Studies of the Photo-Fries Reaction in Solid Poly(phenyl acrylate)

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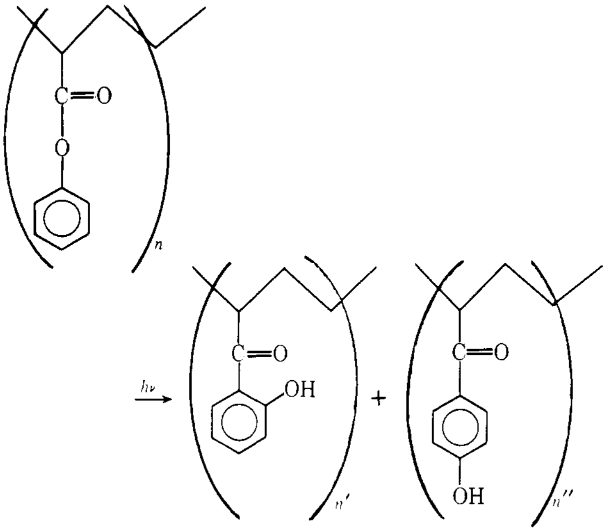
ABSTRACT: Relative quantum yields for the formation of *o*- and *p*-hydroxyphenone groups from poly(phenyl acrylate) via the photo-Fries rearrangement reaction were measured as a function of temperature and of the wavelength of excitation. No significant discontinuity occurred in the quantum yields of photo-Fries products at T_g (332 K). The quantum yields increased with temperature with an apparent activation energy of 1.2 and 1.8 kcal mol^{-1} for the ortho and para products, respectively, up to 294 K but showed no further variation with temperature above this transition, which is tentatively identified as being due to motion of the phenyl ester group. This, as well as the constancy in quantum yields and distribution of the photoproducts with the wavelength of excitation, lends support to a reaction mechanism involving caged radical species.

The photo-Fries reaction in both small organic molecules and polymers has been investigated extensively since the discovery of the reaction by Kobsa[1] and Anderson and Reese.[2] Several review papers on the reaction have been published.[3] The scope of the reaction has been extended from phenyl esters and phenyl carbonates to include other compounds containing the phenoxy group, such as phenoxyacetic acid,[4] acetanilides,[5] phenyl ethers,[6] and hydroxyphenyl cinnamates.[7] When the photo-Fries reaction is carried out in solution, phenols from the corresponding phenyl esters are consistently obtained as side products.

All available evidence on the mechanism of the photo-Fries reaction suggests that the rearrangement is intramolecular. Two different intramolecular mechanisms have received popular support in the literature. In the first mechanism, the excited state of the phenyl ester molecule reacts in a concerted fashion, the acyl and phenoxy portions of the molecule remaining bonded to each other throughout the entire course of the rearrangement.[8] The other mechanism, known in general as the cage recombination mechanism, involves the homolytic cleavage at the C–O bond of the ester linkage, giving rise to acyl and phenoxy radicals which are held within a solvent cage.[1] Recombination of the two radicals inside the solvent cage results in the reformation of the starting ester, or the corresponding *o*- and *p*-acylcyclohexadienones, which then tautomerize to the hydroxyphenone products. Diffusion of the radical fragments from the solvent cage followed by hydrogen abstraction from the solvent allows for the formation of cleavage products such as phenol. The multiplicity of the excited state leading to the reaction has not been unambiguously identified. Naphthalene (a triplet quencher), ferric acetylacetonate (a paramagnetic quencher), acetophenone (a triplet sensitizer), and oxygen were found to have no effect on the photo-Fries reaction.[8] Based on quenching and sensitization experiments, it is generally believed that the reactive state does not involve a triplet.

It has been demonstrated that many photochemical reactions shown by small organic molecules can be induced to occur in polymers when the same chromophores are bonded to a polymer backbone.[9] The rearrangement of poly(phenyl acrylate) (PPA) to polymeric *o*- and *p*-hydroxyphenone groups can be taken as a typical representation of the photo-Fries reaction in a polymeric system (eq 1).

