Quantitative correlation of ethyl acetate diffusion and crystallinity in poly(vinylidene fluoride): photoacoustic *FT*i.r. approach

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The mobility of ethyl acetate (EAc) as a function of crystallinity in poly(vinylidene fluoride) (PVF_2) has been quantified utilizing methodology based on the recently developed rheo-photoacoustic Fourier transform infrared spectroscopy (RPA *FT*i.r.). The diffusion measurements obtained with the photoacoustic cell, combined with the independent sorption and X-ray measurements, indicate that the crystalline phase of the polymer is impermeable to EAc. Spectroscopic RPA *FT*i.r. measurements agree with the independently determined diffusion coefficients and the theoretical predictions relating diffusion to the per cent crystalline phase in PVF_2. This study indicates that RPA *FT*i.r. methodology is highly sensitive to the gas phase analysis and, with the use of proper calibration procedures, can be applied to a quantitative analysis of diffusion in polymers.

(Keywords: ethyl acetate; diffusion; crystallinity)

INTRODUCTION

Transport properties of polymers can reveal important information about their microstructures because diffusion of small molecules in polymers depends upon free volume of the network as well as other properties related to the free volume content. Such variables as temperature[1,2], size and shape of penetrant[3–5], penetrant concentration[6–8], and the degree of crystallinity[3,9] also affect transport properties. Crystalline regions in particular play an important role because they are believed to be impermeable to diffusants, and consequently, diffusant molecules are forced to follow longer and more tortuous paths through the amorphous regions. This is why an interplay between the amorphous fractional free volume and the size of the diffusant molecules is important. Furthermore, the mobility through the amorphous phase is reduced due to the inclusion of parts of the polymer chains in one or more crystallites, diminishing the amorphous phase free volume that acts as the diffusion medium, thus reducing permeability.

Recently, we[10] reported a novel rheo-photoacoustic Fourier transform infrared (RPA *FT*i.r.) methodology that allows us to differentiate the diffusion rate of ethyl acetate (EAc) in poly(vinylidene fluoride) (PVF_2) under various conditions. While the differences in mobility between PVF_2 samples following various degrees of mechanical deformation were qualitatively assessed, no quantitative approach leading to the determination of diffusion coefficients was given. This study focuses on a quantitative extension of the previously introduced experimental RPA *FT*i.r. methodology[11–13].

EXPERIMENTAL

Sample preparation and spectral measurements

Films of PVF_2, 140 ± 10 μm thick and with approximately 40% crystallinity, were obtained from Westlake Corp. The PVF_2 samples with a smaller crystalline content were obtained by heating the polymer to 180°C for 10 to 35 min, followed by quenching the specimens in an acetone/dry ice bath. An analytical grade of EAc was purchased from Aldrich Chemical Co. and was used as received.

Photoacoustic *FT*i.r. spectra were collected in a specially designed rheo-photoacoustic *FT*i.r. cell[10–12]. In essence, the cell consists of an ordinary photoacoustic *FT*i.r. cell equipped with a stress–strain device. The cell design and the procedures involved for collecting *FT*i.r. spectra have been described elsewhere[10,11]. X-ray diffraction was used to determine and differentiate the degree of crystallinity in PVF_2. A description of the instrumentation and experimental parameters used to obtain the X-ray diffractograms were provided earlier[13].

Diffusion coefficient determination

The half time of desorption, $t_{1/2}$, is the time required for half of the initial weight of EAc to evaporate from the polymer specimen. It was determined by measuring the loss of EAc from saturated films using an analytical balance with a sensitivity of 0.1 mg. Based on these data, the diffusion coefficients were determined using the equation[14,15]:

$$D_d = 0.05 \frac{L^2}{t_{1/2}} \qquad (1)$$

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where D_d is the desorption diffusion coefficient, L is the sample thickness and $t_{1/2}$ is the half-time of desorption. The amount of EAc sorbed by PVF$_2$ was obtained by subtracting the weight of the dry polymer from that of the same polymer specimen saturated with EAc.

