

## Diffusion of *m*-Nitroaniline into Polyacrylonitrile

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### Synopsis

The diffusion of nonionic penetrant, *m*-nitroaniline, into polyacrylonitrile was studied in detail on a range of temperature from 50.6°C to 95.0°C. The penetrant distribution in polymer is Fickian, which is different from that of cationic dye, Malachite Green reported earlier. The diffusion coefficient  $D$  increases with the rise of temperature. The sharp inflection point (72°C) of the Arrhenius plot,  $\log D$  versus  $1/T$ , corresponds to  $T_g$  of polyacrylonitrile in the presence of water, which is lower than that measured in the dry state by a dynamic mechanical testing method. The activation energy is constant below  $T_g$  (ca. 10 kcal/mole), suddenly reaches a maximum at  $T_g$ , and then gradually decreases with increasing temperature. General trends of Arrhenius plot for different polymer-penetrant systems are discussed. The temperature dependence of penetrant diffusion above  $T_g$  can be described by a general form of the WLF equation,  $\log a_T = \log (D_{T_g}/D_T) = -C_1^g(T - T_g)/(C_2^g + T - T_g)$ , where the values of  $C_1^g$  and  $C_2^g$  were calculated to be 4.03 and 24.54, respectively. A comparison was made between *m*-nitroaniline and Malachite Green. The difference in the respective  $T_g$  and the constants  $C_1^g$  and  $C_2^g$  of the WLF equation in polyacrylonitrile is attributed to the size of the penetrants and their ionic character. The surface concentration increases below  $T_g$  and decreases above  $T_g$  with rise in temperature.

### INTRODUCTION

The study of diffusion in polymers has become quite important for the consideration of the dyeing mechanism<sup>1</sup> and polymer structure.<sup>2-4</sup> Much work has been done on the diffusion of cationic dye in polyacrylonitrile.<sup>5-9</sup> Rosenbaum<sup>6</sup> showed that diffusion of cationic dye in polyacrylonitrile is Fickian and governed by an interchange mechanism in which dye penetrates by interchange between the mobile occupied sites and unoccupied ones farther inside the fiber. He derived Fick's law from the second-order kinetics of such an interchange with a diffusion coefficient proportional to site concentration. The present authors<sup>5</sup> have carried out experimental work on the diffusion of a cationic dye, Malachite Green, in polyacrylonitrile and found that the distribution of cationic dye in polyacrylonitrile is anomalous, i.e., non-Fickian. The diffusion coefficient has a strong concentration dependence which can be well explained by the chemical potential gradient model given by Atherton et al.<sup>10</sup> A wide range of temperature was taken to study the temperature dependence of dye diffusion, and it was found that

such dye diffusion could be described by a general form of the WLF equation.<sup>11</sup>

Many reports have been published on the diffusion and dyeing of synthetic fibers with disperse dyes. Majury,<sup>12</sup> Bird et al.,<sup>13-15</sup> Campbell,<sup>16</sup> and Fortess et al.<sup>17</sup> published a number of papers about the dyeing and diffusion of cellulose acetate. Again, Sand<sup>18</sup> described in detail the evaluation of diffusion measurements with a high resolution microphotometer and showed the concentration profiles to correspond to Fick's law diffusion. The important point is noted here that little work has been done on the disperse dye in polyacrylonitrile, though recently Hoten et al.<sup>19</sup> investigated the dyeability of a polyacrylonitrile fiber, Exlan, with disperse dyes having different substituents at 90°C and 100°C in equilibrium.