The primary photophysical and photochemical processes of poly(aryl esters) and poly(aryl carbonates) have been investigated extensively because photo-Fries rearrangement products in such polymers offer the possibility of generating internal UV stabilizers in bulk polymers.[10]



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When a photochemical reaction occurs in the solid phase, one would normally expect a much smaller quantum yield than for the same photochemical reaction carried out in solution, but this is not always the case.[11] The present study was made to determine the role of molecular mobility in the solid-phase photo-Fries reaction in poly(phenyl acrylate).

Experimental Section

Phenyl acrylate was obtained from Polyscience Corp. and purified by distillation under vacuum. Poly(phenyl acrylate) was prepared by free-radical polymerization in a sealed tube at 78 °C for 19 h of the neat liquid monomer containing 0.5 wt % of lauroyl peroxide as initiator. The polymer was dissolved in benzene and then reprecipitated three times with petroleum ether. The polymer had a molecular weight in excess of one million and a glass transition temperature of 59 °C. Clear films of uniform thickness were obtained by casting a benzene solution of the purified polymer onto a distilled water surface. Final removal of the residual solvent and water from the films was achieved by drying in a vacuum desiccator for 3 days. All polymer films used for the present studies were on the order of 0.01 mm thick.

During the course of the studies, two different light sources were used. One was an A.E.I. Me/D medium pressure mercury arc lamp. A 2.5-cm path length filter solution made up from 6.9 g of $NiSO_4 \cdot 6H_2O$ and 2.1 g of $CoSO_4 \cdot 7H_2O$ in 100 mL of distilled water was used to isolate the 220 to 340 nm ultraviolet region of the lamp. The other light source was a super pressure mercury point source Model SP 200 from Bausch and Lomb. Monochromatic light was obtained with a high-intensity grating monochromator from the same company. The intensity output of the SP 200 light source at different wavelengths was measured by a Hewlett Packard Model 8334A radiant flux detector. The incident light intensities were displayed directly on a Hewlett Packard Model 8330A radiant flux meter in units of milliwatts per second.

The optical arrangement for the irradiation of polymer films is shown in Figure 1. The PPA film used for irradiation was supported between two quartz plates which were fitted into a thermostated

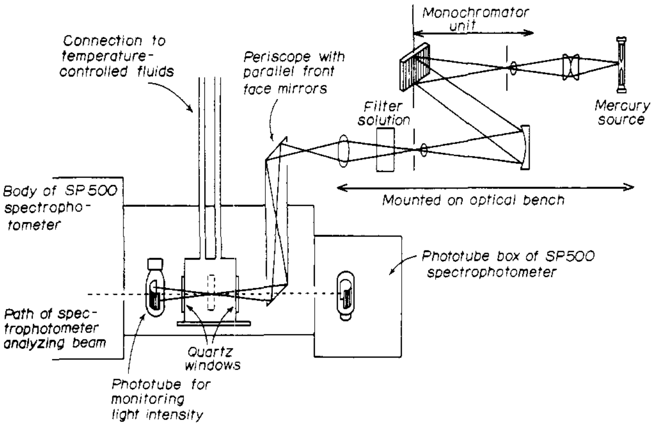


Figure 1. Optical path of the irradiating light and components of the irradiation system.

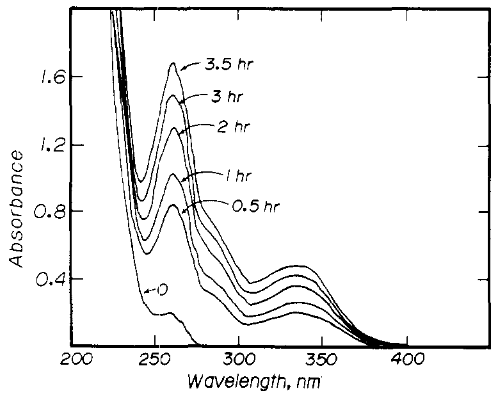


Figure 2. Absorption spectra of a PPA film after different periods of irradiation at room temperature, using light of wavelengths between 220 and 340 nm from the A.E.I medium-pressure mercury lamp.

