

## Diffusion Coefficient of Diallyl Terephthalate Monomer into Thin Polymer Film

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Attenuated total reflection infrared spectroscopy (ATR-FTIR) was used to measure diffusion of diallyl terephthalate monomer (DAT) into a polyDAT film. The assembly, consisting of an ATR crystal, polymer film and a monomer, was heated to a desirable interdiffusion temperature, the spectra thus obtained were deconvoluted and the diffusion coefficient of DAT monomer into polymer was calculated by least square regression technique at various temperatures from 21 °C to 50 °C and, various film thicknesses from 60  $\mu\text{m}$  to 180  $\mu\text{m}$ .

*Key words:*

Diffusion, diffusion coefficient, Fourier transform infrared attenuated total reflectance (FTIR-ATR), diallyl phthalate, diallyl terephthalate

### Introduction

To provide proper reaction conditions for various polymerization reactions, basic physico-chemical properties of materials need to be known, and one among them is the diffusion coefficient, which is used for fundamental understanding of diffusion controlled reactions, and enables the evaluation of the apparent rate constants. Diffusion coefficients for various polymer materials, such as PMMA, PS, PVC and others were previously determined by applying a number of experimental techniques.<sup>1–10</sup> However, no diffusion coefficient for more complicated systems, such as diallyl phthalate (DAP) has been reported in the available literature. DAP is a monomer which is employed as a characteristic engineering plastic material in the electronic and optic industries. The polymerization of DAP is described as free radical crosslinking polymerization with strong diffusion limitations from the beginning of the reaction.<sup>11–13</sup> Diallyl terephthalate (DAT), an isomer of most frequently used DAP, has better initial physical properties, such as higher refractive indexes and density. PolyDAT has excellent properties such as dimensional stability and rigidity under heat, impact heat, great moisture resistances, as well as other excellent electrical and optical properties.<sup>11–13</sup>

The purpose of this study is to determine: (i) diffusion coefficient of DAT monomer conversion into polyDAT film; (ii) the dependence of diffusion coefficient on temperature.

### Experimental

The monomer diallyl terephthalate (DAT) from Daiso Co. Ltd. and commercial initiator dicumyl peroxide (DCPO) from Hercules, were used.

Spectra were obtained with *Perkin-Elmer SPECTRUM 1000* spectrometer using horizontal Zinck/Selenide (Zn/Se) ATR crystal. The spectrometer was maintained at a room temperature within the range of  $21 \pm 1$  °C. The sampling surfaces of the crystals were 70 mm x 10 mm with a thickness of 3 mm, and the refractive index of Zn/Se crystal was 2.40. The normal vectors of the optical entry and exit faces were inclined 45° from the sampling surfaces. The sampling operation data for FTIR-ATR experiments are shown in Table 1.

Table 1 – Operational data used in FTIR-ATR experiments

Data (FTIR)	Value
Resolution	2.0 $\text{cm}^{-1}$
Starting wave number	650 $\text{cm}^{-1}$
Ending wave number	4000 $\text{cm}^{-1}$
Sample scans	32
Signal gain	1
Scan velocity	0.3 $\text{cm s}^{-1}$
Sampling time	7.9 s

The polymer film was cast directly onto Zn/Se crystal. The monomer was polymerized with  $w = 10$  % of DCPO, with variable temperature regime between  $50$  °C and  $150$  °C, to obtain high final monomer conversions (above 96 %). The crystal with polymer film was then put into a vacuum oven, to obtain complete polymerization. Polymer films of various thicknesses 60, 120 and  $180$   $\mu\text{m}$ , were prepared to obtain the optimal film thickness for diffusion coefficient measurements. The spectra were recorded at  $21$ ,  $35$  and  $50$  °C in air atmosphere, to obtain temperature dependence of diffusion coefficients. The reference spectra were taken, using blank Zn/Se crystal in identical experimental conditions.

The thickness of polymer film was measured by casting a mixture of DAT monomer and initiators directly onto an iron plate with the similar dimensions as the Zn/Se crystal. The polymerization was carried out in the same experimental conditions as the film polymerization on crystal. Measurements of film thicknesses were made using a profilometer (Festina 1000), on various film positions. An aluminium slab (thickness  $\sim 1$  mm) with an open rectangular interior opening, centered above the area of film-optical contact, was then placed on the top of the polymer film. This aluminium barrier was held in place over the polymer film by clamps and formed a reservoir to maintain the permeate solution of monomer directly above the film. Detailed representation of ATR cell is shown in Figure 1.