Following the pioneering work Barrer<sup>20</sup> on the diffusion and inner molecular motion of polymer, i.e., hole formation, it was generally recognized that there is an intimate and close relationship between diffusion and the glass transition temperature of polymers. In a report on diffusion-controlled transitions in high polymers by Kanamaru et al.,<sup>21</sup> the diffusion process was treated as one of the relaxation phenomena, characteristic of polymers. They studied the temperature dependence of diffusion coefficients of different polymer-penetrant systems, and their results show that the general trend of the  $\log D$  versus  $1/T$  plot may be attributed to the presence of a few typical relaxation mechanisms which begin to occur at different temperatures corresponding to each of their different relaxation times. Boyer<sup>22</sup> mentioned in his review as regards the dependence of  $D$  on  $T_g$  that both quantitative and qualitative changes are expected in  $D$  below and above  $T_g$ , because the activated diffusion step depends on the segmental motion which sets in at  $T_g$ . Kokes et al.<sup>23</sup> in the study of diffusion of acetone in PVAc found that diffusion above  $T_g$  was Fickian and below  $T_g$  was non-Fickian.

In the present work, unlike the previous one, a different penetrant, *m*-nitroaniline, which is a model substance of disperse dye, was used in the diffusion experiment. The purpose of this work is to study the diffusion behavior of nonionic penetrant in polyacrylonitrile over a wide range of temperature and to compare the results with those of cationic dye diffusion published earlier.<sup>5</sup> The transition phenomenon and thermal properties of polymers are also discussed in detail.

## EXPERIMENTAL

### Film

The substrate used in the experiment was polyacrylonitrile (PAN) film which was prepared in the laboratory from Vonnell W (Mitsubishi Rayon Co., Ltd.). Vonnell was dissolved in dimethylformamide (12% by weight) and was kept for more than three days for uniform solution which was essential for preparing film of uniform thickness. A thin coating of poly-

mer was made on a glass plate and dried in an electric drier. The drying temperature and the time were as follows: 60°C, 115°C, and 140°C for 3, 3 and 5 hr, respectively. The solvent was completely removed and was confirmed by examining the 1663 cm<sup>-1</sup> band (carbonyl stretching in DMF) in the infrared spectra. The thickness of the film was about 5 μ and measured accurately by a Minicom thickness gauge (Tokyo Seimitsu Co.). In each film the standard deviation of the mean value was within 3.6%.

### Penetrant

The penetrant, *m*-nitroaniline (mp 112–114°C, *pK<sub>a</sub>* = 2.46 in H<sub>2</sub>O at 25°C) was of JIS special grade. The absorption maximum in water and on film was 225 and 235 mμ, respectively.

### Diffusion Apparatus and Procedure

The film prepared in the above way was cut to 33 cm × 3 cm and treated in water at 98°C for 24 hr. The pretreated film was rolled on a glass tube at 40°C in water. During rolling special care was taken so that no bubble was between the consecutive layers of the film. Diffusion experiments were carried out in a 500-ml diffusion bottle fitted with a reflux condenser. The penetrant concentration was 1.0 g/l distilled water which was chosen in such a way that an infinite penetrant bath condition was held throughout the experiment. The pH of the penetrant bath was maintained at 6.9 by using phosphate buffer (0.01 mole/l KH<sub>2</sub>PO<sub>4</sub>–Na<sub>2</sub>HPO<sub>4</sub>) at room temperature. After diffusion, the optical density of the respective layers at 235 mμ was measured by a Shimadzu SV-50A spectrophotometer. The concentration of the penetrant on the film was confirmed to obey the Lambert–Beer law. Experiments were carried out on a wide range of temperature from 50.6°C to 95.0°C (±0.1°C).

### Calculation of Diffusion Coefficient *D*

In the present experiment the cylindrical film roll may be reasonably taken as a semi-infinite medium within a limited diffusion time because the thickness of the film roll is very small in comparison with the diameter of the glass tube. The equation of diffusion along the radial direction of the film can be expressed by Fick's second law,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where *D*(cm<sup>2</sup>/min) is the constant diffusion coefficient, *C*(mole/g) is the concentration of the penetrant in polymer, *t*(min) is the time, and *x*(cm) is the distance. As the dyebath is infinite, the boundary and the initial conditions are given by eqs. (2) and (3), respectively:

$$C = C_s, \quad x = 0, \quad t > 0 \quad (2)$$

$$C = 0, \quad x > 0, \quad t = 0 \quad (3)$$

where  $C_s$  (mole/g) is the surface concentration. On applying the Laplace transform, the solution of eq. (1) satisfying the conditions (2) and (3) is given by

$$C = C_s \operatorname{erfc} x/2\sqrt{Dt} \quad (4)$$

where

$$\operatorname{erfc} x = 2/\sqrt{\pi} \int_x^\infty e^{-\xi^2} d\xi \quad (5)$$

The adsorption amount of the penetrant  $\bar{C}_i$  of the  $i$ th layer in the film roll of layer thickness  $\epsilon$  is given by

$$\bar{C}_i = \int_{(i-1)\epsilon}^{i\epsilon} C dx = 2C_s\sqrt{Dt} \left( \operatorname{ierfc} \frac{(i-1)\epsilon}{2\sqrt{Dt}} - \operatorname{ierfc} \frac{i\epsilon}{2\sqrt{Dt}} \right) \quad (6)$$

$i = 1, 2, \dots, n$

where

$$\operatorname{ierfc} x = \int_x^\infty \operatorname{erfc} \xi d\xi \quad (7)$$

It is notable here that  $\bar{C}_i$ , if expressed in concentration units, is the average concentration of the  $i$ th layer.

Putting

$$\epsilon/2\sqrt{Dt} = \zeta \quad (8)$$

the following relation is obtained

$$\frac{\bar{C}_{i+1}}{\bar{C}_i} = \frac{\operatorname{ierfc} i\zeta - \operatorname{ierfc} (i+1)\zeta}{\operatorname{ierfc} (i-1)\zeta - \operatorname{ierfc} i\zeta} \quad (9)$$

It is understandable from eq. (9) that for different values of  $i = 1, 2, \dots, n$  and  $\zeta$ , different respective curves are drawn (Fig. 1).<sup>24</sup> The value of  $\zeta$  corresponding to experimental value  $\bar{C}_{i+1}/\bar{C}_i$  is obtained directly from the curves in Figure 1 for different layers  $i = 1-6$  and the average value of  $\zeta$  is used for the calculation of diffusion coefficient.<sup>24</sup>

On rewriting eq. (8), the diffusion coefficient is calculated from

$$D = \frac{\epsilon^2}{4t\zeta^2} \quad (10)$$

$$= \eta^2/\zeta^2 \quad (11)$$

where

$$\eta = \epsilon/2\sqrt{t} \quad (12)$$

In this paper eq. (11) was used for the calculation of diffusion coefficient  $D$ . The surface concentration was obtained by extrapolating the concentration-distance curve to the surface ( $x = 0$ ), and the  $C_s$  value for particular temperature was obtained by averaging the different values corresponding to different diffusion times at that temperature. A  $C_i/C_s$  versus  $\epsilon/2\sqrt{t}$

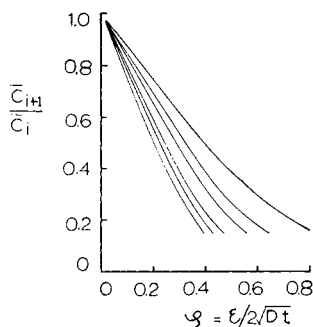


Fig. 1. Graph for the determination of the value of  $\zeta$  directly from  $\bar{C}_{i+1}/\bar{C}_i$ . Data of Sekido and Matsui.<sup>24</sup>

plot was drawn at a particular temperature for different times. Different values of  $c_i = C_i/C_s$  were selected for corresponding  $\eta = \epsilon/2\sqrt{t}$  at regular intervals. The values of  $\frac{c_{i+1}}{c_i} \left( = \frac{C_{i+1}}{C_i} \right)$  can be directly obtained from the optical density of the respective layers without being converted into concentration.