RESULTS AND DISCUSSION

Although the primary objective of this study is to develop a quantitative methodology for monitoring diffusion coefficients in polymeric substances, the first step requires an accurate determination of PVF$_2$ crystallinity. This issue is particularly essential because of the commonly accepted fact that crystalline regions do not allow permeation of small molecules. As a result, penetrant molecules diffusing through the network are forced to diffuse through the amorphous phase regions. Therefore, knowing the crystalline phase content will allow an assessment of the amorphous volume available for diffusion.

In an effort to determine the amount of crystalline phase, the method described by Alexander[16] will be used. This approach enables us to correlate the X-ray peak intensity obtained from a diffractogram pattern to the degree of polymer crystalline content. *Figure 1* represents a typical diffractogram of the α phase of PVF$_2$. As no diffractogram for the totally amorphous PVF$_2$ polymer is available to ascertain the shape of the amorphous halo (dotted area), it was assumed that, for a purely amorphous polymer network, the two more intense peaks are separated such that the contribution of the crystalline phase at point B falls to zero counts s^{-1}. With this in mind, a curve connecting points A, B and C was used to establish the shape of the amorphous contribution to the overall X-ray intensity. The shaded area of the peaks above the curve was determined and taken to be proportional to the crystalline content of the polymer, whereas the height of the amorphous halo between points B and D was assumed to be proportional to the amorphous content. By plotting the X-ray intensity of the amorphous scattering as a function of the integrated intensity of the crystalline peaks, *Figure 2* was obtained, and the degree of crystallinity was calculated using the following relationship[16]:

$$\alpha_c = \frac{1}{\left(1 + \frac{PI_a}{QI_c}\right)} \tag{2}$$

where α_c is the weight per cent crystallinity, P and Q are the axis intercepts at 100% and 0% crystallinity, respectively, I_a is the intensity of the amorphous halo at point B and I_c is the integrated crystalline peak intensity. From the calibration plot shown in *Figure 2*, the crystallinity of the as-received PVF$_2$ was found to be $40 \pm 1\%$. In an effort to establish the validity of this approach, the crystallinity of the same polymer was also examined using density measurements. The density was found to be 1.76 g cm^{-3}. Using the values of 1.90 and 1.67 g cm^{-3} for the densities of the crystalline and amorphous phases, respectively[17], a value of 39% crystalline phase was determined.

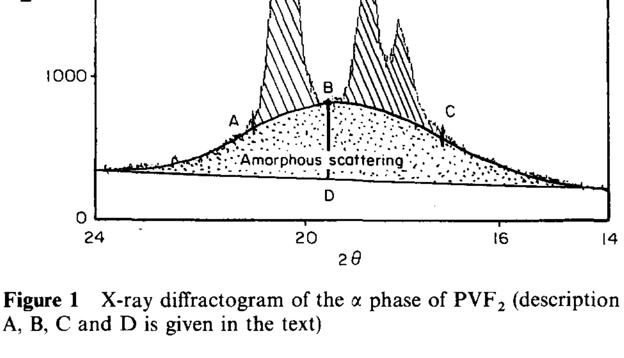

Figure 1 X-ray diffractogram of the α phase of PVF$_2$ (description of A, B, C and D is given in the text)

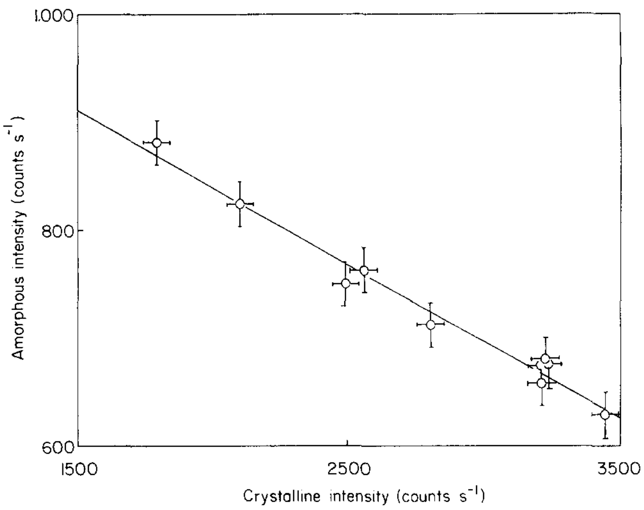

Figure 2 Plot of the amorphous X-ray band intensity determined from *Figure 1* at point B as a function of the integrated intensity of the crystalline peaks