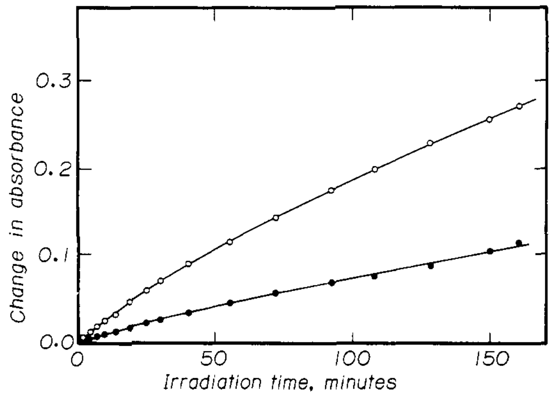
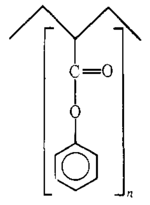
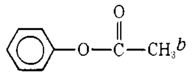
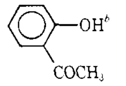
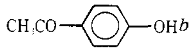


Figure 3. Plots of the differential absorbance changes of an irradiated PPA film with time of irradiation at 25 °C: (○) 265 nm; (●) 335 nm.

Table I
Molar Extinction Coefficients of Poly(phenyl acrylate), Phenyl Acetate, and *o*- and *p*-Hydroxyphenones

	Solvent	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
	1,2-Dichloroethane	259	260[a]
	Cyclohexane	259	290
	Cyclohexane	249 325	9270 3740
	Cyclohexane	259	12200

[a] Calculated from base molecules of the monomeric chromophore. [b] Reference 14.

aluminum cell block in the cell compartment of a UNICAM SP 500 spectrophotometer. The light from the lamp, collimated by a quartz lens, passed through the filter solution, then through a periscope arrangement into the PPA film in the aluminum block and then to the phototube. The lamp, the monochromator, the quartz lens, and the filter solution were all rigidly mounted on an optical bench. The light intensity from the lamp was monitored by a 1P28 photomultiplier tube, powered by a Lambda Model 25 regulated dc power supply and protected by a neutral density filter. Approximate absolute light intensities were estimated by actinometry using 2-undecanone[12] or potassium ferrioxalate solution.

The formation of para and ortho rearranged products from the photo-Fries reaction of PPA films was followed by the absorbance changes at 265 and 335 nm of the irradiated films relative to a nonirradiated film of similar thickness. These two bands at 265 and 335 nm correspond to absorption due to *p*- and *o*-hydroxyphenone groups on a polymer chain, respectively. Six or more absorbance points were taken at each wavelength at various times of irradiation.

The fluorescence and phosphorescence spectra of PPA were measured on a Perkin-Elmer Model MPF 2A fluorescence spectrophotometer with phosphorescence accessories. The phosphorescence spectrum of a PPA film was measured at approximately −150 °C without degassing. A weak fluorescence spectrum of a solution of PPA in 1,2-dichloroethane was also obtained. The transition temperatures involving the motion of subgroups on a PPA polymer chain were measured by the procedure of Somersall et al.[13] by observing the change in phosphorescence intensity as a function of temperature.

Results and Discussion

Figure 2 shows the change in absorption spectra of a thin PPA film with the time of irradiation. The new absorption band with λ_{max} at 335 nm could be interpreted as due entirely to the presence of *o*-hydroxyphenone groups. The intensification of the absorption band with λ_{max} at 265 nm was similarly assigned as due predominantly to *p*-hydroxyphenone groups on a polymer chain. Examination of individual absorption spectra of monomeric model compounds *o*- and *p*-hydroxyacetophenones showed that these assignments of absorbance peaks might in fact be justified.[14] However, since the exact absorption spectra of *o*- and *p*-hydroxyphenone groups on a polymer chain are unavailable, the quantum yields calculated from differential absorbance measurements, especially involving the para products, can only be considered approximate.

The total amounts of *o*- or *p*-hydroxyphenone groups formed as a result of irradiating PPA films are found from the equation

$$C_{II} = \frac{A_{total} - A_{I}}{\epsilon_{II}} \text{ mol cm}^{-2}$$

where C_{II} is the concentration of either *o*- or *p*-hydroxyphenone groups, ϵ_{II} is the corresponding molar extinction coefficient, A_I is the absorbance of the starting PPA at a certain wavelength, and A_{total} is the total absorbance of the irradiated PPA film at the same wavelength as A_I. Therefore ($A_{total} - A_I$) represents the differential absorbance due to the formation of products. Figure 3 shows a typical plot of the changes of absorbance at 265 and 335 nm with the time of irradiation. The initial slopes were taken and used in the calculation of quantum yields of both the *o*- and *p*-hydroxyphenone groups on the assumption that they have the same extinction coef-

