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ESTIMATION OF DIFFUSION PARAMETERS FOR POLYMER FILMS BY TG

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ABSTRACT

Dynamic thermogravimetric techniques (TG) have been utilized to estimate diffusion parameters during the desorption of water from Nylon 6 and Plexiglas films. Thus, values of activation energy of diffusion (E_D) and diffusion constants (D) could be calculated from expressions derived for the estimation of these parameters from TG traces. In the case of Nylon 6, it was found that values of D were dependent upon heating rate (RH). Values of E_D and $D[(RH) \rightarrow 0]$ obtained were in reasonably good agreement with values reported from static (isothermal) measurements. Average values of E_D (uncorrected) obtained for Nylon 6 and Plexiglas were, respectively, 7.0 ± 0.4 and 10.7 ± 1.2 kcal.mole^{-1}; whereas, corresponding values of $D[303\,^{\circ}\mathrm{K}$ and $(RH) \rightarrow 0]$ were, 2.2×10^{-9} and 2.9×10^{-8} cm^2.sec^{-1}. Advantages and limitations of the method employed are described.

INTRODUCTION

Diffusion constants (D) and activation energies (E_D) are invariably estimated using isothermal techniques. Further, in the case of diffusion of poor solvents in polymer films, weight changes are generally followed using an oven with an external spring-balance arrangement. The polymer film is attached to this balance and suspended inside the constant temperature oven and periodic readings are made (static thermogravimetry). In connection with the preceding, it appeared that dynamic thermogravimetric techniques (TG) would be more advantageous[1] in estimating diffusion parameters (by desorption) which involve weight losses. Thus, there are the following advantages in using TG rather than isothermal methods.

(*a*) Considerably less data are required. Diffusion parameters may be determined over various temperature ranges from the results of a single experiment,

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whereas, several separate experiments are required for each temperature range if isothermal methods are employed.

(*b*) The continuous recording of weight loss *vs*. temperature generally ensures that no features of the diffusion kinetics are overlooked.

(*c*) A single sample is used for the entire TG trace, thereby avoiding a possible source of variation in the estimation of diffusion parameters.

(*d*) In the isothermal method, premature diffusion may occur in the sample during the equilibration period and this may make subsequent kinetic data difficult to analyze properly.

(*e*) A TG trace could yield information as to whether values of D (and E_D) are dependent upon solvent concentration.

However, several major disadvantages of TG may be noted. Less precise control of sample temperature is possible than with static methods. Also, the TG apparatus causes limitations on the sample size. Despite the preceding, it appeared appropriate to investigate the feasibility of employing TG to estimate values of D and E_D and this is the aim of the present paper.

It may be mentioned here that Beyerlein and coworkers[2] recently reported on the use of TG in sorption studies. However, they employed expressions for diffusion which were originally[3] derived for polymer pyrolyses. Further, effects of variables, such as heating rate (RH), were not investigated.

EXPERIMENTAL

Starting materials

The following polymer films were employed: unoriented Nylon 6 film (Capran 77C, Allied Chemical Co.), density = 1.13–1.14, crystallinity ≈30%, viscosity average molecular weight ≈22,000; and polymethylmethacrylate (Plexiglas, Rohm and Haas) film. The film thicknesses ranged from 5.5 mil (for Nylon) to 6.5, 55.5, and 58.8 mil (for polymethylmethacrylate). The sample sizes varied from 20.44 to 47.20 mg for Nylon, and from 45.53 to 197.95 mg for polymethylmethacrylate. Distilled water was used as the poor solvent.

Apparatus

The polymer film samples were placed in a 950 DuPont Thermogravimetric Analyzer. The TG apparatus was programmed for heating rates which varied from 0.2 to 4.0 deg.min^{-1} for Nylon 6, and from 0.5 to 6.0 deg.min^{-1} for polymethylmethacrylate. An atmosphere of purified nitrogen (approx. 40 cm^3.min^{-1}) was maintained around the sample during each run. Isothermal runs were also carried out with this instrument.

