

A STUDY OF SOME PHOTOCROSSLINKABLE RESINS USING i.r. SPECTROSCOPY

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Abstract—The kinetics of photoinduced crosslinking of a number of polymers containing chalcone units have been studied. The concentration of the chalcone groups and the nature of the backbone were varied in a controlled manner. The rates of photocrosslinking cannot be analysed by the simple application of solution kinetics. Factors which affect the rate of cure (e.g. concentration of chalcone units, thickness of films and temperature) were examined and reasons are given for the failure of the simple kinetic model.

INTRODUCTION

i.r. Spectroscopy has been used extensively in the field of polymer chemistry, and more specifically Azuma *et al.* [1] have studied photosensitive rubbers containing pendant cinnamate using this technique. These workers used their results to develop a kinetic model for these systems. The model however was based on solution kinetics. A similar kinetic model has also been used to study the crosslinking of furylacryloyl pendant groups [2]. This paper will show how this model is essentially invalid. The effects of varying the concentration of the chromophores, film thickness and temperature are also studied as is the applicability of the statistical model presented in a separate paper [3].

Although it is widely accepted that i.r. radiation is appreciably attenuated within the first few micrometers of a polymer film, this view has never previously been substantiated. Results are detailed showing this to be the case.

Polymers 1-8 contain 1,3-diphenyl-prop-2-en-1-one as, the photoactive unit, whereas polymers A-F contain 1,5-diphenyl-penta-1,4-dien-3-one.

i.r. SPECTRA OF POLYMERS

The bands used to follow the irradiation of the polymers are either the C=C double bond stretch around 1600 cm⁻¹, the conjugated C=O stretch which absorbs around 1645-1665 cm⁻¹ (depending upon the system), and the C-H out-of-plane deformation, which for the *trans* configuration lies between 960-980 cm⁻¹. These particular bands are picked out in Fig. 1, the spectrum of polymer A.

When using i.r. spectroscopy quantitatively, it is necessary to define a particular datum line so that results from different experiments are directly comparable. The method used is the baseline technique and consists of drawing a line tangential to two points on the spectrum. Any number of baselines can be drawn, the question of which to use depends upon experimental conditions. In this case a line was drawn between approx. 1800 cm⁻¹ and 780 cm⁻¹, as the 980 cm⁻¹ band almost completely disappears on

irradiation. This would lead to gross inaccuracies if individual base lines were drawn.

Spectra of polymers 1, 5, 8 and E are shown in Fig. 2. Since the extent of absorption at a particular frequency is dependent upon film thickness, it would be useful to know accurately the thickness of the films employed. Film thicknesses of polymers can be obtained from the density of the polymers using:

$$l = \frac{M}{Ax\rho},$$

where M = mass of film; ρ = density of polymer; A = area of film; l = thickness.

In order to reduce weighing errors which can be large when two large weights are subtracted to find a small difference, a substrate with a high surface area-to-weight ratio is required. If the curing of the film is to be monitored using i.r. spectroscopy then a substrate transparent to i.r. radiation would be an advantage. Large thin KBr discs meet these requirements, hence the use of 80 mm KBr discs in these studies. Another advantage of the discs is that they can be easily removed using water, thus enabling the backs of the films to be studied.

RESULTS AND DISCUSSION

Tables 1 and 2 give some useful data on polymers 1-8 and polymers A-F.

The carbonyl bands from the hydantoin moiety occur at 1765 and 1705 cm⁻¹ and should be unaffected by irradiation. However the 1705 cm⁻¹ is affected because on irradiation, the central carbonyl group of the chromophores becomes deconjugated when the C-C bonds undergo [2 + 2] cycloaddition and thus it will shift its absorption to the 1705 cm⁻¹ region. The 1765 cm⁻¹ band remains unaffected and, after determining the extinction coefficient as measured from the baseline (using many different thicknesses of film), this band was used to monitor thickness and also to act as an internal standard. The extinction coefficient, taken as an average of 28 results was measured as $207 \pm 20 \text{ l mol}^{-1} \text{ cm}^{-1}$.