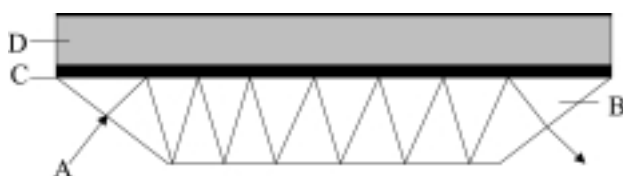


Fig. 1 – FTIR – ATR cell for *in situ* measurement of monomer/polymer diffusion: A. Infrared light beam, B. ATR crystal, C. Polymer film, D. Reservoir with monomer

Each experiment was started by pipetting 4 mL of monomer onto the polymer film in the provided reservoir. Spectra (sample minus background spectra of air) were then obtained at pre-determined time intervals throughout the experiments, which were conducted *in situ*.

## Analysis

The equation describing Fickian diffusion of a penetrant through a thin polymer film, measured at one side of the film using FTIR-ATR method, was developed before.<sup>14–18</sup> Only the final equation used for diffusion coefficient determination is reported

$$\frac{A(t)}{A_{\text{eq}}} = 1 - \frac{8}{\pi d_p \left( 1 - \exp\left(-\frac{2\delta}{d_p}\right) \right)} \cdot \sum_{n=0}^{\infty} \frac{\exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4\delta^2}\right) \cdot \left[ \frac{\pi(2n+1)}{2\delta} \cdot \exp\left(-\frac{2\delta}{d_p}\right) + (-1)^n \cdot \left(\frac{2}{d_p}\right) \right]}{(2n+1) \cdot \left( \frac{4}{d_p^2} + \left(\frac{\pi(2n+1)}{2\delta}\right)^2 \right)} \quad (1)$$

where  $A(t)$  is the integrated infrared absorbance of diffusing penetrant at time  $t$ , and  $A_{\text{eq}}$  is its value at equilibrium,  $d_p$  is the penetration depth of the evanescent wave,  $\delta$  is the average polymer film thickness,  $n$  is the number of terms, while all other constants arise from the physics of attenuated total reflection.<sup>19–22</sup> It was assumed that refractive index of polymer does not change during monomer penetration, therefore the depth of penetration  $d_p$  is assumed to be constant.<sup>14</sup> The only fit parameter is the diffusion coefficient  $D$ , which was obtained by regressing the eq. 1 to experimental data.

## Results and discussion

The purpose of the present report was to determine the diffusion coefficient of monomer in a thin polymer film using ATR technique. The FTIR spectra of pure DAT monomer and polymer film are shown in Figure 2, where three peaks are shown over the presented band range. The peak at the band value of  $1648$   $\text{cm}^{-1}$  represents C=C double bond vibrations and the peaks at the band of  $1609$   $\text{cm}^{-1}$  and  $1576$   $\text{cm}^{-1}$  represent the first and the second benzene ring vibrations. When necessary, the peak areas were integrated using 40 % to 60 % of Gauss and Lorentz distribution, and the same experimental protocol developed by Jin and Meyer<sup>22</sup> was used. Figure 3 shows the time-involved spectra of the DAT monomer diffusion in polymer film. The peak