Final values reported are based on a least-squares treatment using a Hewlett-Packard 9100A programmable calculator. This calculator was also programmed to estimate values of T_0 by trial-and-error (described in the Theory section), as well as other derived values.

Procedure

The films were soaked in distilled water for several days, at both 30 and 60°C, until the weight of water absorbed (equilibrium concentration of water) was constant. Prior to weighing the samples, they were gently blotted with filter paper to remove surface water. It was found that for any particular sample, the equilibrium water content was independent of temperature. Thus, for the Nylon, the final equilibrium weight of a certain film was identical at either 30 or 60°C. Similar results were obtained for the polymethylmethacrylate. [However, in the case of Plexiglas, the equilibrium water concentration may become temperature dependent well above the T_g (*cf.* Results and Discussion section)]. Further, final identical weights were obtained when the commercial samples were dried prior to soaking in water or soaked without prior drying.

The soaked polymer film was quickly placed into the TG apparatus and the weight loss of the sample was recorded starting with ambient temperature. In the temperature range employed, the polymer films should not be thermally degraded (*cf.* Fig. 1).

THEORY

When desorption occurs by diffusion of a poor solvent (*e.g.* water) in a polymeric film under isothermal conditions, and the film contains a uniform initial distribution of solvent, and the surface concentrations of solvent are maintained at zero, we can consider the following two cases.

Case 1. — For short times (and low conversions)^4

$$1 - \frac{W_t}{W_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}} \tag{1}$$

where, W_t = weight of solvent in film at any time, t; W_∞ = equilibrium weight of solvent in film; D = diffusion coefficient; and l = one-half the film thickness.

When Eqn. 1 is differentiated with respect to t and the following expressions are utilized,

$$(\mathrm{RH}) = \mathrm{d}T/\mathrm{d}t \tag{2}$$

$$D = D_0\, \mathrm{e}^{-E_\mathrm{D}/RT} \tag{3}$$

Eqn. 4 is obtained,

$$-\frac{\mathrm{d}W}{\mathrm{d}T} = \frac{2\, W_\infty D_0\, \mathrm{e}^{-E_\mathrm{D}/RT}}{(\mathrm{RH})\,\pi l^2\,(1 - W/W_\infty)} \tag{4}$$

where, W = weight of solvent in film at any temperature, T; and, (RH) = rate of heating = constant.

Upon integration, Eqn. 4 becomes,

$$\int_{W_\infty}^{W}(W-W_\infty)\,\mathrm{d}W=\frac{2W_\infty^2 D_0}{(\mathrm{RH})\pi l^2}\int_{T_0}^{T}\mathrm{e}^{-E_\mathrm{D}/RT}\,\mathrm{d}T$$

$$=\frac{2W_\infty^2 D_0}{(\mathrm{RH})\pi l^2}\left[\left(\int_0^{T}\mathrm{e}^{-E_\mathrm{D}/RT}-\int_0^{T_0}\mathrm{e}^{-E_\mathrm{D}/RT}\right)\mathrm{d}T\right] \tag{5}$$

By employing approximations previously reported[5], Eqn. 5 becomes,

$$1+\left(\frac{W}{W_\infty}\right)^2-2\left(\frac{W}{W_\infty}\right)=\frac{4D_0RT^2P}{(\mathrm{RH})\pi l^2E_\mathrm{D}}\left[1-\left(\frac{P_0}{P}\right)\left(\frac{T_0}{T}\right)^2\mathrm{e}^{-E_\mathrm{D}/R(1/T_0-1/T)}\right]\mathrm{e}^{-E_\mathrm{D}/RT} \tag{6}$$

where, $P=(1-2RT/E_\mathrm{D})$; $P_0=(1-2RT_0/E_\mathrm{D})$; and T_0 = initial temperature at which the TG trace begins to depart from the horizontal (zero conversion). Since P_0/P is generally close to unity throughout a run and letting $P=P_{\mathrm{av.}}$, Eqn. 6 finally becomes,