## RESULTS AND DISCUSSION

At each temperature diffusion was carried out for several lengths of time. The constancy of surface concentrations for different corresponding times was demonstrated by extrapolating the concentration-distance curve (Fig. 2). The plot of  $C_i/C_s$  versus  $x/(2\sqrt{t})$  lies on the same curve independent of time (Fig. 3). Diffusion coefficients were calculated from this smooth curve, and the constancy of the value of diffusion coefficient  $D$  in Table I clearly shows that the distribution of nonionic penetrant in polyacrylonitrile is Fickian, which is quite different from the case of cationic penetrant,<sup>5</sup> where the distribution is non-Fickian (Fig. 4) and the diffusion coefficient has strong concentration dependence. This is a remarkable

TABLE I  
Constancy of Diffusion Coefficient at 74.5°C<sup>a</sup>

<i>i</i> th layer	$\eta \times 10^{-5}$ , cm-min <sup>-1/2</sup>	$C$	$C_{i+1}/C_i$	$\epsilon/2\sqrt{Dt}$
1	2.00	0.890	0.764	0.200
2	6.00	0.680	0.752	0.185
3	10.00	0.512	0.706	0.189
4	14.00	0.362	0.662	0.194
5	18.00	0.239	0.577	0.212
6	22.00	0.138	0.608	0.188
7	26.00	0.084		

<sup>a</sup>  $\epsilon/2\sqrt{Dt} = 1.168/6 = 0.194$ ;  $D = 4.25 \times 10^{-10}$  cm<sup>2</sup>/min;  $C_s = 18.86 \times 10^{-4}$  eq/g.

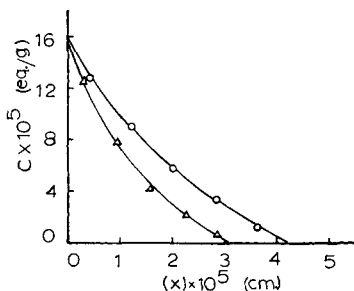


Fig. 2. Diffusion profiles of *m*-nitroaniline into polyacrylonitrile at 77.3°C: (Δ) 8<sup>1</sup>/<sub>2</sub> hr; (○) 21<sup>1</sup>/<sub>4</sub> hr.

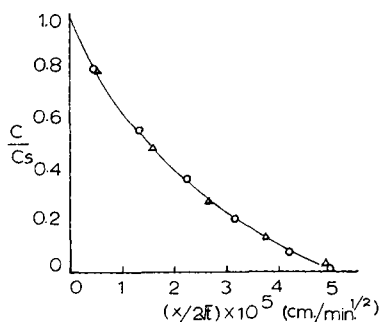


Fig. 3. Diffusion profiles of *m*-nitroaniline into polyacrylonitrile independent of time at 77.3°C: (Δ) 8<sup>1</sup>/<sub>2</sub> hr; (○) 21<sup>1</sup>/<sub>4</sub> hr.

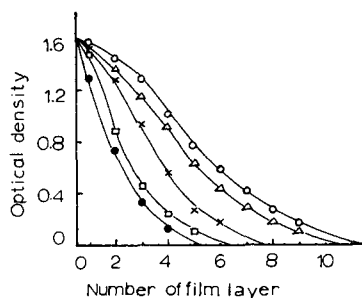


Fig. 4. Diffusion profiles of Malachite Green into polyacrylonitrile at 98°C: (○) 24 hr; (Δ) 20 hr; (×) 9<sup>1</sup>/<sub>2</sub> hr; (□) 5 hr; (●) 3 hr.

difference in the diffusion behavior of cationic and nonionic penetrant into polyacrylonitrile. The cationic penetrants are adsorbed on the acidic sites of polymer by an ion-exchange mechanism whereas the nonionic penetrants are adsorbed by a dissolution mechanism which is governed by the Nernst distribution law. It is notable here that, as mentioned earlier, Rosenbaum<sup>6</sup> shows the concentration independence of cationic dye diffusion in polyacrylonitrile and Sand<sup>18</sup> in the case of disperse dye in polyamide-6 has

TABLE II  
Temperature Dependence of Diffusion Coefficients and Surface Concentrations