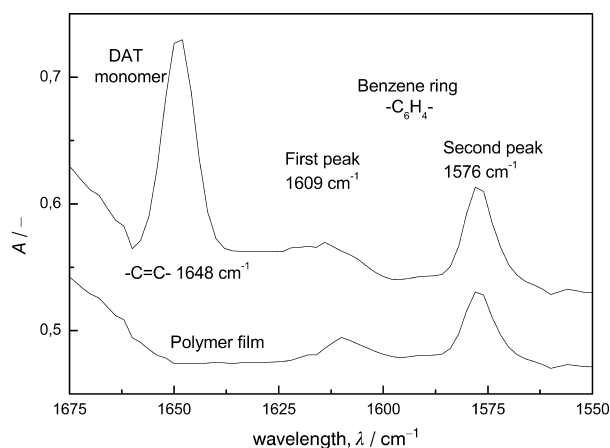


Fig. 2 – FTIR-ATR spectra of pure DAT monomer and polymer film

at the band value of  $1648\text{ cm}^{-1}$  starts increasing as the diffusion starts and the integrated area under this peak has been used for  $A/A_{\text{eq}}$  calculation. Results of  $A/A_{\text{eq}}$  are shown as function of time in Figure 4 a and b, for different film thicknesses and experimental conditions. The last measured points of  $A/A_{\text{eq}}$  were measured approximately one day after the last measurements for all temperatures and film thickness, respectively, to be sure that final equilibrium value was reached. The  $A_{\text{eq}}$  is the equilibrium absorbance of the final homogeneous system, which was determined by the integration of the recorded spectra in the infinity time, when no changes among the last three measured spectra could be detected.  $A_{\text{eq}}$  is directly proportional to the total amount of monomer absorbed into the polymer, and it appears to decrease in a linear fashion with the treatment temperatures, as shown in Figure 5. At higher temperature less monomer is absorbed in polymer film when the equilibrium was obtained. The same tendency was observed in other systems.<sup>14</sup> In addition it was observed that  $A_{\text{eq}}$  values rise while film thickness decreases at constant experimental temperature. The values are higher in thinner films, which may be attributed to a greater amount of monomer, which penetrates into polymer film. Similar observations were made by other authors.<sup>14</sup>

The thicknesses of polymer films on iron plates were measured to obtain all the necessary data for diffusion coefficient determination. The measured average film thicknesses used for calculation, are presented in Table 2, where initially cast on film thickness and measured film thickness of polyDAT films used for diffusion coefficient calculation are presented. The differences between initially cast on and measured thickness of polymer film are probably a consequence of material shrinkage during the polymerization. The diffusion coefficient of DAT monomer into polymer film at various conditions

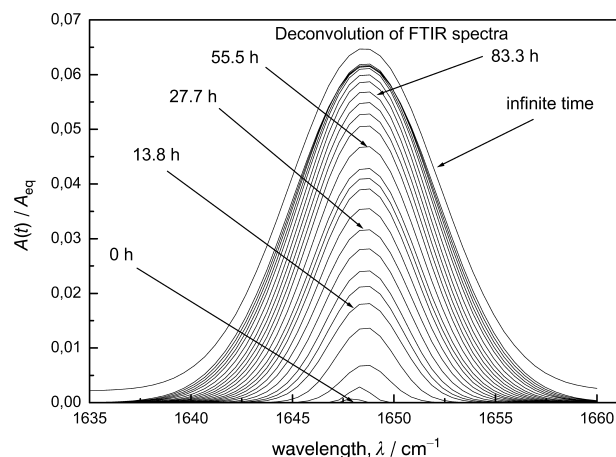


Fig. 3 – FTIR-ATR spectra at different times of the peak at  $1648\text{ cm}^{-1}$  band value, at  $120\text{ }\mu\text{m}$  film thickness and temperature  $35\text{ }^{\circ}\text{C}$

Table 2 – Initially casted ( $\delta_{\text{cast on}}$ ) and measured film thickness ( $\delta_{\text{exp}}$ ) used for least square regression (the average of three measurements) for various experimental temperatures

$T/^{\circ}\text{C}$	21 $^{\circ}\text{C}$	35 $^{\circ}\text{C}$	50 $^{\circ}\text{C}$
$\delta_{\text{cast on}} / \mu\text{m}$			
60	–	$55.1 \pm 7.2$	–
120	$119.1 \pm 7.2$	$118.2 \pm 9.8$	$111.2 \pm 14.1$
180	–	$172.3 \pm 14.5$	–

were determined by regressing the eq. 1 to experimentally measured data by using least square regression technique,<sup>14–17</sup> and results are shown in Figure 4a and b. From the obtained diffusion coefficients, the activation energy of diffusion  $E_D$ , and the pre-exponential factor  $A_D$ , were obtained from the slope of  $\ln D$  versus  $1/T$  for  $120\text{ }\mu\text{m}$  films. It was observed that the diffusion coefficients apparently follow Arrhenius behaviour quite well after the eq. 2.

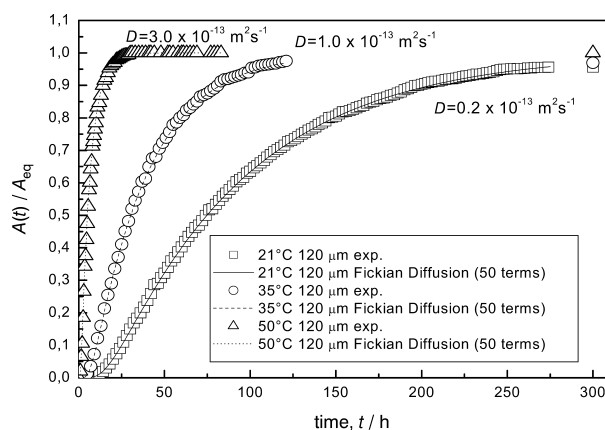


Fig. 4 a –  $A(t)/A_{\text{eq}}$  versus time, with 50 terms approximation of diffusion Fickian model for  $120\text{ }\mu\text{m}$  film thickness at various experimental temperature