We[13] demonstrated in an earlier study that, if the EAc vapour contained in the RPA *FT*i.r. cell is purged away between spectral collections, the relationship between the intensity of the carbonyl band due to gas phase EAc at 1768 cm^{-1} and diffusion time is exponential and can be expressed by:

$$I_{PA} = Ae^{-xt^{1/2}} \quad \text{or} \quad \ln I_{PA} = \ln A - xt^{1/2} \tag{3}$$

where I_{PA} is the photoacoustic *FT*i.r. intensity of the carbonyl normal vibrations at 1768 cm^{-1} of the gas phase EAc, x is the rate at which EAc diffuses out of the polymer, A is a constant and t is the time of diffusion in minutes.

As shown in *Figure 3*, a plot of natural log of I_{PA} as a function of the square root of time results in two straight lines having, in all cases, correlation coefficients of 0.995 or better. Conceptually, the exponential relationship seems to be justified since the concentration of EAc in the polymer decreases over the course of the experiment and, as shown in many studies[6,7], the diffusion coefficients of polymers exhibit an exponential dependence on diffusant concentration. In our case, the rate of diffusion is reflected in the slope, x, of the plot in *Figure 3*. This is because the more rapidly EAc migrates to the surface and evaporates, the faster the intensity of the carbonyl band decreases as the cell is being purged between spectral collections.

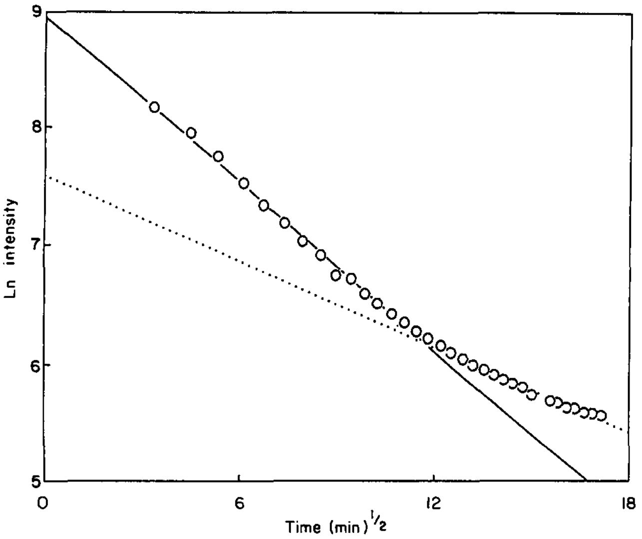

Figure 3 Natural log of EAc carbonyl band intensity at 1768 cm^{-1} recorded using photoacoustic detection plotted as a function of the square root of time of the experiment

Table 1 Data used for the generation of *Figures 4* and *7*

% Crystallinity, α_c ($\pm1\%$)	x^a	$D_d \times 10^6$ (cm^2 min^{-1})^b
22	0.236	1.80
29	0.223	1.52
30	0.220	1.45
32	0.218	1.41
36	0.211	1.26
37	0.208	1.19
40	0.204	1.10
43	0.198	0.97

[a] x, exponent in equation (3)
[b] D_d, desorption diffusion coefficient

The effect of crystallites on the mobility of diffusant molecules in polymeric amorphous phases has been studied extensively[3,9,17–21]. Based on Maxwell's equations for electrical conductance in dilute suspensions, Kulkarni and Mashelkar[22] developed a relationship between the diffusion coefficient, D, and the crystalline fraction, α_c. The validity of the relationship was demonstrated for several systems[22] and for the idealized case is given by:

$$D_S = D_A\left(\frac{1}{1+\alpha_c/2}\right) \tag{4}$$

where D_S and D_A are the diffusivities of the semicrystalline and the amorphous polymers, respectively.

