# NG-Migration into Double-Base Inhibitors. II. Diffusion

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**SYNOPSIS**

The maximum sorption of nitroglycerine (NG) in polymeric material was measured in Part I. The results of the sorption is used to determine the average diffusion coefficient for each polymer, utilizing Fick's second law. These values are compared to the chlorine content in the polymer backbone to ascertain whether the chlorine has any influence in lowering the diffusion coefficient. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The measurement techniques of diffusion coefficients in polymers have been well discussed by Crank and Park.[1] The measurement technique used in this experiment is based on the use of initial rates of sorption.[2]

It is possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted against the square root of time. Thus, in the early stages of an sorption experiment, for a constant diffusion coefficient $D$ and a sheet of thickness $L$, we have that

$$\frac{M(t)}{M(\infty)} = \frac{4}{\pi^{\frac{1}{2}}}\left[\frac{Dt}{L^2}\right]^{1/2} \qquad (1)$$

where $M(t)$ is the absorption percentage at time $t$, and $M(\infty)$, the maximum amount absorbed for a particular liquid at constant pressure and temperature.

If the initial gradient,[3] $I = d[M(t)/\mathrm{M}(\infty)]/d(t/L^2)^{1/2}$, is observed in a sorption experiment in which $D$ is concentration-independent, then the average diffusion coefficient $D$[4-6] deduced from Eq. (1) is

$$\bar{D} = \frac{\pi I^2}{16} \qquad (2)$$

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## EXPERIMENTAL

The experimental procedures are described in Part I.[7]

## RESULTS

The results for the sorption, as described in Part I, is used for Part II. The results of Part I are displayed in Table I.

The values for $M(\infty)$ from Table I were used to calculate the values of $M(t)/M(\infty)$. These values and the calculated values for $t^{1/2}/L$ were used to draw the graphs depicted in Appendix 1. The slope, $I$, for the graphs were determined by hand and the values for the calculated slopes are given in Table II. The average diffusion coefficient was calculated using eq. (2).

## DISCUSSION

The graphs for the average diffusion coefficients in Table II vs. the chlorine content in the backbone are shown in Figures 1 and 2.

The commercial polymers and the synthesized polymers have diffusion coefficients that are in the same order. One can thus expect that the diffusion coefficients of other thermosets will be in the same order of magnitude with respect to NG-migration.

**Table I The Values for the Constants (Sorption Curves), According to Margolin's Formula**

| Sample No. | Constant $a$ | Constant $b$ | $M(\infty) = 1/b$ |
|---|---|---|---|
| C6610 | 0.0498 | 0.0314 | 31.84 |
| FR976D | 0.0713 | 0.0135 | 74.07 |
| EE170 | 0.1022 | 0.0159 | 62.89 |
| E840 | 0.1255 | 0.0213 | 46.95 |
| C1 | 0.0089 | 0.4590 | 2.18 |
| C2 | 0.2400 | 0.0380 | 26.32 |
| C3 | 0.0827 | 0.0232 | 43.10 |
| C4 | 0.0458 | 0.0202 | 49.50 |
| C5 | 0.0314 | 0.0284 | 35.21 |
| H1 | 0.1799 | 0.0224 | 44.64 |
| H2 | — | — | — |
| H3 | — | — | — |
| H4 | 0.0074 | 0.0435 | 22.98 |
| H5 | 0.0496 | 0.0272 | 36.76 |
| M1 | 0.2478 | 0.0227 | 44.05 |
| M2 | 0.1828 | 0.0229 | 43.68 |
| M3 | 0.1074 | 0.0214 | 46.73 |
| M4 | 0.1081 | 0.0197 | 50.76 |
| M5 | 0.1322 | 0.0188 | 53.19 |
| 1H | 0.1799 | 0.0224 | 44.64 |
| 2H | 0.1192 | 0.0133 | 75.19 |
| 3H | 0.0671 | 0.0129 | 77.51 |
| 4H | 0.0684 | 0.0143 | 69.93 |
| 5H | 0.0496 | 0.0272 | 36.76 |
| 1M | 0.2478 | 0.0227 | 44.05 |
| 2M | 0.7842 | 0.0206 | 48.54 |
| 3M | 0.1370 | 0.0250 | 40.00 |
| 4M | 0.1864 | 0.0228 | 43.86 |
| 5M | 0.1322 | 0.0188 | 53.19 |

Although polymer C6610 has a lower $M(\infty)$ than that of the other commercial polymers, it shows a higher diffusion coefficient. This is because this polymer reaches its saturation point very quickly as well as being a polyester polyol. The other commercial polymers are polyether polyols and, as such, contain a lower percentage oxygen.