By using the extinction coefficient to determine the thickness of the films of polymers 1-8 and A-F and then relating the absorbance obtained to one that

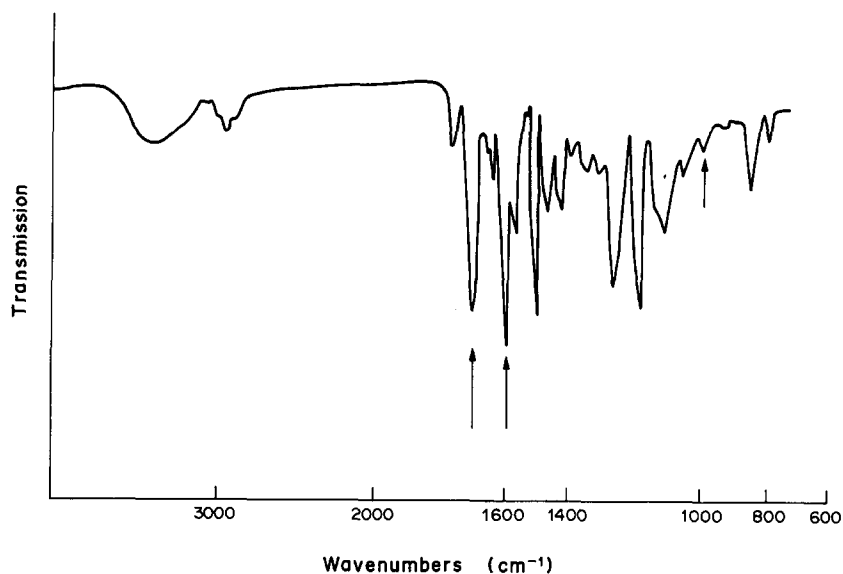


Fig. 1. i.r. Spectrum of film of polymer A on KBr disc.

would be obtained at a standard film thickness of 3×10^{-6} m, it was possible to obtain calibration graphs of absorbance against concentration for the various bands.

The best straight lines, i.e. those that obey Beers law, were obtained by using the 1600 and 984 cm^{-1} absorptions. However the tendency of the latter to disappear as the reaction proceeds meant that the

former was used to follow the reactions in most cases. The 1650 cm^{-1} band, due to the unsaturated carbonyl group, tended to merge with the adjacent carbonyl band due to the hydantoin unit, and thus is of limited use.

Using the calibration curve for the 1600 cm^{-1} band, it was possible to follow the effect of irradiation on the average concentration of chromophore in a

