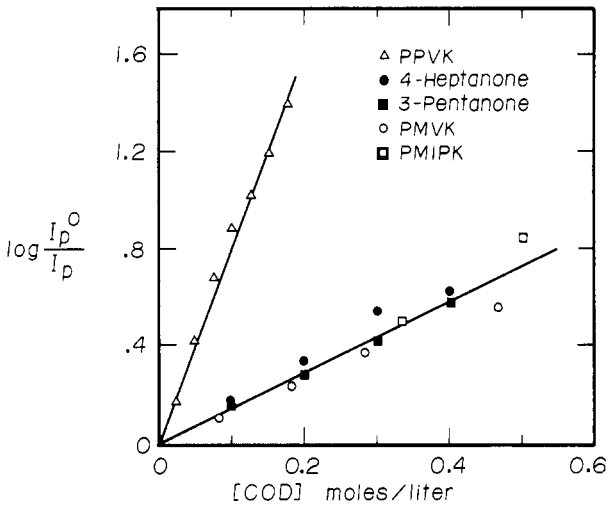

Figure 3. Phosphorescence quenching with COD in H_4furan–ether at 77°K.

energy transfer. Plots of log I_p^0/I_p *vs.* [COD] for the polyketones and for small ketones are shown in Figure 3. The size of the quenching spheres are similar for PMVK, PMIPK, and for the small ketones, whereas for PPVK the critical sphere has a radius R_0 = 19 Å. If the energy transfer in the polymer is random,[16] some intermolecular migration may take place where the local chromophore concentration is high, as in the films. The smaller value of R_0 in solid solution could imply that this intermolecular contribution is not shown in solid solution at low chromophore concentrations. Alternatively, migration of the triplet excitons may be dependent on the nature of the frozen matrix. In any case, energy migration does take place in the aromatic ketone polymers where it does not in the aliphatic polymers.

George[17] has recently considered models for triplet quenching when exciton diffusion takes place and has outlined two extreme cases in polymers. Energy trapping may be limited either by the final M → Q transfer step (M is the unit chromophore), or on the other extreme, by the rate of migration M → M. We have observed that in the case of phosphorescence quenching of naphthalene polymers[16,18,19] the Stern–Volmer diffusion model describes the results, whereas in the case of the ketone polymers, the static Perrin model is more appropriate. In both cases the results demonstrate that intramolecular triplet migration takes place. However, it would seem that in the case of the aromatic π,π^* triplet states, the trapping is tending to the limit controlled by M–M migration, whereas in the case of the n,π^* ketone triplet states, the migration is faster than the final transfer step. A theoretical approach to this question seems justified.

Acknowledgments. The authors acknowledge the financial support of the National Research Council of Canada.

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Photochemistry of Ketone Polymers. X. Chain Scission Reactions in the Solid State

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ABSTRACT: The quantum yield of chain scission was determined in the solid state for a number of polymers containing pendant ketone groups. Copolymers of methyl methacrylate with methyl vinyl ketone (PMMA–MVK) and styrene with phenyl vinyl ketone (PS–PVK) showed higher quantum yields with increasing temperature in the glassy state. Above the glass transition temperature (T_g) the quantum yield for chain scission increased rapidly to the same value as that obtained for the same polymer in solution. A homopolymer of phenyl vinyl ketone (PPVK) showed the opposite effect below T_g, but above T_g a constant quantum yield equal to the solution value was obtained. The variation in quantum yields is interpreted in terms of polymer chain mobility.

The degradation of polymeric materials on outdoor exposure can often be attributed to photochemical reactions arising from absorption of ultraviolet radiation by ketone groups present on the polymeric backbone. In polyethylene, for example, the ketone groups are known to be formed by air oxidation on extrusion and moulding.

It has been shown[1-4] that ketones in polymeric material undergo some of the same photochemical reactions as their low molecular weight analogs. The most important of these are the Norrish type I and type II reactions. In polymers where the carbonyl carbon is on the backbone, both of these reactions will lead to lowering of the molecular weight.

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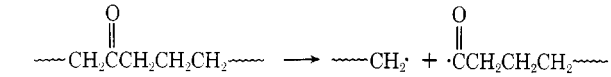

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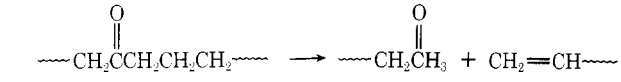

When the ketone group is on a side chain, the type I reaction will not cause scissioning of the main chain and only

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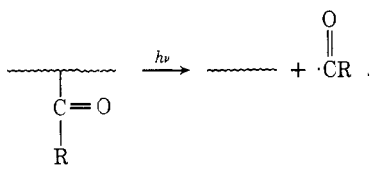
those polymers that have the carbonyl group directly bound to the backbone will degrade by the type II mechanism

Type I



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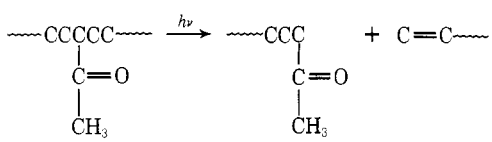