Keeping the above relationships in mind, let us attempt to correlate the x values obtained from equation (3) for specimens exhibiting different crystallinity contents and relate them to the $1/[1+(\alpha_c/2)]$ term in equation (4). *Table 1* lists the x and the corresponding α_c values and *Figure 4* illustrates graphically the relationship between x and the $1/[1+(\alpha_c/2)]$ term in equation (4). According to *Figure 4*, x is inversely proportional to the degree of crystallinity and this assessment appears to be in agreement with the generally accepted concept that polymer crystallites are impermeable to organic penetrants[8,18,19]. Therefore, slower rates of diffusion are observed for semicrystalline polymers than for amorphous ones. Further evidence for the EAc non-permeability of the crystalline PVF$_2$ regions can be found by measuring the amount of EAc absorbed in saturated films. *Figure 5* represents the weight of EAc absorbed per unit weight of dry PVF$_2$ plotted as a function of the crystalline content in the film. Extrapolation of the line to zero sorbance results in an intersection close to 100% crystallinity, again indicating that the crystallites are impermeable to the EAc.

So far, we have shown that the term x in equation (3) is related to the rate of diffusion and depends upon the PVF$_2$ crystalline content. At this point, it is appropriate to return to the main theme and relate the spectroscopic data obtained in the RPA *FT*i.r. experiment to a standard diffusion coefficient. In this case, the desorption coefficient, D_d, introduced in the Experimental section, will be used as a convenient and independent means of determining the polymer's diffusion properties. *Figure 6* represents a plot of diffusion coefficients obtained from equation (1), and plotted as a function of x values obtained for the corresponding specimens. Based on these data, a linear relationship between x and D_d is obtained:

$$D_d \times 10^6 = A + Bx \tag{5}$$

where $A = -3.34$ and $B = 21.78$ are the experimental constants, and their physical meaning is most probably polymer system dependent. Since x can be determined

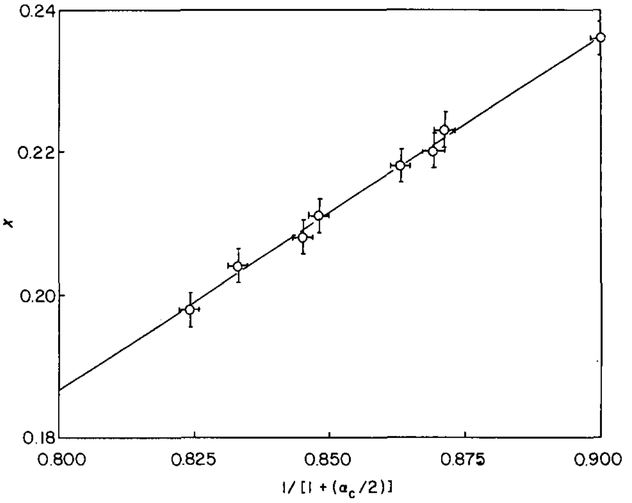

Figure 4 Exponent x (equation (3)) plotted as a function of $1/[1+\alpha_c/2)]$ (equation (4))

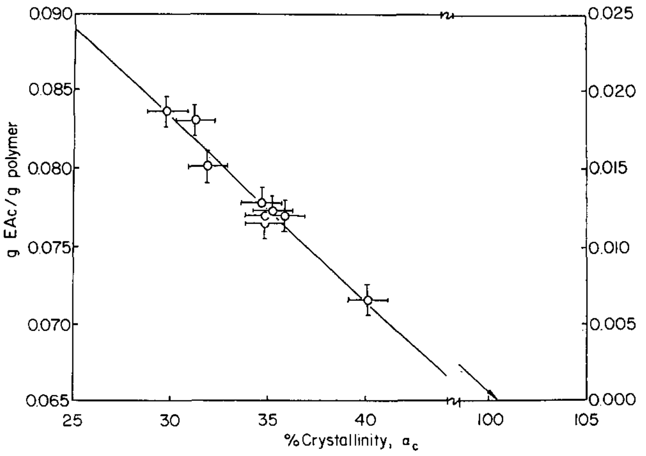

Figure 5 Amount of EAc absorbed in PVF$_2$ per gram of dry polymer plotted as a function of the crystalline content (α_c) of the film