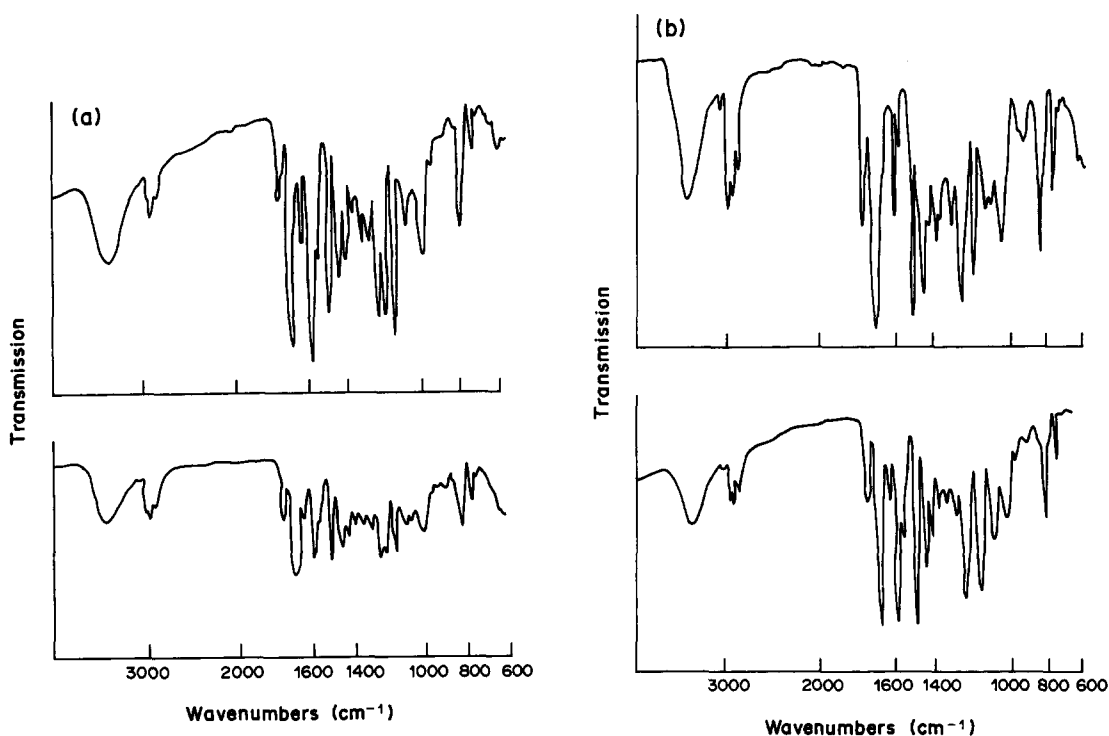


Fig. 2. (a) i.r. Spectrum of films of polymer 1, and polymer 5 on KBr disc. (b) i.r. Spectrum of films of polymer 8 and polymer E on KBr disc.

Table 1. Compositions and densities of polymers 1-8

Polymer	Conc. of Chalcone (mol/l)	Conc. of DMH ^a (mol/l)	Conc. of BADGE ^b (mol/l)	Density (kg/m ³)
1	3.21	2.44	—	1440
2	3.14	2.65	0.30	1550
3	2.41	2.29	0.51	1310
4	1.91	2.07	0.71	1180
5	1.36	2.06	1.15	1140
6	0.75	2.15	1.68	1110
7	0.26	2.26	2.29	1160
8	—	2.26	2.51	1140

^aDMH = 5,5-dimethylhydantoin; ^bBADGE = Bisphenol A diglycidyl ether.

Table 2. Compositions and densities of polymers A-F

Polymer	Conc. of DBA ^a (mol/l)	Conc. of DMH (mol/l)	Conc. of BADGE (mol/l)	Density (kg/m ³)
A	2.39	2.12	0	1175
B	2.34	2.24	0.25	1260
C	2.12	2.32	0.51	1270
D	1.77	2.19	0.72	1196
E	1.22	2.11	1.16	1126
F	0.76	2.18	1.71	1146

^aDBA = dibenzalacetone diglycidyl ether.

4×10^{-6} m film of polymer. The thickness was determined by both weighing and using the extinction coefficient: both methods gave a result of 4×10^{-6} m. The observed absorbances were corrected for thickness so that the calibration curve would be applicable.

The results in Table 3 are shown graphically in Fig. 3.

Table 3. Concentration of chromophore in a film of polymer 1 after various times of irradiation

Time (sec)	Conc. (ml ⁻¹)	Time (sec)	Conc. (ml ⁻¹)
0	3.08	180	2.55
30	2.88	300	2.35
60	2.76	420	2.22
90	2.69	540	2.12
120	2.61	570	2.09

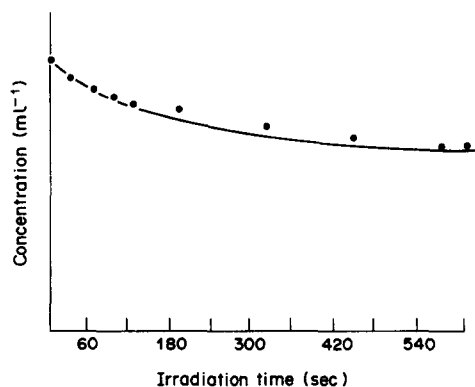


Fig. 3. Graph showing change in chromophore concentration (measured at 1600 cm^{-1}) vs irradiation time.