The C1–C5 samples show an increase in the diffusion coefficient with decreasing chlorine content. The same phenomenon is shown by the synthesized polymers, especially if looking at the MDI cross-linked polymers.

The diffusion coefficient that was calculated for C1 cannot be trusted. This is due to the sample being broken during NG-migration readings, giving too little data for proper calculations.

Samples H1–H5 show no significant pattern due to inadequate data. Samples 1H–5H, however, show a certain trend, the same as was described for the MDI cross-linked samples (sample 5H's data must be omitted due to insufficient data for diffusion coefficient calculations).

The diffusion coefficients for the "blends" (M2–M4) are slightly higher than the coefficients for the random polymers (2M–4M). This is to be expected as the more "homogeneous" random polymer has its chlorine groups interdispersed in the backbone, which makes the delocalization of the charge on the

**Table II The Values for the Slope, $I$, the Average Diffusion Coefficient, and Cl % in the Backbone**

| Sample No. | $I$ (cm $s^{-1/2}$) | Av. Difference Coefficient ($cm^2$ $s^{-1}$) ($/10^6$) | % Cl |
|---|---|---|---|
| C6610 | 0.01854 | 67.49 | 0.00 |
| FR976D | 0.00955 | 17.72 | 0.00 |
| EE170 | 0.01426 | 39.93 | 0.00 |
| E840 | 0.01350 | 35.79 | 0.00 |
| C1 | 0.03600 | 254.47 | 24.80 |
| C2 | 0.01166 | 26.70 | 18.60 |
| C3 | 0.01192 | 27.90 | 12.40 |
| C4 | 0.01671 | 54.83 | 6.20 |
| C5 | 0.02456 | 118.44 | 0.00 |
| H1 | 0.01367 | 36.69 | 29.02 |
| H2 | — | — | 21.74 |
| H3 | — | — | 14.46 |
| H4 | 0.03406 | 227.78 | 7.21 |
| H5 | 0.01556 | 47.54 | 0.00 |
| M1 | 0.00963 | 18.21 | 19.54 |
| M2 | 0.01162 | 26.51 | 14.60 |
| M3 | 0.01172 | 26.97 | 9.66 |
| M4 | 0.01308 | 33.59 | 4.83 |
| M5 | 0.01386 | 37.72 | 0.00 |
| 1H | 0.01367 | 36.69 | 29.02 |
| 2H | 0.00840 | 13.86 | 20.76 |
| 3H | 0.00945 | 17.53 | 13.29 |
| 4H | 0.01264 | 31.37 | 9.27 |
| 5H | 0.01556 | 47.54 | 0.00 |
| 1M | 0.00963 | 18.21 | 19.54 |
| 2M | 0.00680 | 9.08 | 18.27 |
| 3M | 0.01088 | 23.24 | 11.70 |
| 4M | 0.01082 | 22.99 | 8.09 |
| 5M | 0.01386 | 37.72 | 0.00 |