$$\ln\left\{\frac{f(W)}{MT^2}\right\}=-\frac{E_\mathrm{D}}{RT}+\ln\frac{4D_0RP_{\mathrm{av.}}}{(\mathrm{RH})\pi l^2E_\mathrm{D}} \tag{7}$$

where, $M\equiv1-\left(\frac{T_0}{T}\right)^2\mathrm{e}^{-(E_\mathrm{D}/R)[(T-T_0)/TT_0]}$ and $f(W)\equiv1+\left(\frac{W}{W_\infty}\right)^2-2\left(\frac{W}{W_\infty}\right)$.

Case 2. — For long times (and high conversions)[4]

$$W_t/W_\infty=\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\mathrm{e}^{-D(2n+1)^2\pi^2t/L^2} \tag{8}$$

where, L = film thickness. Since the series in Eqn. 8 converges rapidly at relatively long times, and letting $n=0$, Eqn. 8 becomes

$$W_t/W_\infty\approx\frac{8}{\pi^2}\mathrm{e}^{-D\pi^2t/L^2} \tag{9}$$

Upon differentiation and utilizing Eqns. 2 and 3, Eqn. 9 becomes

$$-\frac{\mathrm{d}W}{\mathrm{d}T}=\frac{W\pi^2D_0\mathrm{e}^{-E_\mathrm{D}/RT}}{(\mathrm{RH})L^2} \tag{10}$$

Upon integration of Eqn. 10 and carrying out a similar treatment as in *Case 1*, Eqn. 11 is obtained

$$\ln\frac{W_\infty}{W}=\frac{\pi^2D_0RT^2PM}{(\mathrm{RH})L^2E_\mathrm{D}}\mathrm{e}^{-E_\mathrm{D}/RT} \tag{11}$$

or

$$\ln\left\{\frac{\ln\frac{W_\infty}{W}}{MT^2}\right\} = -\frac{E_D}{RT} + \ln\frac{\pi^2 D_0 R P_{av.}}{(RH)\, L^2 E_D} \tag{12}$$

In connection with Eqn. 12, it may be remarked here that if a first-order reaction is assumed, *i.e.*

$$-dW/dt = kW \tag{13}$$

and if a treatment similar to that already described is carried out, Eqn. 13 yields,

$$\ln\left\{\frac{\ln\frac{W_0}{W}}{MT^2}\right\} = -\frac{E}{RT} + \ln\frac{ZRP_{av.}}{(RH)E} \tag{14}$$

where, W_0 = initial weight of material undergoing reaction; and, E = activation energy of the reaction. Beyerlein and coworkers[2] utilized an expression similar to Eqn. 14 to estimate activation energies of desorption (E in Eqn. 15)

$$\ln\left\{\ln\frac{W_0}{W}\right\} = -\frac{E}{RT} + \text{constant} \tag{15}$$

Values of E_D, D_0 (and consequently D) may be estimated from Eqns. 7 and 12 as follows. At relatively high conversions (and temperatures), $T_0 \ll T$, and therefore, $M \approx 1$. Thus, for example, for relatively long times (*cf.* Eqn. 12), values of W and T at relatively high conversions are employed (with $M \approx 1$) in a plot of ln [ln $(W_\infty/W)/T^2$] *vs.* $1/T$ to afford preliminary values of E_D and D_0. Then, values of W and T at lower conversions (and values of T) are substituted into Eqn. 12 to estimate M and consequently T_0 (by trial-and-error). Once T_0 is known, a plot of the left-hand side of Eqn. 12 *vs.* $1/T$ may be made to obtain more accurate values of E_D, D_0, and D (for any particular temperature). In the case of the diffusion of water through the polymer films studied, the average value of T_0 was about 268 °K. Since the TG runs commenced at ambient temperature, it was not possible to obtain data at very low conversions and it was therefore not possible to employ Eqn. 7. Thus, Eqn. 12 only was used to estimate values of E_D and D_0 for the diffusion of water in Nylon 6 and Plexiglas. It was assumed that dynamic equilibrium obtained at the higher diffusion temperatures (and higher conversions) and that there was no chemical reaction between water and polymer over the temperature range of interest.