Application of first and second order solution kinetics is shown in Figs 4a and 4b. Neither plot yields a straight line, thus indicating that the solid state reaction does not follow simple rate kinetics developed for solutions. This is because on irra-

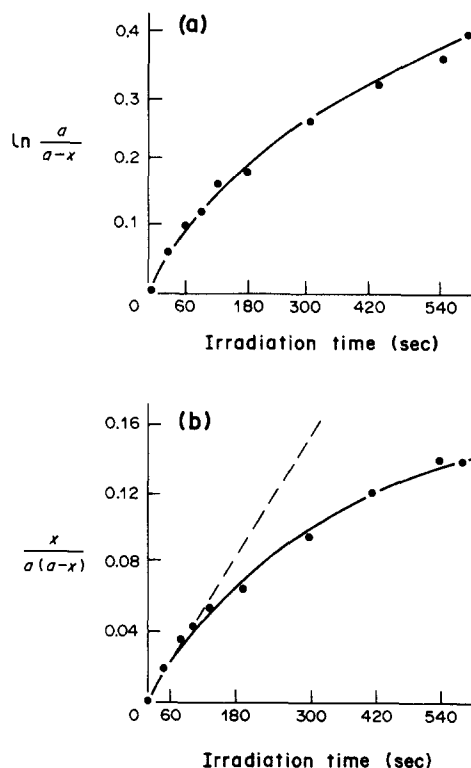


Fig. 4. (a) First order plot for disappearance of chromophore (unsaturated ketone) upon irradiation of polymer 1. (b) Second order plot for disappearance of chromophore (unsaturated ketone) upon irradiation of polymer 1.

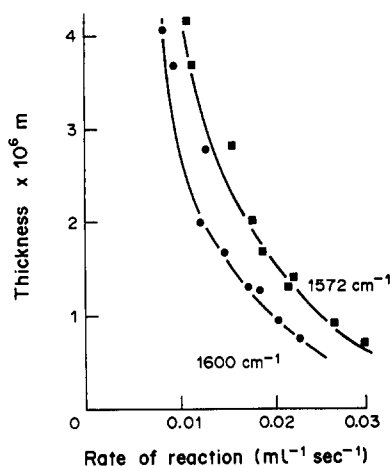


Fig. 5. Rate of reaction vs thickness of film for polymer 1 monitored at 1600 cm⁻¹ (●) and 1572 cm⁻¹ (■).

diation the concentration is no longer uniform unlike solution reactions, i.e. there is a concentration gradient through the film. No account has been taken of the chromophores, isolated in the solid matrix after the surrounding chromophores have reacted; they absorb incident radiation but cannot react thereby reducing the effective light intensity.

A rate equation has been developed, based on the kinetic model of Azuma *et al.* [1], in which some account of unreactive sites has been taken. The model is not successful because no allowance is made for the attenuation of the incident intensity I_0 by chromophores in unreactive sites. Initially this is not significant; however once cure has passed to the lower region of the film the incident intensity is greatly attenuated [3].

Because of the failure of the models to yield a true rate constant, the mean gradients between 0–60 sec of the plots of concentration vs time are used in order to obtain a degree of comparison between experiments.

Plots of rate of reaction vs thickness produced curves in most cases. However plots of rates of reaction vs the inverse of thickness yielded straight lines which only tailed off at high thicknesses (see Figs 5 and 6), thus for thin films, the thinner the film the faster the reaction. However this result is only an apparent result which arises from the method of measurement, i.e. transmission spectroscopy. In fact the rate of reaction is dependent upon the light intensity, the value of which at any particular depth in the film is dependent upon the concentration of unreacted chalcone chromophores between the point and the surface. Thus a concentration gradient will be set up in the film. After a specific irradiation time, cure will reach the same depth in all films which are sufficiently thick to prevent light transmission. Since transmission i.r. spectroscopy measures the concentration of chromophores in the film, there will be an apparent increase in concentration of unreactive chromophores, the greater the thickness of the film. As a consequence, this form of spectroscopy will give rise to apparent dependence of reaction rate upon the