Table II
Irradiation of Poly(phenyl acrylate) (PPA) and Phenyl Acetate (PA)[a]

	Solvent	ϕ_o	ϕ_p	ϕ_p/ϕ_o
PA	Cyclohexane	0.18 ± 0.02	0.20 ± 0.02	1.1
PA	Cyclohexane[b]	0.17 ± 0.02	0.15 ± 0.02	0.9
PA	1,2-Dichloroethane	0.18 ± 0.02	0.22 ± 0.02	1.2
PPA	1,2-Dichloroethane	0.12 ± 0.02	0.23 ± 0.02	1.9
PPA	Solid film (air)	0.10 ± 0.02	0.13 ± 0.02	1.3
PPA	Solid film (N_2)	0.10 ± 0.02	0.14 ± 0.02	1.4

[a] Irradiation at 250 nm in air at 23 °C except where otherwise stated. [b] Reference 14.

Table III
Irradiation of Poly(phenyl acrylate) Films at Different Excitation Wavelengths in Air at 23 °C

Excitation wavelength, nm	Light intensities, I_0^i, quanta s^{-1} cm^{-2}	ϕ_o	ϕ_p	ϕ_p/ϕ_o
300	3.3×10^{15}	0.00	0.00	
260	9.9×10^{13}	0.09 ± 0.02	0.13 ± 0.02	1.4
250	1.3×10^{15}	0.10 ± 0.02	0.13 ± 0.02	1.3
240	8.3×10^{14}	0.08 ± 0.02	0.11 ± 0.02	1.3
232	2.1×10^{14}	0.09 ± 0.02	0.12 ± 0.02	1.3

ficients as the corresponding monomeric model compounds, the *o*- and *p*-hydroxyacetophenones, in solution. This assumption was encouraged by the observation that the λ_{max} and ϵ_{max} values of phenyl acetate are close to those of poly(phenyl acrylate). Table I shows the λ_{max} and ϵ_{max} of PPA, phenyl acetate, and *o*- and *p*-hydroxyacetophenones. ϵ_{355} for *o*-hydroxyphenone groups was taken as 3740 L mol^{-1} cm^{-1} and ϵ_{265} for *p*-hydroxyphenone groups was taken as 9000 L mol^{-1} cm^{-1}.[14]

Infrared spectra of irradiated PPA films showed an increase in OH absorption in the region 3200 to 3400 cm^{-1} and the appearance of a well-defined peak at 1640 cm^{-1}. When unfiltered light from the A.E.I. mercury lamp was used for irradiation, photoyellowing of the PPA film occurred rapidly. The yellow portion of the irradiated film was no longer soluble in benzene or other solvents, indicating the formation of a cross-linked polymer. This is not surprising since both ortho and para products absorb more strongly than PPA and further photochemical reactions might be expected on prolonged irradiation with high light intensity from an unfiltered lamp.

Irradiation of PPA under Various Conditions. Table II shows the quantum yields for the formation of ortho and para products, ϕ_o and ϕ_p, respectively, for phenyl acetate (PA) and PPA under various conditions of irradiation. Literature values of ϕ_o and ϕ_p for PA in cyclohexane are also included for comparison. The quantum yields in our study, determined from the UV absorbance change in cyclohexane, are in good agreement with the data of Shizuka et al.[14]

The quantum yields of ortho product from poly(phenyl acrylate) are only slightly lower in the solid phase than in solution, indicating that the formation of the ortho product is not appreciably affected by chain mobility at 23 °C. Complications due to the formation of phenol when the photo-Fries reaction is carried out in solution may account for the differences in quantum yields of para product observed.[15] However, it does seem that the formation of both phenol and the para product requires more group mobility than that of the ortho product. Neither ϕ_o nor ϕ_p for the photo-Fries reaction of PPA films was affected by oxygen, which is consistent with a "cage" radical mechanism.