RESULTS AND DISCUSSION

Nylon 6

In Fig. 1 is shown a typical TG trace for Nylon 6. The conditions involved in this run (Run No. N9 in Table I) are: (RH) = 4.0 deg.min^{-1}; nitrogen gas flow rate = 40 cm^3.min^{-1}; $L = 5.5$ mil; $W_\infty = 2.06$ mg. Utilizing values of W and T at high conversions (86–92%) and assuming $M = 1$, a linear regression treatment of derived data, *i.e.*, $\ln[\ln(W_\infty/W)/T^2]$ *vs.* $1/T$, afforded values of $E_D/2 = 3325$ and $\ln[\pi^2 D_0 R P_{av.}/(\mathrm{RH}) L^2 E_D] \equiv B = -1.99$. From these values, and values of W and T at lower conversions (65–70%), values of M, and consequently of T_0, could be calculated. In this manner, $T_0 = 274 \pm 1$ °K for this particular run. From this average value of T_0, values of $\ln[\ln(W_\infty/W)/MT^2]$ *vs.* $1/T$ could be calculated over a wide range of conversion (42–92%) and a linear regression analysis of the linear plot obtained (*cf.* Fig. 2) afforded values of $E_D/2 = 3461$ and $B = -1.60$. From a comparison between the uncorrected values ($M = 1$) and corrected values ($M \neq 1$) of E_D and D_0, it can be seen that it can be assumed that $M = 1$ with little error in these values. In Table I are summarized values (corrected and uncorrected) of E_D, D_0, and D(303 °K) for Nylon 6. In calculating values of D_0 (and D), a value of $P_{av.} = 0.8$ was used for all the runs. From the table, it can be observed that D(303 °K) and D_0 are dependent on values of (RH) whereas, the value of E_D is relatively independent of (RH). Thus, over a range of (RH) = 0.2–4.0 deg.min^{-1}, E_D (av., uncorrd.) = 7.0 ± 0.4 kcal.mole^{-1}. However, as shown in Fig. 3, a plot of D(303 °K) *vs.* (RH) clearly indicates that D is dependent on (RH). A linear regression analysis of data involving (RH) values from 0.2 to 0.7 deg.min^{-1} afforded a limiting [(RH) = 0] value of D(303 °K, uncorrd.) = 2.2×10^{-9} cm^2.sec^{-1} and D(303 °K, uncorrd.) = 2.0×10^{-9} cm^2.sec^{-1}. In connection with these values, it may be noted here that three isothermal desorption runs were carried out at 311.7, 315.4, and 327.3 °K for the diffusion of water in Nylon 6. From Eqn. 1, a plot of W_t/W_∞ *vs.* $t^{\frac{1}{2}}$ should afford a