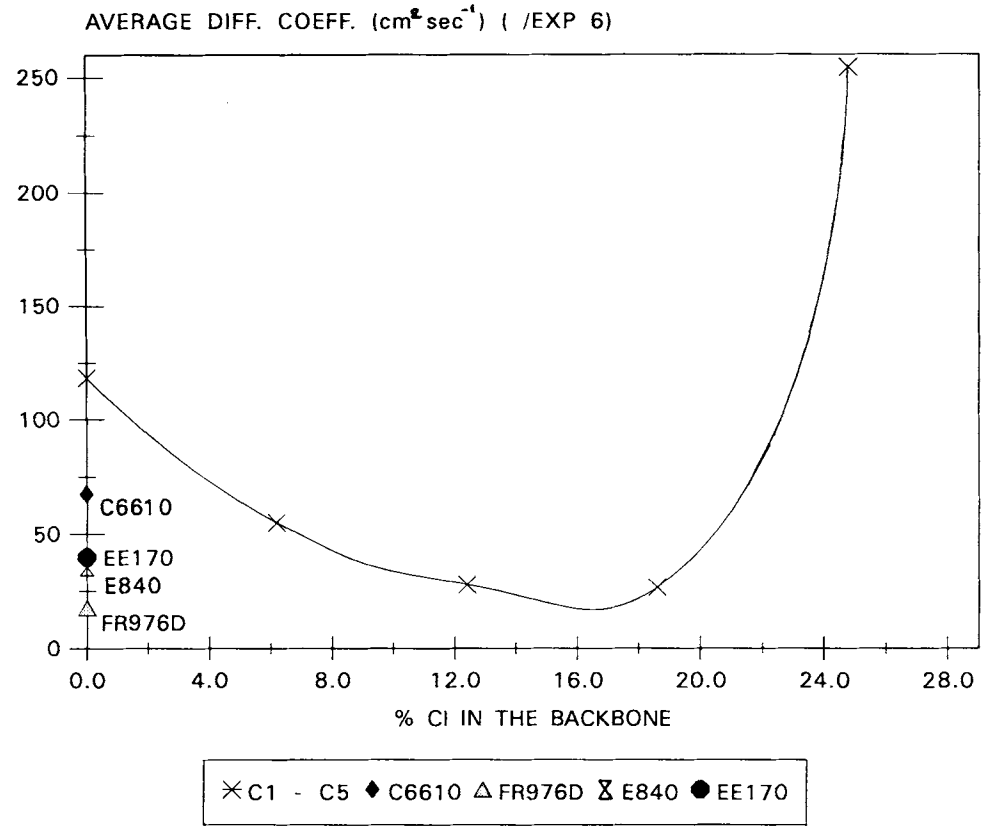



**Figure 1** Graphs of average diffusion coefficients vs. chlorine % in the backbone.

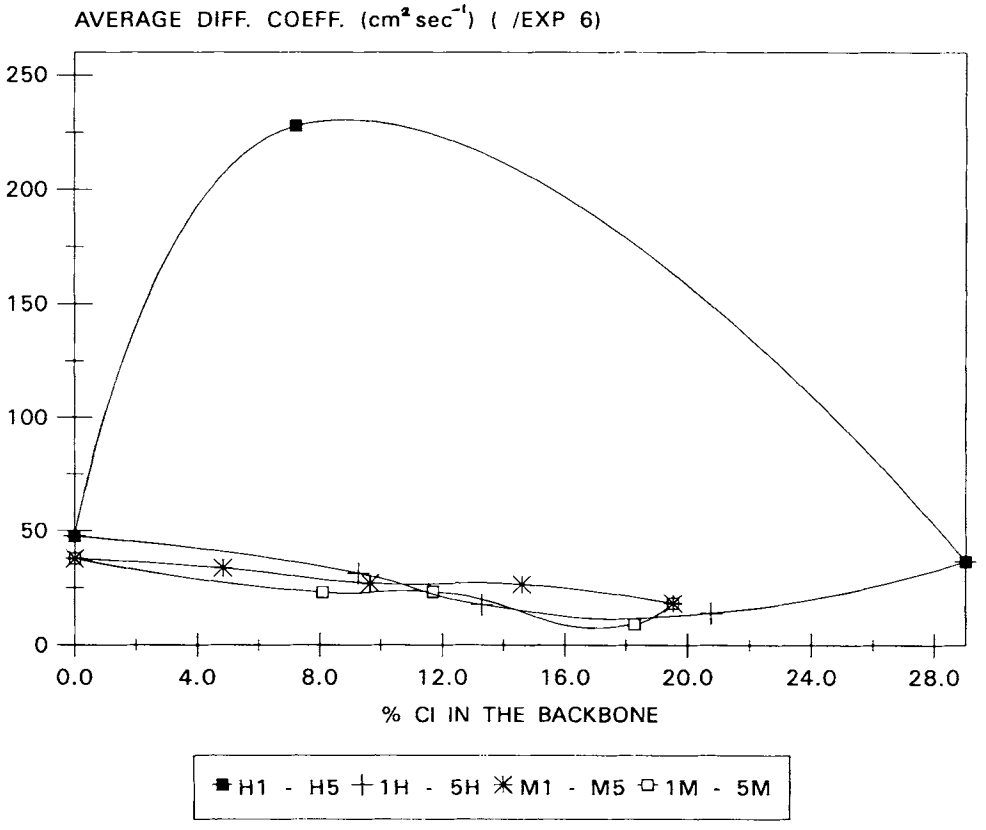



**Figure 2** Graphs of average diffusion coefficients vs. chlorine % in the backbone.