Effect of the Wavelength of Excitation. Table III shows the values of ϕ_o and ϕ_p and their relative ratios ϕ_p/ϕ_o for the irradiation of PPA films at five different wavelengths of excitation. Light intensities were determined by potassium ferrioxalate actinometry and the use of a Hewlett-Packard Model 8334A radiant flux meter. The wavelengths of excitation were chosen so that both the first and second benzenoid bands of the PPA absorption were irradiated. Despite the large changes in light intensity at different wavelengths of excitation, the values of ϕ_o and ϕ_p were the same within experimental error. Excitation into the second benzenoid band produced essentially the same results in ϕ_o and ϕ_p as excitation into the first band. The invariance of the quantum yields with wavelength is consistent with the suggestion that the photo-Fries reaction proceeds from a single excited state and that internal conversion from the second benzenoid state to the first state is both rapid and efficient. Our results also militate against the possibility that a less intense, underlying n,π* state had been excited directly. Were that the case, one would normally expect a more dramatic change in the quantum yields and product distribution upon irradiating the PPA with a wide range of excitation wavelengths. The insensitivity of

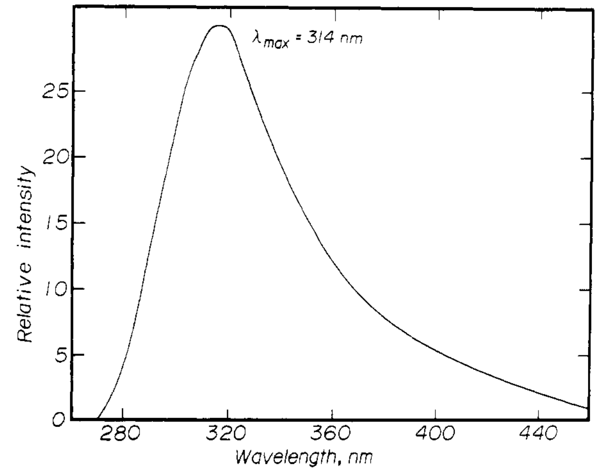


Figure 4. Fluorescence spectrum (uncorrected) of PPA in 1,2-dichloroethane at room temperature; excitation at 270 nm, emission band pass 10 mμ.

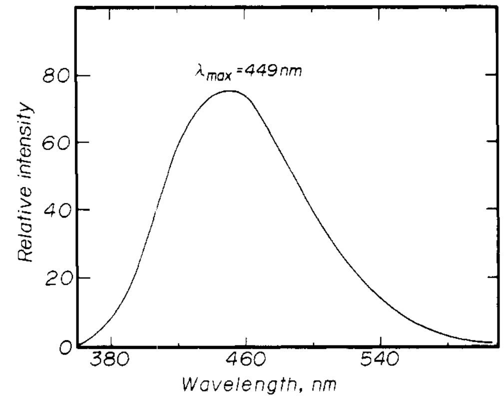


Figure 5. Phosphorescence spectrum (uncorrected) of PPA at −150 °C; excitation at 270 nm and emission band pass 6 mμ.

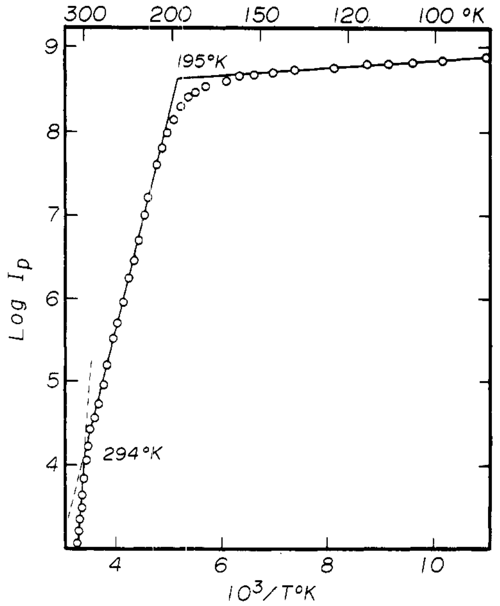


Figure 6. Arrhenius plot of PPA phosphorescence.