Temp, °C	$D$ , cm <sup>2</sup> /min	$C_s \times 10^5$ , eq/g
50.6	$1.02 \times 10^{-10}$	2.24
59.0	$1.66 \times 10^{-10}$	7.53
64.0	$1.78 \times 10^{-10}$	18.44
71.0	$2.75 \times 10^{-10}$	14.50
72.0	$2.78 \times 10^{-10}$	19.30
74.5	$4.25 \times 10^{-10}$	18.86
77.0	$1.42 \times 10^{-9}$	14.65
77.3	$1.11 \times 10^{-9}$	16.10
79.0	$2.06 \times 10^{-9}$	14.50
82.5	$4.33 \times 10^{-9}$	12.60
83.8	$5.49 \times 10^{-9}$	14.10
87.5	$7.30 \times 10^{-9}$	12.38
89.0	$15.40 \times 10^{-9}$	10.25
92.3	$20.70 \times 10^{-9}$	10.30
95.0	$25.60 \times 10^{-9}$	12.90

shown that concentration profile corresponds to Fick's law diffusion. The results of McGregor et al.<sup>25</sup> for acid dye diffusion and of Sand<sup>18</sup> for disperse dye diffusion in polyamide shows that diffusion behavior of both ionic and nonionic penetrant in polyamide is more or less analogous to that of polyacrylonitrile. The Fickian diffusion of disperse dye in polyacrylonitrile was confirmed experimentally, and this behavior was found to be similar to that in all other synthetic fibers.

The diffusion coefficients at different temperatures from 50.6°C to 95.0°C and corresponding surface concentrations are shown in Table II. The value of  $D$  increases with increasing temperature. In the plot of  $\log D$  versus  $1/T$  (Fig. 5) there is a sharp change at 72°C which is ascribed to  $T_g$  of polyacrylonitrile during diffusion with *m*-nitroaniline. In this connection Kanamaru et al.<sup>21</sup> studied the temperature dependence of diffusion coefficients for a number of polymer-penetrant systems and reported four types of general pattern of  $\log D$  versus  $1/T$  plot which may be attributed to

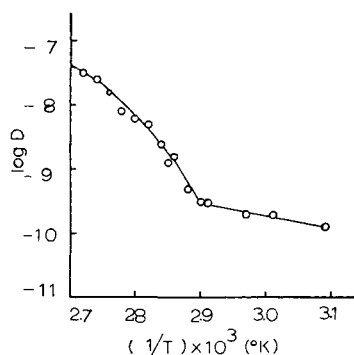


Fig. 5. Arrhenius plot of diffusion coefficient  $D$  of *m*-nitroaniline into polyacrylonitrile.

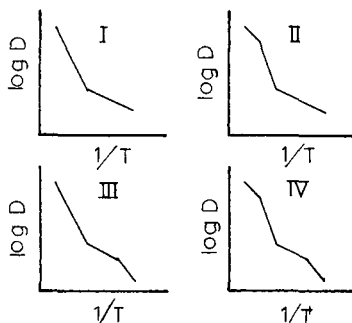


Fig. 6. Typical  $\log D$  vs.  $1/T$  plots for different polymer-penetrant systems.<sup>21</sup>

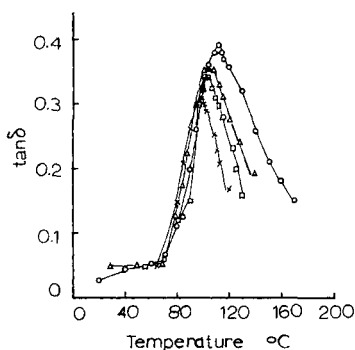


Fig. 7. Dynamic mechanical property of polyacrylonitrile: (O) 110 cps; ( $\Delta$ ) 35 cps; ( $\square$ ) 11 cps; ( $\times$ ) 3 cps.