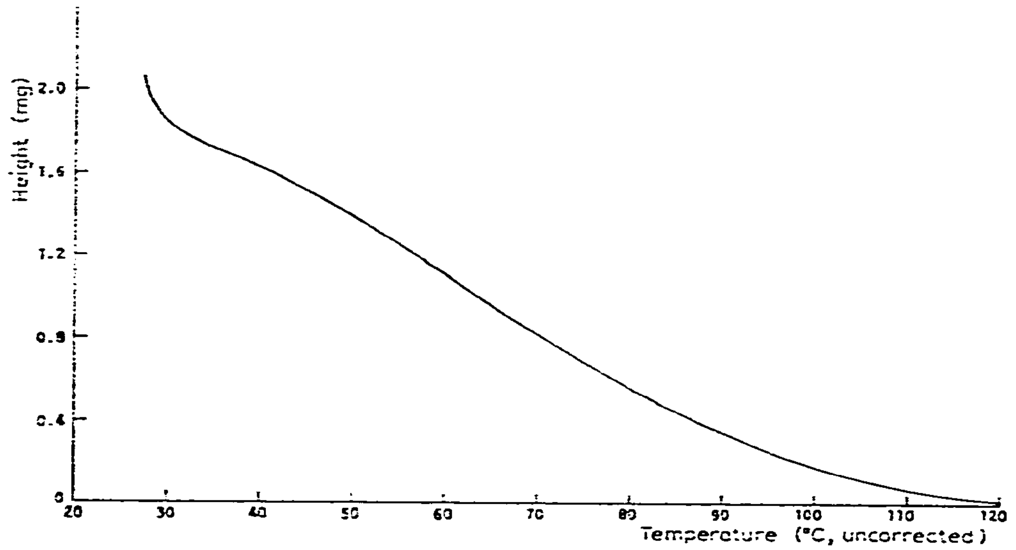

Fig. 1. TG trace for desorption of water from Nylon 6. (RH) = 4.0 deg.min^{-1}, $W_\infty = 2.06$ mg, $L = 5.5$ mil, nitrogen flow rate = 40 cm^3.min^{-1}.

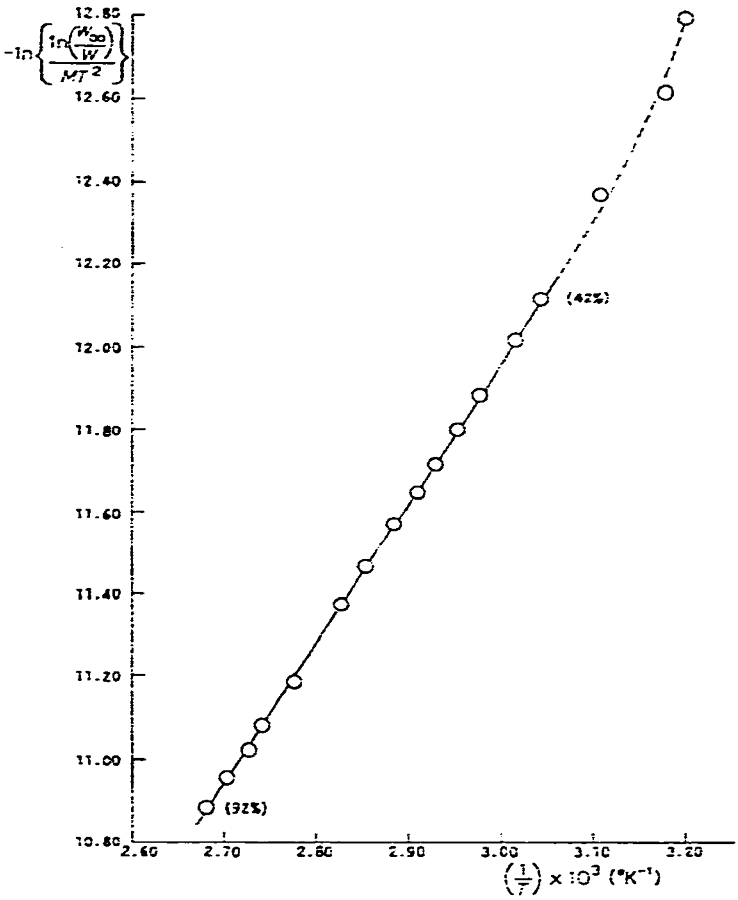

Fig. 2. Plot of $-\ln \frac{\ln(W_\infty/W)}{MT^2}$ *vs.* $1/T$ for Nylon 6 (data from Run N9). (RH) = 4.0 deg.min^{-1}, W_∞ = 2.06 mg, L = 5.5 mil, nitrogen flow rate = 40 cm^3.min^{-1}, T_0 = 274°K, $E_D/2$ = 3325 cal.mole^{-1} (M = 1). The numbers along the curve denote percentage conversion.