ϕ_o and ϕ_p in the photo-Fries reaction of PPA films to the wavelength of excitation is consistent with a similar study of phenyl acetate in solution.[16]

Recently, a reaction mechanism of the photo-Fries reaction involving both a concerted and dissociative pathway was proposed.[3b,17,18] According to this dual pathway, the excited phenyl ester chromophore in one of its excited states cleaves at the phenoxy ester bond to give a pair of radicals, which recombine subsequently to form photo-Fries products and phenol. Concomitantly the molecule in another of its excited states rearranges concertedly to the photo-Fries products via the formation of a radical pair. Humphrey et al.[17,18] proposed that the ortho Fries product formation involves a concerted cyclization of the aryloxyl $^1\pi^*$ state, whereas a "conformation dependent radiation process populates a π^* carbonyl state leading to the dissociation of the phenolate ester bond". Our wavelength studies are not inconsistent with such a mechanism.

Nature of the Excited State. The absorption spectrum of the PPA film is similar to that of many phenyl esters and carbonates.[14,18,19] The lowest excited singlet is a π,π^* state localized on the phenoxy system. The carbonyl n,π^* state is generally believed to be in the 210-nm region and therefore would be completely obscured by the much more intense benzenoid absorptions.[20] In the present experiments, the population of the carbonyl n,π^* state by direct excitation seems likely to be unimportant.[17]

Figure 4 shows the fluorescence spectra of undegassed PPA in 1,2-dichloroethane at room temperature. No phosphorescence could be observed at room temperature. But when the temperature was lowered, the PPA film phosphoresced strongly, showing a structureless broad band with λ_{max} at 448 nm (Figure 5). No further attempts were made to identify the nature of the emissive state in either fluorescence or phosphorescence. The phosphorescence intensity decayed over approximately three orders of magnitude from 77 to 300 K. Somersall et al. found that Arrhenius plots of phosphorescence intensities of several families of ketone copolymers showed discontinuities at the temperatures corresponding to the onset of characteristic subgroup motions in the polymer.[13] The PPA polymer film showed typical behavior (Figure 6) indicating transitions at 195 and 294 K. We attribute the former to the onset of rotational motion of the phenyl ring and the latter to the movement of the entire ester group. Apparent activation energies obtained from the slopes of the Arrhenius plots were 5.3 and 17.8 kcal mol^{-1}, respectively.

Table IV
Effect of Temperature on the Photo-Fries Reaction of Poly(phenyl acrylate) in the Solid Phase[a]

Temp, °K	Initial rate of absorbance change: A at 265 nm × 10^3, min^{-1}	Initial rate of absorbance change: A at 335 nm × 10^3, min^{-1}	A_{265}/A_{335}
380	4.60	1.95	2.4
368	4.81	1.92	2.5
353	5.75	2.37	2.4
338	4.95	1.93	2.6
326	4.74	1.97	2.4
309	4.42	2.03	2.2
298	4.42	1.98	2.2
290	4.01	1.71	2.3
269	3.83	1.47	2.6
249	2.33	1.35	1.7
220	1.20	0.94	1.3
180	0.58	0.54	1.1

[a] Irradiation at 250 nm in air.

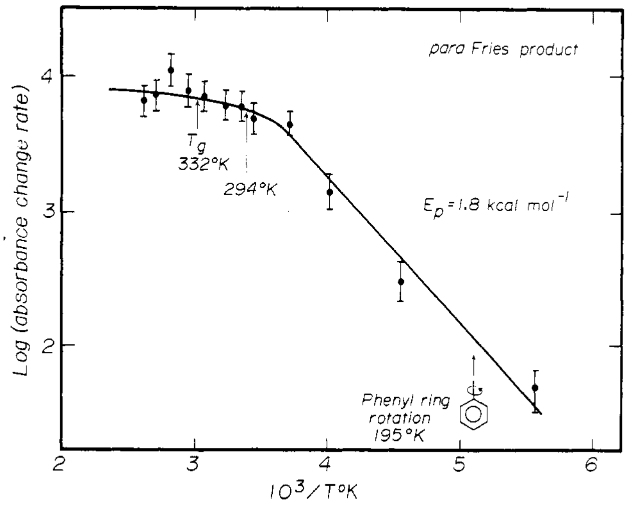


Figure 7. Arrhenius plot of the formation of p-hydroxyphenone groups as measured by absorbance changes at 265 nm. The transition temperatures of the polymer are also included.