the presence of several relaxation mechanisms for which relaxation begins to occur at different temperatures corresponding to their different relaxation times (Fig. 6). Similarly, in the diffusion of gases in poly(vinyl acetate) in relation to the second-order transition, Mears<sup>26</sup> obtained an inflection point a few degree below the glass transition temperature which was explained in terms of a two-phase structure for polymer: one is solid amorphous or glasslike phase and the other is liquidlike phase in which the segments of the polymer chains possess some freedom for rotation or torsional oscillation at a frequency comparable with or greater than the jump of diffusing atoms. Many others<sup>20,22,27</sup> showed that the transition in polymers could be detected well by the inflection point of the  $\log D-1/T$  plot. Now, the plot of  $\log D$  versus  $1/T$  in Figure 5 does not properly, though partly, fit to any of the four general types as shown in Figure 6. It more or less resembles the general type II. There is a downward tendency in Figure 5 but no sharp inflection point like  $T_3$ . The sharp inflection point in Figure 5 may be reasonably assigned as the diffusion-controlled transition temperature  $T_0$  of the polymer for the particular penetrant *m*-nitroaniline in the presence of water. But previously with Malachite Green in the same polymer the inflection point of the  $\log D-1/T$  plot was obtained at



80°C. The difference may be attributed to the molecular size of the penetrant, its ionic character, or both which may be assumed to be responsible for different relaxation times.

The glass transition temperature of polyacrylonitrile under discussion was determined in the dry state by a dynamic mechanical testing method.  $\tan \delta$  was measured by a Vibron Model DDV-II instrument (Toyo Sokki Co., Ltd.), and the plot is shown in Figure 7 for different frequencies.  $T_g$  corresponding to the frequency of 1 cps was found by extrapolation to lie at 98°C. This is in agreement with the value of 104°C obtained by Krigbaum et al.<sup>28</sup> which Andrews et al.<sup>29</sup> explained by hard to resolve combination of two glass transition temperatures at 87°C and 140°C on the assumption that polyacrylonitrile is a doubly hetero-bonded solid structure of secondary intermolecular bonding forces of two types, e.g., van der Waals forces and dipole-dipole association forces between nitrile side groups. It may be easily understood that the above-mentioned inflection points (80°C and 72°C) found during diffusion with Malachite Green and *m*-nitroaniline, respectively, correspond to 98°C, the glass transition temperature of polyacrylonitrile in the absence of water.

TABLE III  
Depression of  $T_g$  in the Presence of Waters and Moisture Regain  
of Various Polymers

Polymer	Degree of depression, °C <sup>a</sup>	Moisture regain at 20°C, 65% RH, % <sup>b</sup>
PAN	20	0.5-2.0
Secondary acetate	75-80	6.5
Dacron	15-20	0.4-0.8
Polyamide	60	4.5

<sup>a</sup> Data of Bryant and Walter.<sup>30</sup>

<sup>b</sup> Data of Murakami.<sup>31</sup>

The glass transition temperature of polymer is depressed by the presence of water. Generally the depression of  $T_g$  for different polymers is as shown in Table III. Rosenbaum<sup>32</sup> reported that water depresses  $T_g$  of polyacrylonitrile by 30-35°C; he explained this in terms of reduction of molecular stiffness by the decrease in repulsion forces in the polymer molecules due to an increase of dielectric constant. It will be more clear that most recently Okajima et al.<sup>33</sup> carried out diffusion of some disperse dyes including model compounds into cellulose tri- and diacetate in the absence of water. They obtained three inflection points at 197, 173, and 90°C for cellulose triacetate. On the other hand, Iwahori et al.<sup>34</sup> measured the diffusion coefficient of similar disperse dyes from aqueous solution into cellulose triacetate by the cylindrical film roll method from 80 to 130°C and obtained an inflection point at 105°C which may correspond to the inflection at 173°C of Okajima et al. Sprague<sup>35</sup> also found an inflection point of

acetate at 87–95°C in water. The depression of  $T_g$  of polymer, in general, in the presence of water may be mainly explained by the imbibition behavior of polymer, i.e., the higher the hydrophobic character of polymer, the less the depression of  $T_g$  (Table III).<sup>30</sup>