adjacent oxygen atoms that much more easy. In the "block" polymers' case, this is not possible.

## CONCLUSIONS

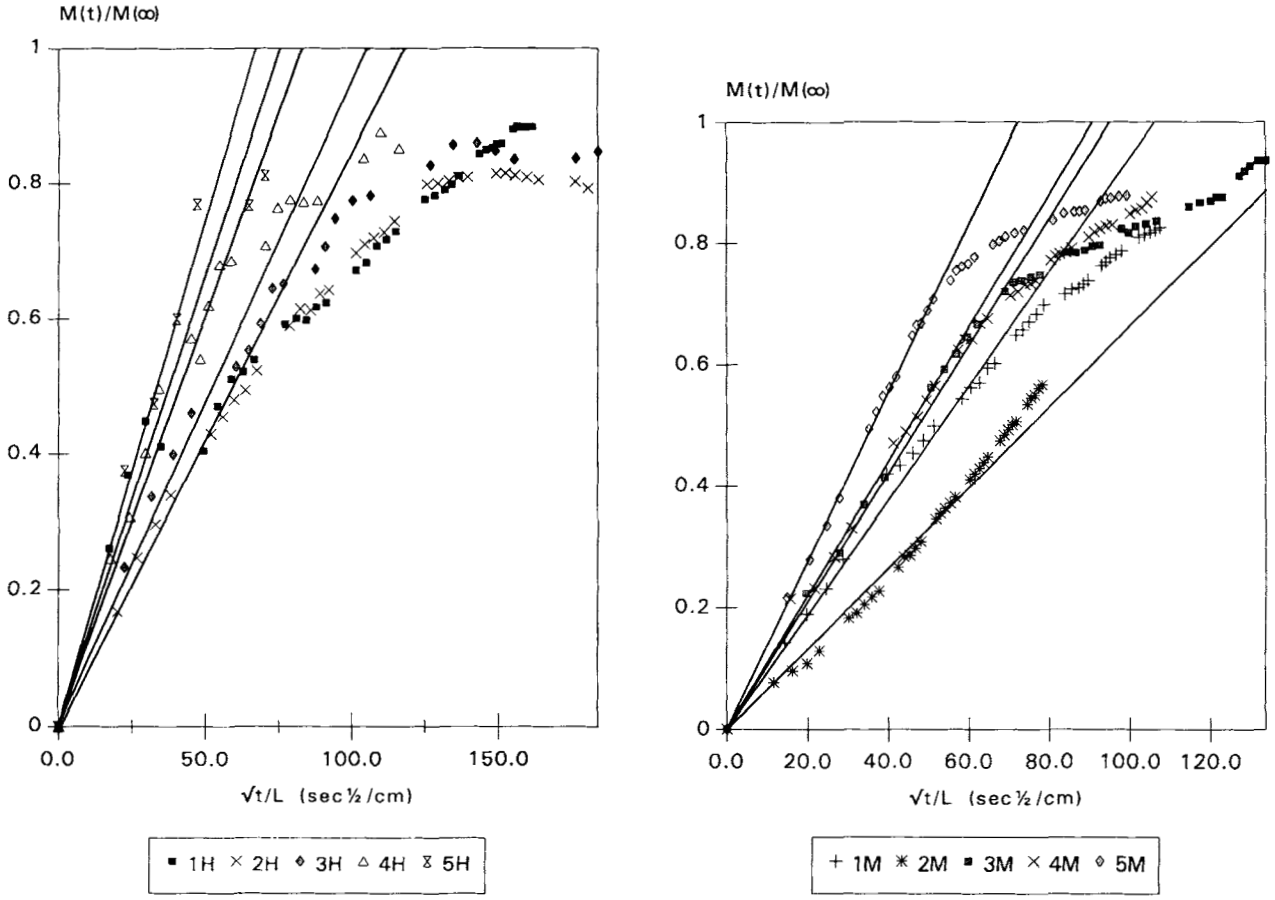
In essentially all cases, Fick's second law approximated successfully the measured sorption data, which indicates that