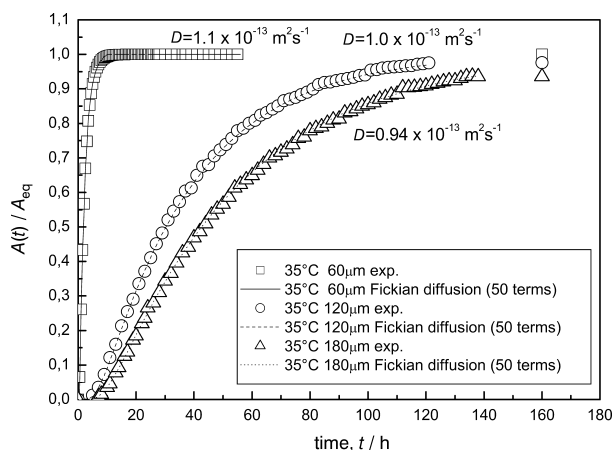


Fig. 4 b –  $A(t)/A_{\text{eq}}$  versus time, with 50 terms approximation of diffusion Fickian model for various film thicknesses, at  $35\text{ }^{\circ}\text{C}$

$$D = (0.28 \pm 0.02) \cdot \exp\left(-\frac{(73.85 \pm 7.40)}{RT}\right) \quad (2)$$

The same type of temperature dependence was observed for other probe diffusions in polymer films of different thickness for various systems.<sup>20,21</sup> Data for pre-exponential factor and activation energy of diffusion coefficient are similar to the results obtained for other systems.<sup>10</sup> The differences are attributed to different measurement techniques and experimental errors.

The effects of different film thicknesses on diffusion coefficients at the constant temperature were estimated and are shown in Figure 4b. It may be noted, that the film thickness does not affect the diffusion coefficient at the constant experimental temperature. The differences of obtained  $D$  for various films, thickness may be attributed to experimental errors or to different polymer film structures which were not completely the same in all film thicknesses, however more experiments will need to be done to confirm these observations. Similar observations were obtained in other monomer polymer systems.<sup>22–27</sup>

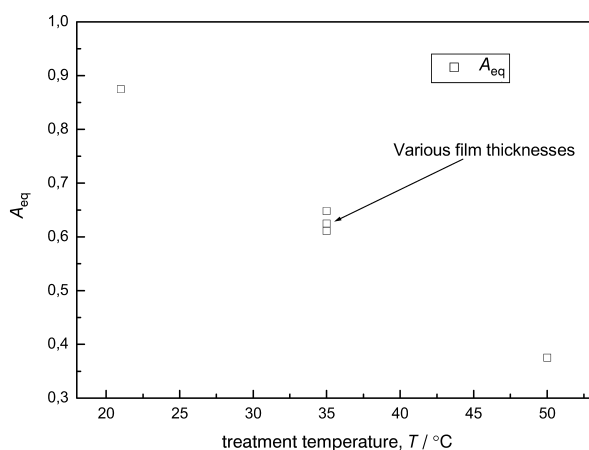


Fig. 5 –  $A_{eq}$  versus treatment temperature

## Conclusions

Based on the current study, the following observations may be made

1. FTIR – ATR technique may be successfully used for diffusion coefficient of DAT monomer into polymer film prediction and could be also applied in other systems,

2. The diffusion coefficients obtained are similar to the results from other systems and other experimental techniques,

3. The Arrhenius dependence of diffusion coefficients on temperature was obtained, and the pre-exponential factor of diffusion coefficient ( $A_D = 0.28 \text{ m}^2 \text{ s}^{-1}$ ), as well as activation energy ( $E_D = 73.85 \text{ kJ mol}^{-1}$ ) were determined.

## Nomenclature

$D$	– diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
$t$	– time, s
$z$	– distance, m
$\delta, \delta_{\text{cast on}}, \delta_{\text{exp}}$	– film thickness, cast on and experimentally, measured
$n$	– number of terms, –
$d_p$	– penetration depth, m
$A(t), A_{\text{eq}}$	– absorbance area at time $t$ and at equilibrium, –
$A_D$	– preexponential factor of diffusion coefficient, $\text{m}^2 \text{ s}^{-1}$
$E_D$	– activation energy of diffusion coefficient, $\text{J mol}^{-1}$
$T$	– temperature, K
$R$	– universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$w$	– mass fraction, %

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