Figure 8 shows the temperature dependence of surface concentration of both Malachite Green and *m*-nitroaniline in polyacrylonitrile. The surface concentration of *m*-nitroaniline decreases with increasing temperature from  $T_g$  upward. This is in agreement with the thermodynamic point of view. But in the case of Malachite Green the surface concentration below  $T_g$  is constant, while at  $T_g$  it suddenly rises, and above  $T_g$  it gradually increases

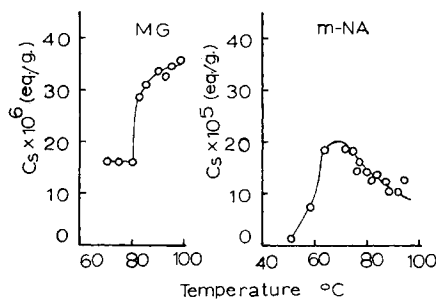


Fig. 8. Temperature dependence of surface concentrations for Malachite Green (MG) and *m*-nitroaniline (m-NA).

with rising temperature. The effect may be explained by the availability of specific sites the number of which depends on temperature. Furthermore, according to Sand<sup>36</sup> the weak acid groups in polymer are ionized with rise of temperature and thus new sites for cationic penetrant are provided.

The activation energy of diffusion was calculated from the relation

$$D = D_0 \exp \{E/RT\} \quad (13)$$

and it was found that below  $T_g$  the activation energy is almost constant at about 10 kcal/mole (Fig. 9), but above  $T_g$  the activation energy gradually decreases with the increase in temperature. It reaches a maximum at  $T_g$ . The activation energy is approximately the same below  $T_g$  in both the cases of Malachite Green and *m*-nitroaniline. This result indicates that below  $T_g$  diffusion occurs through some voids<sup>37</sup> already present in the polymer, mainly around the large endgroups of polymer chain or perhaps due to subgroup motion of the polymer. The maximum activation energy of Malachite Green and *m*-nitroaniline at  $T_g$  is 194 and 89 kcal/mole, respectively. The activation energy maximum at  $T_g$  and gradually decreasing above  $T_g$  agrees with the fact that the penetrant diffusion is similar to other kinetic phenomena in polymer above glass transition temperature and is governed by the movement of the free volume.<sup>5</sup>

It is worthy of mention here that most of the general pattern of dyeing systems correspond to type I of Figure 6 of the four general types given by

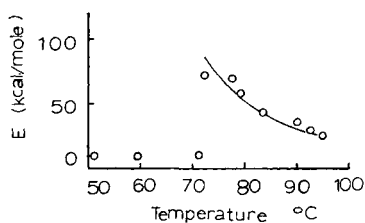


Fig. 9. Variation of activation energy with temperature: (—)  $E = 2.303C_1^g C_2^g RT^2 / (C_2^g + T - T_g)$ ; (O) experimental points.

Kanamaru et al.<sup>21</sup> The typical pattern like that in Figure 5 is a special case for polyacrylonitrile only.

Rosenbaum<sup>6</sup> has studied the temperature dependence of cationic dye diffusion in polyacrylonitrile and described the course of dependence by the WLF equation. The general form,

$$\log a_T = \log (D_{T_g}/D_T) = -C_1^g(T - T_g)/(C_2^g + T - T_g) \quad (14)$$

was used, as was already pointed out by Tobolsky<sup>38</sup> and Ferry<sup>39</sup> that  $C_1^g$  and  $C_2^g$  are not universal constants. Here  $a_T$  is the ratio of relaxation time at temperature  $T$  to its value at reference temperature  $T_g$ ;  $D_{T_g}$  and  $D_T$  are diffusion coefficients at  $T_g$  and  $T$ , respectively. In the present paper the general relation was used, and the values of  $C_1^g$  and  $C_2^g$  were calculated by the least-squares method and found to be 4.03 and 24.54, respectively. Putting the values of  $C_1^g$  and  $C_2^g$  in eq. (14) yields

$$\log a_T = \log (D_{T_g}/D_T) = -4.03(T - T_g)/(24.54 + T - T_g) \quad (15)$$

The solid line in Figure 10 was drawn according to eq. (15), the experimental points being shown as dotted circles. The fit is satisfactory and agrees with the fact that penetrant diffusion in polymer is related to the activated diffusional jump of polymer segments, which sets in at  $T_g$ . In addition,  $C_1^g$  is related to free volume at  $T_g$  and  $C_2^g$  is related to free volume at  $T_g$  as