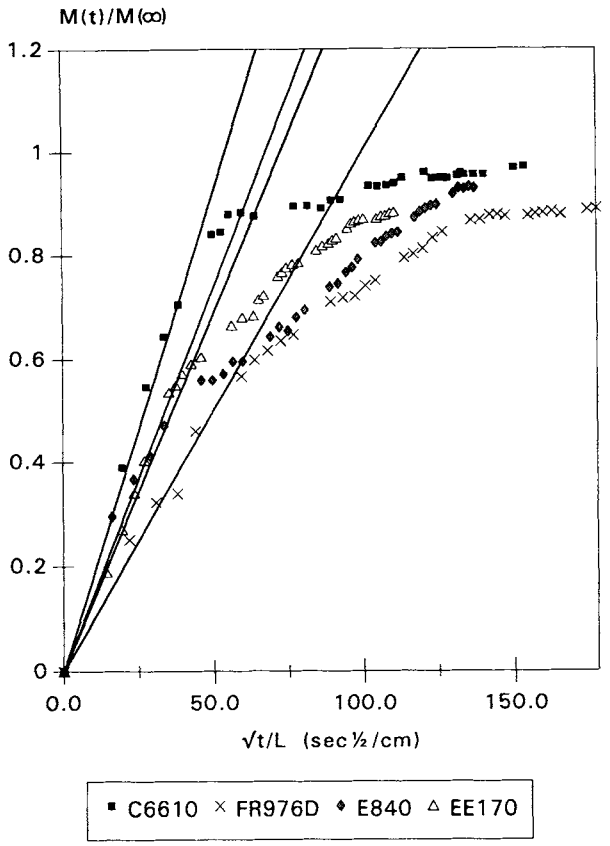
- All the thermosets obey Fickian diffusion.
- The Fickian formula can be used to calculate the average diffusion coefficient for relative comparison between the thermosets.

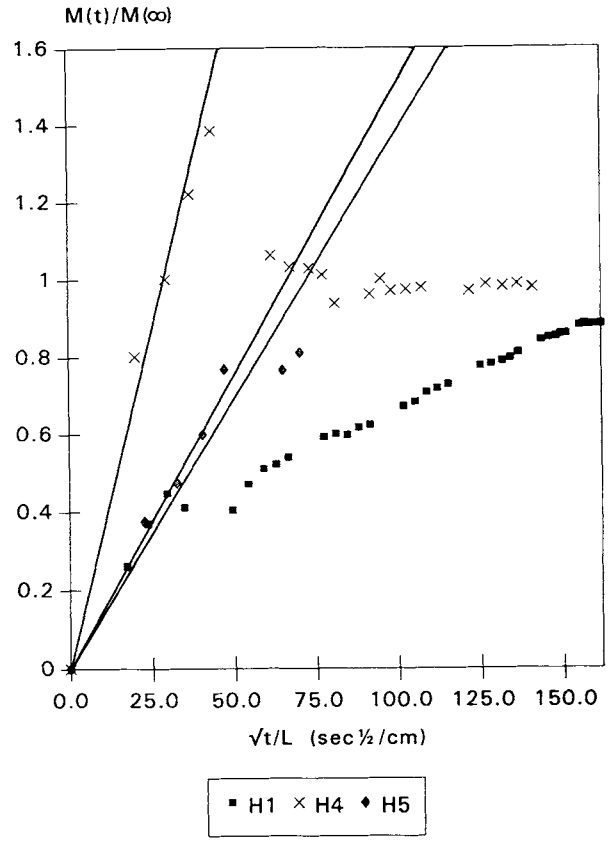
There is no definite correlation between the percentage chlorine in the backbone and the average diffusion coefficients. If the average diffusion coefficients, the sorption values for the polymers, their $T_g$'s, and their elongations are taken as criteria, then samples 2H, 3H, and 4H would be recommended as the "BEST" inhibiting material.