TABLE I

VALUES OF E_D, D_0, AND D(303°K) FOR NYLON 6 UNDER VARIOUS EXPERIMENTAL CONDITIONS

Run No.	(RH) (*deg.min*$^{-1}$)	*Nitrogen flow rate* (*cm*^{3}*.min*$^{-1}$)	E_D(*kcal.mole*$^{-1}$)		$D_0 \times 10^4$ (*cm*^{2}*.sec*$^{-1}$)		D(303°K) $\times 10^9$ (*cm*^{2}*.sec*$^{-1}$)	
			Uncorrd.	*Corrd.*	*Uncorrd.*	*Corrd.*	*Uncorrd.*	*Corrd.*
N1	0.20	40	6.8	6.5	2.0	1.3	3.0	3.0
N2	0.30	40	7.2	6.8	5.4	2.8	3.4	3.6
N3	0.50	10	6.4		1.4		4.0	
N4	0.50	40	7.1	6.9	5.0	3.6	4.1	4.4
N5	0.70	40	6.6	6.1	2.8	1.3	4.9	5.6
N6	1.0	40	7.3	7.0	12.1	7.8	6.5	6.7
N7	1.0	40	7.4		11.5		6.4	
N8	2.5	40	7.6		26.0		9.6	
N9	4.0	40	7.2	6.9	17.0	12.0	11.8	12.6

linear relation, at low conversions, whose slope will yield a value of D. Then a plot of $\ln D$ *vs.* $1/T$ (*cf.* Eqn. 3) should give values of E_D and D_0 (and D). In this manner, $E_D = 8\text{–}9$ kcal.mole^{-1} and $D(303\,^{\circ}K) \approx 14 \times 10^{-9}$ cm^2.sec^{-1}. These values are for relatively high concentrations of water in the Nylon 6 film and indicate that $D(303\,^{\circ}K)$ is dependent upon water content when this is relatively high. [However, there exists doubt concerning the accuracy of these isothermal results since the Arrhenius type plot, $\ln D$ *vs.* $1/T$ was not a good linear fit]. Others[6,7] have also indicated that values of D for Nylon 6 are dependent upon water concentration (increasing with increasing water content). Thus, for an "untreated" Nylon 6 film, $D(25\,^{\circ}C)$ has been reported[7] to be as high as 10×10^{-9} cm^2.sec^{-1} for a relatively high water content of about 7% and as low as 1×10^{-9} cm^2.sec^{-1} for a water content of about 2.5%. [D values are also reported to be a function of the pre-treatment the film has undergone as well as the temperature involved[6] (above or below $T_g = 40\text{–}50\,^{\circ}C$)]. The dependence of D on water content may be utilized to explain, in part, the dependence of D (and D_0) on (RH). Thus, in the following are given heating rate (deg.min^{-1}) and the mean percentage of water in the film over the conversion range [over this range, temperatures were generally above 50 °C (T_g for Nylon 6)] that Eqn. 12 was applied, respectively, 0.2, 8; 0.3, 11; 0.5, 13 (av.); 0.7, 17; 1.0, 27 (av.); 2.5, 45; and 4.0, 35. From this, it would be anticipated, based upon the water concentration dependency, that as (RH) increases (and consequently, the mean water concentration