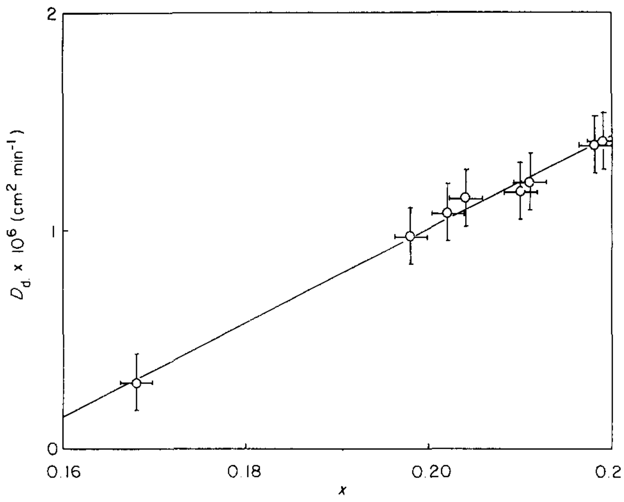

Figure 6 Diffusion coefficients (D_d) determined from equation (1) plotted as a function of x (equation (3))

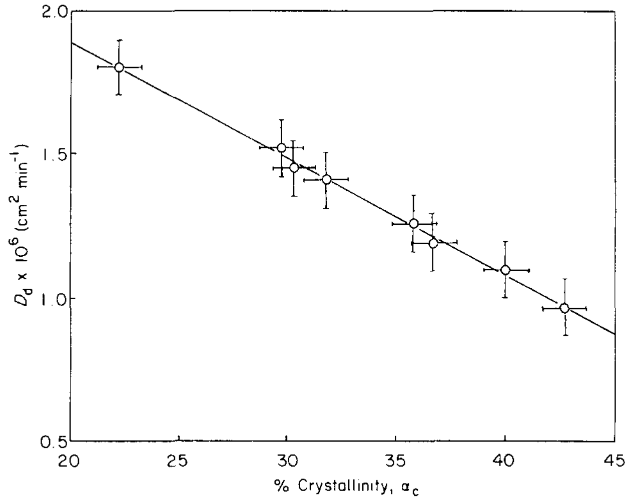

Figure 7 Diffusion coefficients (D_d) calculated from equation (5) and plotted as a function of PVF$_2$ crystallinity (α_c)

from RPA *FT*i.r. experiments, equation (5) allows the determination of D_d by monitoring the elution of vapour in the RPA *FT*i.r. cell. Such an approach makes possible an RPA *FT*i.r. spectroscopic evaluation of D_d in PVF$_2$, as well as in other polymers, regardless of shape or opacity of the polymer. The previously reported method of determining D_d using transmission spectroscopy[23] is limited in this respect.

It has been reported in the literature[8] that the rate of diffusion in polymers is inversely related to the content of crystalline phase. In order to establish the relationship between the diffusion coefficient (D_d) and the crystalline fraction (α_c) for the PVF$_2$/EAc system, the diffusion coefficients, calculated using equation (5), were plotted as a function of α_c, as shown in *Figure 7*. The correlation coefficient between D_d and α_c is again better than 0.995 and this relationship formulates the basis for the assessment that the diffusion coefficient of EAc in PVF$_2$ is proportional to the amorphous fraction of the film. The numerical data used for plotting *Figures 4* and *7* are provided in *Table 1*. It should be noted that the reported diffusion coefficients were obtained under non-equilibrium conditions, namely, the concentration of EAc in the polymer was continuously decreasing throughout the course of the experiment. As a result, the reported D_d values represent an average for a given EAc concentration range in the PVF$_2$ network.

CONCLUSIONS

In this study, we have demonstrated that it is possible to monitor quantitatively the diffusion of EAc in PVF$_2$ using a newly developed rheo-photoacoustic *FT*i.r. technique. The experimental approach involves the previously reported 'photoacoustic umbrella' which does not allow the i.r. light to 'see' the polymer, but only the gas phase diffusing out of the polymer. The mobility and solubility of EAc is directly dependent upon the amorphous phase fraction of the polymer. The spectroscopic diffusion data agree well with the previously proposed theories and independent diffusion measurements. The ability to quantify diffusivity, coupled with the capability of acquiring data from strained polymers, makes RPA *FT*i.r. spectroscopy not only a promising methodology for studying transport properties of polymeric materials, but also polymers experiencing uniaxial strain.

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