Molecular Motion and the Photo-Fries Reaction. Table IV shows the initial absorbance changes at 265 nm (due to para product) and 335 nm (due to ortho product) and their relative

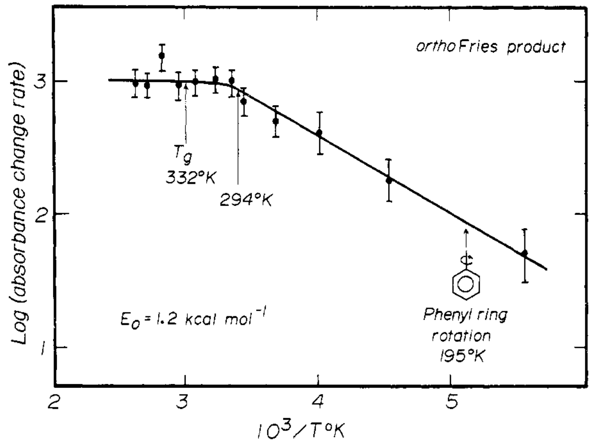


Figure 8. Arrhenius plot of the formation of *o*-hydroxyphenone groups as measured by absorbance changes at 335 nm. The transition temperatures of the polymer are also shown.

ratios for several PPA films in the temperature range −100 to 120 °C. Arrhenius plots for the formation of ortho and para products are included in Figures 7 and 8. Both curves show a level portion at the higher temperatures and a gradual change at low temperatures. The absorbance ratio A_{265}/A_{335} shows a decrease at lower temperatures. The absorbance at 265 nm at room temperature was almost seven times that at 180 K, whereas the absorbance ratio at 335 nm at these two temperatures was only about three times. This difference indicates that the formation of phenol and para products was much more sensitive to temperature than the ortho product. We rationalize this observation on the grounds that the para position of the phenyl ring is separated from the carbonyl carbon by a longer path than the ortho position. The rearranging COR group would therefore have less probability of reaching the more distant para position at lower temperatures when the molecular environment becomes very rigid.

At temperatures slightly above and below T_g (59 °C), no appreciable difference in both ortho and para product yields was detected. Considering that the glass transition involves the onset of large-scale segmental motion of the polymer chain, one would suspect that the intermediate involved in the photo-Fries reaction would not require long-range interaction of the excited chromophore with atoms further down the polymer backbone. If the reaction mechanism of the photo-Fries rearrangement does indeed involve dual pathways, one would not expect abrupt changes in the reaction rate above and below T_g. For the dissociative pathway, the effect of temperature would be limited to its influence on processes subsequent to the cleavage of the C–O bond, such as reorientation and recombination of the pair of radicals. The overall photo-Fries reaction therefore should vary continuously with temperature rather than showing a discontinuity at the glass transition. For the concerted pathway, although a four-membered cyclic transition state is required, it appears that such a configuration can be formed within the "local environment" of the excited chromophore. The vibrational motions of the polymer chain and side groups even at temperatures below T_g are sufficient for the necessary formation of the cyclic structure. The constancy of both ortho and para product yields above and below T_g of the PPA polymer and their insensitivity to oxygen quenching allows us to conclude that the photo-Fries reaction in PPA solid polymer is little affected by bulk diffusion in the polymer matrix.

There is also little correlation between the rate of photorearrangement and the two detected subgroup transitions. The rate of formation of both ortho and para products did not pass through any abrupt changes around these two temperatures, although it is possibly significant that the yields become temperature independent above the transition associated with motion of the phenyl ester group. Rotation of the phenyl ring would not be expected to cause significant changes in the reaction via the dissociative pathway. On the other hand, the lifetime of the four-membered intermediate might be so short that the reaction to the subsequent product was unaffected by ring rotation.

Activation energies below 294 K associated with the formation of ortho and para products, E_o and E_p estimated from the slope of their Arrhenius curves, are equal to 1.2 and 1.8 kcal mol^{-1}, respectively. The higher value for E_p than for E_o is consistent with the rationalization that rearrangement to the para position involves a greater distance. Both E_o and E_p are significantly lower than the activation energy required for the rotation of the phenyl ring (9 kcal mol^{-1}).[21] This may imply that the excited phenyl ester rearranges to its initial product much faster than the rotation of the phenyl ring. The apparent activation energy for diffusion in solution is usually about 2 to 3 kcal mol^{-1}. The present results indicate that the formation of both *o*- and *p*-hydroxyphenone groups in solid PPA requires similar activation energies as for cage processes in simple radical recombinations.

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