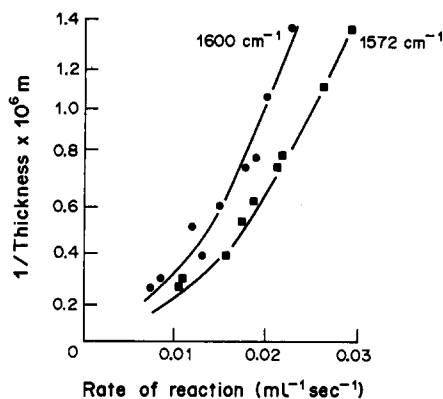


Fig. 6. Rate of reaction vs the inverse of the thickness of film of polymer 1 monitored at 1600 cm⁻¹ (●) and 1572 cm⁻¹ (■).

thickness of the film. Clearly as the thickness of films is increased, the effect of unreacted chromophores will lead to a greater percentage of unreacted chromophores and transmission (i.r. spectroscopy will show that less and less reaction is occurring).

The main error in our results is in the measurement of the film thickness and this in turn was attributed to the confidence in the figure obtained for the extinction coefficient of the 1765 cm⁻¹ band.

Using the 1600 cm⁻¹ band during the study of polymers 1–8, it was possible to show that 49% cure had been achieved in films <6.0 μm thick. However the time taken to attain this degree of cure was excessive and unacceptably long for even thicker films. Thus the model described in a separate paper gives good correlation in this case [3]. It should be noted however that when the 1600 cm⁻¹ band showed 45% cure, the 1572 cm⁻¹ band showed 55% cure.

Experiments on the polymer A series show that maximum cure is around 86% and generally this figure is achieved in <2 min for films approx. 1 μm thick.

The effect of varying the initial concentration of the chalcone was demonstrated for both series. For the series based on chalcone (polymers 1–8), plots of rate of reaction vs the square of the concentration for film thicknesses from 0.8 to 4 μm gave reasonable straight lines, showing that during the initial period the reaction is basically second order. However the restrictions of the solid matrix soon become apparent at longer irradiation times.

Three films of polymer 1 of comparable thickness were cured at different temperatures but under the same light intensity 64 kW/m². The results are shown in Table 4.

A very slight trend of increasing rate of reaction with increasing temperature can be observed. This effect is attributed to the higher mobility of the polymer chain at higher temperatures allowing chromophores to move into reactive positions.

A comparison of the rates of reaction between the two series of polymers is made in Table 5 presenting the results obtained using the 1600 cm⁻¹ band. It can be seen that the inclusion of a second double bond doubles the rate of reaction.

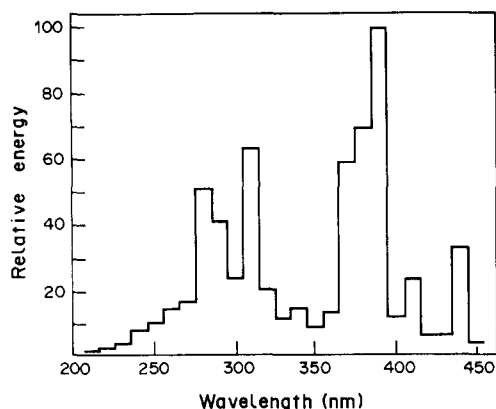


Fig. 7. Spectral output of u.v. curve lamp.

Table 4. Effect of temperature on rate of crosslinking

Temperature (°C)	Thickness (μm)	Conc. (ml)	Rate (ml ⁻¹ sec ⁻¹)
25	3.52	3.06	0.002
40	3.15	3.24	0.003
60	2.79	3.42	0.005

An experiment was performed with a polymer similar to polymer A but containing more chromophore in order to obtain a measurable amount of light absorption. Glass plates, onto which films of various thickness of the polymer were spread, were placed on top of a light intensity meter and exposed to the curing lamp. The intensity of the transmitted light was monitored with time. The results are presented in Table 6. Before each irradiation, the intensity of the light was checked because the detector response varied with temperature.