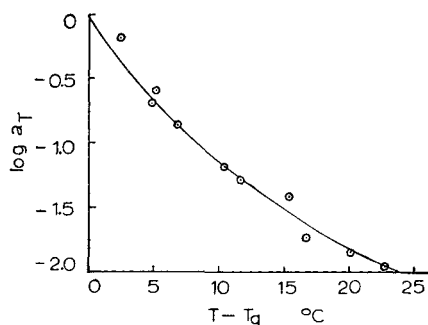
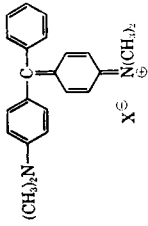
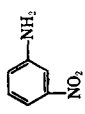


Fig. 10. Fit experimental data to WLF equation: (—)  $a_T = \log D_{T_g}/D_T = -C_1^g(T - T_g)/(C_2^g + T - T_g)$ ; (O) experimental points.

TABLE IV  
Comparison between Malachite Green and *m*-Nitroaniline

Penetrant	Structure	$T_g, ^\circ\text{C}$	$C_1^f$	$C_2^f$	$f_g$	$\Delta\alpha, \text{deg}^{-1}$
Malachite Green	 $(\text{CH}_3)_3\text{N}^+$ $\text{X}^-$ $\text{N}(\text{CH}_3)_2$	80	2.23	6.53°	0.195	$2.99 \times 10^{-2}$
<i>m</i> -Nitroaniline		72	4.03	24.54°	0.108	$4.41 \times 10^{-3}$

well as the thermal expansion coefficient above and below  $T_g$ , by the following relations<sup>38</sup>

$$C_1^g = 1/2.303f_g \quad (16)$$

$$C_2^g = f_g/\Delta\alpha \quad (17)$$

where  $f_g$  is fractional free volume at  $T_g$  and  $\Delta\alpha$  is the difference between the thermal expansion coefficients above and below  $T_g$ . The values of  $C_1^g$ ,  $C_2^g$ ,  $f_g$ ,  $\Delta\alpha$ , and  $T_g$  for Malachite Green and *m*-nitroaniline are summarized in Table IV. On comparing  $f_g$  and  $\Delta\alpha$  of Malachite Green and *m*-nitroaniline, the difference may be qualitatively explained by the size of the penetrants. The bigger the size of the penetrant, the greater is the value of  $f_g$  and  $\Delta\alpha$  which has a direct effect on the glass transition temperature of polymer. It is reasonable that  $C_1^g$  and  $C_2^g$  are different from polymer to polymer and penetrant to penetrant. But quantitatively, the values of  $f_g$  and  $\Delta\alpha$  are too large in comparison with the universal value 0.025 and  $4.8 \times 10^{-4}$ , respectively. Though the values of  $C_1^g$ ,  $C_2^g$ ,  $f_g$ ,  $\Delta\alpha$ , and  $T_g$  can be explained by the size of the penetrant only, yet one cannot neglect the other possibility, i.e., the ionic character of the penetrant, the effect of which is still not known. Malachite Green and *m*-nitroaniline are of ionic and nonionic character, respectively, and it can be reasonably suggested that the above difference of constants and glass transition temperature is due to the size of the penetrants as well as their ionic character, hence the difference in diffusion mechanism. In the case of the diffusion of ionic penetrants the relaxation time is concerned only with the polymer endgroups, while in the diffusion of nonionic penetrants it is involved with the segmental motion of the main chain and side groups which is responsible for diffusion and is directly related with the size of the penetrants.

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