a, equal to 96 ± 1

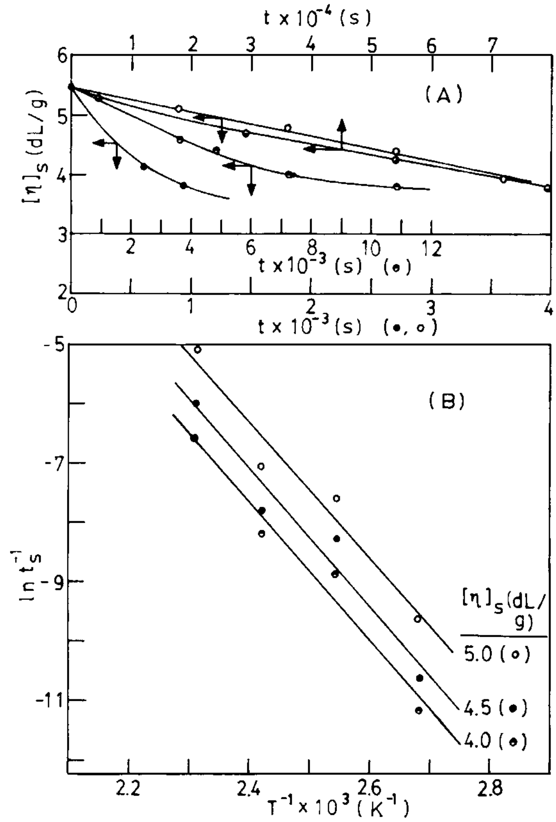

Fig. 3. (A) Plots of $[\eta]_s$ against t for a natural rubber at various temperatures (°C): (●) 160; (○) 140; (◓) 120; (◒) 100. (B) Plot of ln t_s^{-1} against T^{-1} for the foregoing systems.

kJ mol^{-1}. The average literature value of E_a for *NR* is cited as 92 kJ mol^{-1}.[3] These results are indeed in essential agreement.

Attempts to compute the rate constant k have been unsuccessful at the exact values of A, n and $\bar{P}_n^0$ are virtually unknown. Despite this shortcoming, the present analysis indeed makes the E_a a parameter of easy access. Apparently, the classical DSV also rests on eq. (9) but with $F(b, b_s)$ equal to unity. This means that, in the strict sense, it is valid only for the most probable distribution. Hence, the proposed method is more general and versatile, and should be applied in place of the standard technique in any event.

Davis and Golden have handled the kinetic data of thermal degradation by[7,17]

$$ln[\eta]_s = -aln(t + t_0) + C'' \tag{22}$$

where t_0 and C'' are the characteristics parameters of the model.[18] Since the equation is particularly effective for excessive chain scission, it is best applied in connection with eqs. (15) and (16). Taking the boundary condition $[\eta] = [\eta]_0$ at $t = 0$, eq. (22) is recast to

$$\frac{[\eta]_s}{[\eta]_0} = (1 + t/t_0)^{-a} \tag{23}$$

Comparing eq. (23) with eq. (15) results in

$$(1 + \bar{\alpha}) = (1 + t/t_0)F^{1/a} \tag{24}$$

The Arrhenius equation for k is written as

$$k = k_0 \exp(-E_a/RT) \tag{25}$$

where k_0 and R are respectively the preexponential factor, and gas constant. Manipulation of eqs. (16), (24), and (25) at $t = t_0$ yields

$$\ln t_0 = \ln I + \frac{E_a}{RT} \tag{26}$$

where

$$I = \frac{F_\infty^{1/a} + (F_\infty^{1/a} - 1)/\beta}{k_0 \bar{P}_n^0} \tag{26a}$$

with β being an adjustable parameter. In order to satisfy eq. (15), β must be large. Accordingly, eq. (26a) is reduced to

$$I = \frac{F_\infty^{1/a}}{k_0 \bar{P}_n^0} \tag{27}$$

It follows that a plot of ln t_0 against T^{-1} would produce a straight line with intercept and slope rendering the information on k_0 and E_a respectively. Such linear plots are demonstrated in Figure 4 for polycarbonate (PC), and poly(tetramethylene oxide) (PTMO).[7,17] Here, the t_0 datum at each temperature was derived by extrapolating the asymptotic linear part of the curve of log$[\eta]_s$ against log t to $[\eta]_s = [\eta]_0$ where $t = t_0$. The PTMO was prepared by the polymerization of tetrahydrofuran/phosphorous pentafloride complex in vacuum as well as in air. Figure 4 reports the E_a for these samples to be 198 (in vacuum) and 215 kJ mol^{-1} (in air), whereas the conventional DSV technique cites a common value of 208 kJ mol^{-1} for the two cases. The E_a values of the PC are 171 and 165 kJ mol^{-1} obtained respectively by the present procedure and the classical approach. Clearly, the E_a data estimated by the two distinct treatments are indeed comparable, considering the possible experimental and algorithm errors involved. Perhaps, a striking feature of eq. (26) is its dependability and simplicity in that it requires less input information to produce the precise results. However, additional data on a, $\bar{P}_n^0$ and b are essential for estimating the absolute value of k.

In conclusion, we have determined the E_a of random scission event for NR, PC, and PTMO by a novel viscometry. The method employs only the $[\eta]$ data collected over either the initial or final stage of the degradation process. It is workable for $D_0 \leq 10$ which practically covers a broad spectrum of commercially important polymers. Although the present and classical viscometric methods seem to produce equivalent results in this study, the former is theoretically

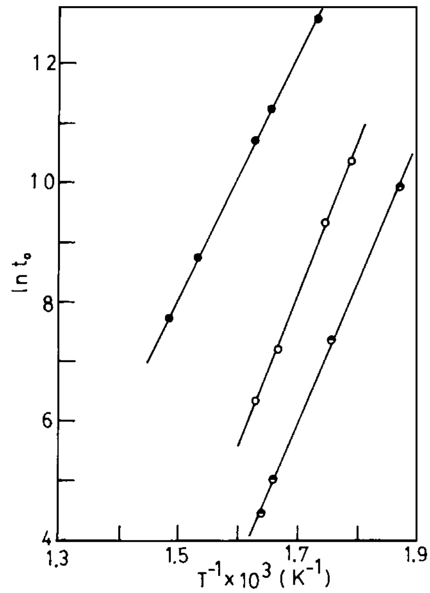

Fig. 4. Plots of ln t_0 against T^{-1} for polycarbonate (●), poly(tetramethylene oxide) prepared in air (○), and in vacuum (◓).

more rigorous in that it makes allowance for the variation of molecular weight distribution with extent of conversion.

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