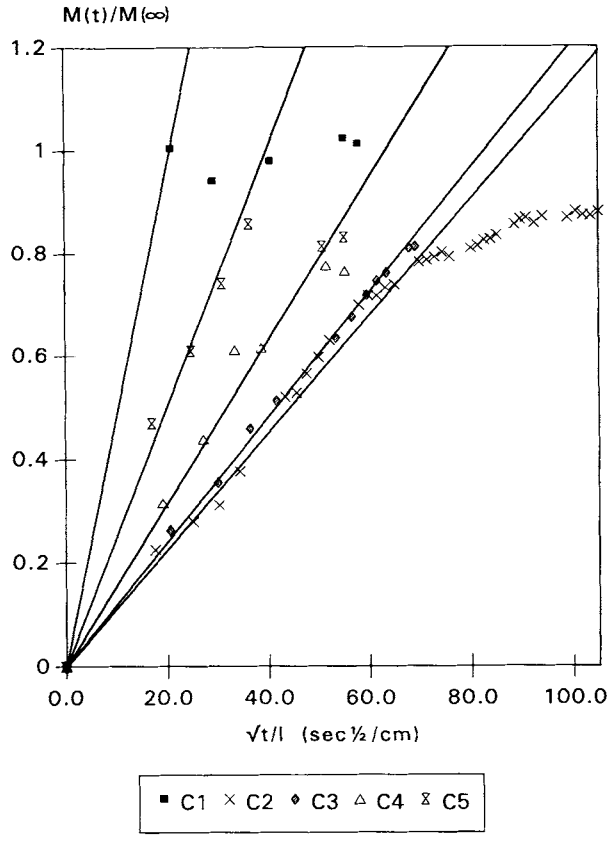
I would like to thank the company SOMCHEM, Division of DENEL, for the use of their facilities.

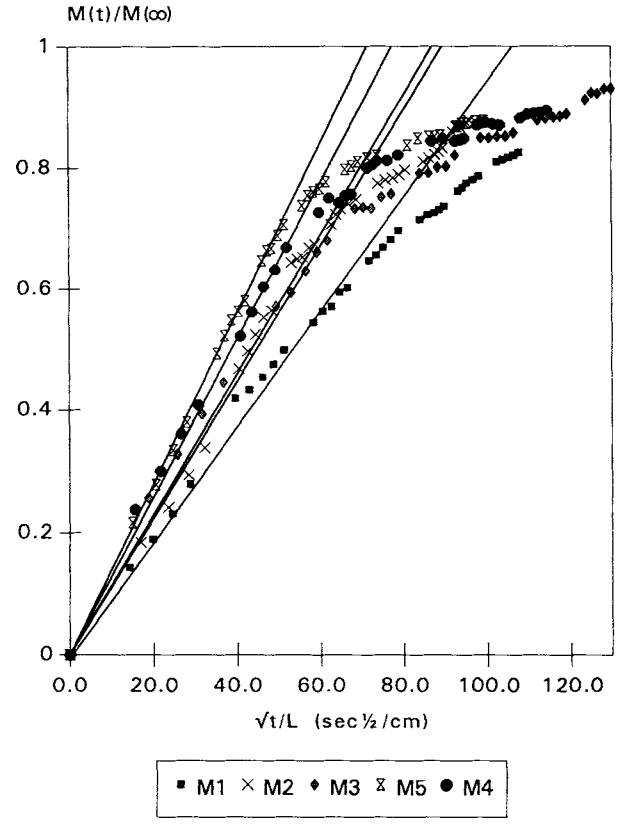
## APPENDIX 1: GRAPHS OF $M(t)/M(\infty)$ vs. $\sqrt{t}/L$






**Appendix 1** *(Continued from the previous page)*

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