The results show that light which initiates photocrosslinking eventually penetrates 4×10^{-6} m into the sample. However before an appreciable amount of the radiation reaches a depth of 5×10^{-6} m, it is attenuated to such an extent that it is not possible to

detect any cure which is initiated. The film will still absorb a little more radiation as demonstrated by the 11.2×10^{-6} film, but this is insufficient to initiate a significant amount of reaction. This high attenuation of light by films in which the concentration of chromophore has been reduced to about 15% of the original concentration is attributed to the high extinction coefficients of the chromophore below 400 nm.

EXPERIMENTAL

The i.r. spectra were obtained on a Perkin-Elmer 599 spectrometer. In general, samples were placed in a sample holder which had a 15×5 mm hole cut into it. This was done to standardize the surface area of the sample presented to the beam.

Most films were prepared on a 40 mm KBr disc made using approx. 3 g of KBr placed in a 40 mm Specac press. A pressure of 25 tons was applied for 3 hr.

Intensity measurements were made using a Macom, radiometer/photometer R101. The lamp used for curing was an 1800 W medium pressure lamp. (Thorn Lighting 91-7480).

The distance between the lamp and the sample was 23 cm. The light from the lamp was restricted through a 7 cm dia circular hole so that filter solutions could be inserted between lamp and the sample. The spectral output of the lamp can be seen in Fig. 7. The temperature of the curing apparatus was 80–100° and samples were always brought to this temperature in an oven prior to irradiation.

Films were laid down using K-bars from RK print coat instruments. Temperature in the irradiation chamber was controlled at 60° using a flat vessel through which cooled water was pumped. This arrangement had a secondary effect of reducing the intensity from 77 kW/m² to 64 kW/m². Further reduction of temperature to 40 and 25° was achieved by placing icebaths inside the chamber.

The synthesis of the polymers is described in a separate paper [4].

CONCLUSION

It has been demonstrated that solution kinetics do not apply for solid state reactions. It has been further demonstrated that i.r. spectroscopy is limited when

Table 5. Comparison of the rate of reaction of the two series of polymers

Series A-F			Series 1-7		
Conc. (ml ⁻¹)	Thickness	Rate (ml ⁻¹ sec ⁻¹)	Conc. (ml ⁻¹)	Thickness (μm)	Rate (ml ⁻¹ sec ⁻¹)
3.32	0.82	0.045	3.76	0.75	0.023
3.32	1.99	0.039	3.14	2.02	0.012
3.28	3.42	0.028	2.84	3.70	0.009
3.43	1.75	0.035	2.73	1.79	0.013
2.25	3.58	0.022	2.73	3.79	0.010
2.17	1.21	0.029	2.46	0.89	0.016

Table 6. The intensity of light measured through film of a polymer similar to polymer A

Thickness (μm)	I_0 (Wm ⁻²)	I_g (Wm ⁻²)	I_{gr} at $t = 0$ (Wm ⁻²)	I_{gr} at $t = 60$ sec (Wm ⁻²)	I_{gr} at $t = 600$ sec (Wm ⁻²)
0.9	77,000	68,000	61,000	66,000	66,000
3.9	77,000	72,000	58,000	60,000	60,000
5.1	77,000	67,000	57,000	57,000	57,000
11.2	77,000	72,000	58,000	58,000	58,000

I_0 = Incident intensity.

I_g = Intensity measured through glass plate.

I_{gr} = Intensity measured through glass plate and film at various times.

faced with concentration gradients set up by curing the polymer.

However i.r. spectroscopy has again proved useful in showing that the rate of cure is dependent upon film thickness, concentration of chromophores and temperature.

It has also shown that polymers containing a second double bond in the chromophore cures twice as quickly as those with only one double bond.

An attempt to correct a kinetic model so as to include provision for unreactive sites has had limited success due to the failure to include factors for light absorbed by unreactive sites and concentration gradients.

It has also been shown that films of polymer A thicker than 4×10^{-6} m will not cure at the bottom due to a lack of light penetration.

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