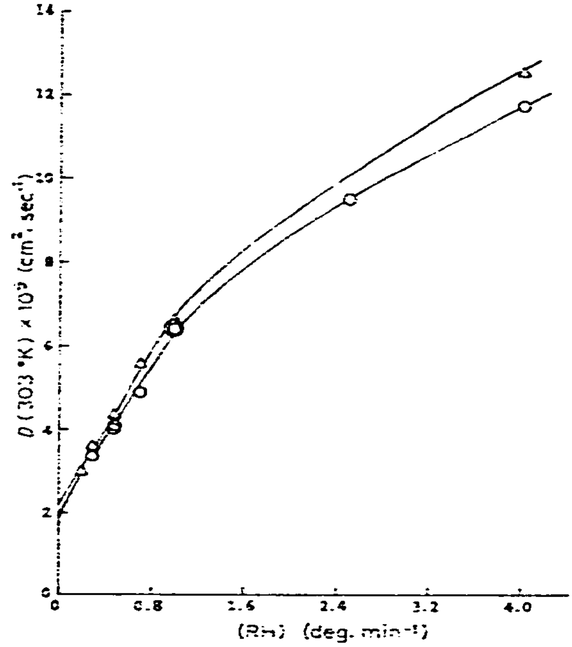

Fig. 3. Plot of $D(303\,^{\circ}K)$ *vs.* heating rate, (RH), for desorption of water from Nylon 6. ○—○, uncorrected $D(M = 1)$; △—△, corrected $D(M \neq 1)$.

in the film), values of D_0 (and D) would increase, as observed. Further, limiting values of $D[(\mathrm{RH}) = 0]$ may be compared with reported values of D obtained from initial data involved in sorption studies (the concentration of water in the film may be considered to be very low during the early sorption stages). Asada and Onogi[6] reported a value of $D(303\,°\mathrm{K}) = 1.3 \times 10^{-9}$ cm^2.sec^{-1} (for zero water concentration). However, these workers also reported that values of E_D were temperature dependent, varying from about 14 at 50°C (T_g) to about 6.5 kcal.mole^{-1} at 25°C.

TABLE II

VALUES (UNCORRECTED) OF E_D, D_0, AND $D(303\,°\mathrm{K})$ FOR PLEXIGLAS UNDER VARIOUS EXPERIMENTAL CONDITIONS

Run No.	(RH) (*deg.min*$^{-1}$)	*Nitrogen flow rate* (*cm*^{3}.*min*$^{-1}$)	E_D (*kcal.mole*$^{-1}$)[a]	D_0 (*cm*^{2}.*sec*$^{-1}$)	$D(303\,°\mathrm{K}) \times 10^8$ (*cm*^{2}.*sec*$^{-1}$)[b]
P1	0.50	40	9.3	0.12	2.94
P2	1.0	40	9.7	0.21	2.85
P3	2.0	40	9.5	0.15	3.03
P4	4.0	40	11.8	7.7	3.01
P5	5.0	40	11.9	8.5	2.93
P6	6.0	40	11.9	11.2	3.57

[a] E_D(av.) = 10.7 ± 1.2 kcal.mole^{-1}. [b] $D \times 10^8$(av.) = 2.9 ± 0.1 cm^2.sec^{-1} (excluding Run P6).

Polymethylmethacrylate (*Plexiglas*)

Adopting an approach similar to that employed for Nylon 6, it was found that corrected ($M \neq 1$) and uncorrected ($M = 1$) values of E_D and $D(303\,°\mathrm{K})$ were in very good agreement and that it was therefore unnecessary to correct for values of M. Thus, from data obtained for the desorption of water from Plexiglas (*cf.* Run No. P6 in Table II) employing TG techniques, it was found that $T_0 = 275\,°\mathrm{K}$ and that uncorrected ($M = 1$) values of E_D and $D(303\,°\mathrm{K})$ were, respectively, 11.9 kcal.mole^{-1} and 3.2×10^{-8} cm^2.sec^{-1} whereas, the corresponding corrected ($M \neq 1$) were, 11.7 kcal.mole^{-1} and 3.3×10^{-8} cm^2.sec^{-1}. The various results obtained for Plexiglas and the various experimental conditions used are summarized Table II. Values of $P_{\mathrm{av.}}$ varied from 0.82 to 0.89.

From Table II, it can be seen, contrary to the results obtained for Nylon 6, that in the case of Plexiglas, values of E_D, D_0 (and D) are independent of (RH) from 0.50 to 2.0 deg.min^{-1}, the average values being $E_D = 9.5 \pm 0.1$ kcal.mole^{-1}, $D_0 = 0.16 \pm 0.03$ cm^2.sec^{-1}, and $D \times 10^8 (303\,°\mathrm{K}) = 2.94 \pm 0.06$ cm^2.sec^{-1}. Further, over the higher range of values of (RH), 4.0–6.0 deg.min^{-1}, values of E_D and D_0 are higher, but approximately constant; thus, $E_D = 11.9 \pm 0.0$ kcal.mole^{-1} and $D_0 = 9.1 \pm 1.3$ cm^2.sec^{-1}. Except for $D(303\,°\mathrm{K})$ at $(\mathrm{RH}) = 6$ deg.min^{-1}, the order of magnitude of the $D(303\,°\mathrm{K})$ values at (RH) = 4.0 and 5.0 is similar to that at the lower values of (RH). Average values of $D \times 10^8$ cm^2.sec^{-1} at 293, 310.4, and 323 °K were also calculated and are, respectively, 1.7 ± 0.1; 4.7 ± 0.4; and, 9.3 ± 1.0. These values were estimated over the entire range of (RH) employed, *i.e.*, 0.5–6.0 deg.min^{-1}. Values reported for $D \times 10^8$ cm^2.sec^{-1} (for polymethylmethacrylate) at 293, 303, 310.4, and 323°K are[8–12], respectively, 0.5 and 0.9; 1.6 and 1.8; 0.9, 1.4, and 2.3; 4.3, 13.0, and 13.3. Reported values of E_D for polymethylmethacrylate are[8–10], 10.1, 10.4, 11.6, and 14.9 kcal.mole^{-1}. It should be noted here that a fair comparison of TG values of E_D and D with values from isothermal measurements must take into consideration the following. For several water–polymer systems it has been observed[10] that values of D appear to depend on the method of measurement, *e.g.*, transient *vs.* steady-state techniques. It has also been reported[10,12] that D values are dependent upon the water concentration in polymethylmethacrylate and that E_D and D_0 values depend upon whether the diffusion temperature is below or above the value of T_g (about 90°C). The water concentration factor should not affect the TG values obtained (on a relative basis) since the mean water contents varied only between 22–28% over the conversion range that Eqn. 12 was applied. However, for Runs P1–P3 (Table II), the temperature values encountered varied from about 105 to 180°C (these values are above the T_g value) whereas, for Runs P4–P6, temperatures employed ranged from 45 to 77°C (below the T_g value). These temperature ranges arose due to the utilization of much larger sample thicknesses for Runs P1–P3 as compared with Runs P4–P6 (about 58 as against 7 mil). Although consideration of T_g may account, in part, for the differing E_D values in Table II, it may be remarked that whereas, E_D appeared to decrease for temperatures above T_g, an opposite trend was reported by Ryskin and coworkers (*cf.* Ref. 10). In this connection, it may be mentioned that above the T_g it has been reported[13] that the equilibrium water concentration commences to change markedly. Such an effect may markedly influence diffusion parameter values obtained for Plexiglas from TG techniques.

Based upon results obtained from TG techniques for Nylon 6 and polymethylmethacrylate, it appears that values of E_D and D, calculated from water desorption data, may be obtained with reasonably good reliability from such techniques. However, in order to minimize the possible effects of heating rate and T_g, low values of (RH) and samples with similar dimensions should be employed. It is planned to extend these TG techniques to other solvent–polymer systems. In the case of water, it was not possible (under the experimental conditions used) to apply Eqn. 7 due to the relatively high volatility of water ($T_0 \approx 268$°K). However, this expression, as well as Eqn. 12, may be applicable in cases where solvents are much less volatile than water (higher T_0). In such cases, it should be possible to obtain a fairly complete spectrum of values from a single thermogram. These values could indicate the extent of the dependency of E_D and D_0 (and D) values upon solvent concentration and T_g.

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