Chemical reaction is only one mode of dissipating the absorbed excitation energy. It has been shown that the lowest lying singlet and triplet states are n–π^* states in dialkyl and phenyl alkyl ketones. Thus excitation with ultraviolet radiation with 313 nm (ABS) leads to the promotion of a nonbonding electron to the anti-bonding π^* singlet state. Because of rapid vibrational relaxation (VR) to the lowest vibrational level, even at low temperatures all subsequent processes take place from the ground vibrational level of the excited n–π^* singlet. Intersystem crossing (ISC) (a quantum mechanically forbidden transition) to the lower lying triplet state can take place due to spin-orbit couplings which effectively mixes the singlet and triplet states. Here again vibrational relaxation is very rapid. Fluorescence (F) and phosphorescence (P) are the two radiative processes from the singlet and triplet states, respectively, which dissipate the electronic excitation energy by remitting radiation. In addition to this, radiationless deactivation (RD) can take place, from both the singlet and triplet state, a process by which the excitation energy is converted into vibrational energy of the ground-state molecule. All the above processes compete with each other and their relative effectiveness in deactivating the excited molecule depends on the relative rate constants of the processes originating from the same state. A measure of this efficiency is given by the quantum yield, ϕ_i, which is the fraction of the total energy absorbed that is dissipated by process i.

$$\phi_i = \frac{\text{number of events of process } i}{\text{total number of quanta absorbed}} = \frac{k_i}{\sum_n k_n}$$

where k_n are the processes competing with process i. In ketones at room temperature and above, RD and chemical reactions account for most of the deactivation because the radiative processes are spin and/or symmetry forbidden. In fact, in a forthcoming communication[5] we show that emission becomes important only at low temperatures where molecular motion is greatly reduced. In our present work, emission accounts for less than 1% of the deactivation, and therefore will not be considered further.

It is well known that in low molecular weight ketones, the Norrish type II quantum yield in solution shows very little temperature dependence,[6] and a similar effect was shown by Hartley and Guillet[7] for poly(ethylene–carbon monoxide) in the solid phase at temperatures above about −30°. Below −30° the quantum yield decreases due to the restricted mobility of the polymer chain which decreases the probability of formation of the six-member transition state usually required for this intramolecular rearrangement reaction. The purpose of this investigation was to study further the temperature dependence of the type II reaction in polymers in the solid phase. The polymers investigated were copolymers of styrene with phenyl vinyl ketone (PS–PVK), a copolymer of methyl methacrylate with methyl vinyl ketone (PMMA–MVK) and a homopolymer of phenyl vinyl ketone (PPVK).

Experimental Section

Phenyl Vinyl Ketone. 3-Chloropropiophenone (40 g) was dissolved in 100 ml of absolute ethanol. The solution was heated and 24 g of potassium acetate was added slowly with vigorous stirring. The solution was filtered, 100 ml of chloroform was added, and the alcohol was then removed by washing with water in a separatory funnel. The chloroform was removed on a rotary evaporator and the phenyl vinyl ketone was distilled under vacuum. Care was taken to keep ketone in the dark as it was found to be very sensitive to even ordinary light.

Methyl Vinyl Ketone. 3-Buten-2-one was obtained from Aldrich Chemical Co. The ketone was dried over anhydrous calcium chloride overnight, filtered, and distilled under atmospheric pressure.

Methyl Methacrylate and Styrene. These monomers were extracted with aqueous sodium bicarbonate to remove the inhibitor and distilled under vacuum.

Polymerization. PS–PVK and PPVK were polymerized in the bulk at 60° under nitrogen atmosphere, for 24 hr, using benzoyl peroxide as initiator. PMMA–MVK was prepared by heating a solution containing 20 ml of benzene and 0.01 g of benzoyl peroxide under a nitrogen atmosphere at 60° for 24 hr. All the polymers were reprecipitated three times from benzene solution into cooled methanol and then freeze-dried. Number-average molecular weights ($\bar{M}_n$) were determined by osmometry on a Hewlett-Packard Model 502 high-speed membrane osmometer using degassed butyl acetate as solvent.

The molecular weight of PS–PVK was also determined by gel permeation chromatography using a Waters Associates Ana-Prep chromatograph. The machine was calibrated by use of narrow distribution PS samples from Pressure Chemical Co. It was assumed that this calibration curve was also applicable to the PS–PVK samples since the low ketone content was not expected to change the hydrodynamic properties of the polymer. The fact that close agreement was obtained with the osmometric determination confirmed the validity of this assumption (see Table I).

Table I
Molecular Weights and Glass Transition Temperatures of Copolymers of PS–PVK, PPVK, and PMMA–MVK

No.	Polymer	$\bar{M}_n$ (osm)	$\bar{M}_n$ (GPC)	T_g (°C)
B-65	PS–PVK	142,000	144,000	104
B-37	PPVK	75,000		82
A-165	PMMA–MVK	90,800		102

The glass transition temperatures (T_g) were determined by differential calorimetry using a Perkin-Elmer DSC 1 differential scanning calorimeter. A summary of the molecular weights and glass transition temperature obtained is given in Table I.

Preparation of Polymer Films. Approximately 0.5 g of the polymer was dissolved in 15 ml of spectroscopically pure benzene. The solution was poured onto water in a 4-in. diameter Petri dish. In 24 hr the solvent evaporated, leaving a clear film of approximately 0.5 mm thickness. These films were air-dried for 2 days and then dried at 70° for 1 hr, and finally purified under high vacuum ($<10^{-5}$ Torr) for 2 weeks. This procedure was found to remove even small amounts of the solvent. The films were cut to proper size for irradiation (1 × 4 cm).

Photolysis and Analysis. The polymer films were weighed and placed between two quartz plates. The description of the photolysis apparatus is given elsewhere.[8] Calibration of the photomultiplier for response to radiation intensity was done by ferrioxalate actinometry[9] in a 1-mm path-length quartz cell. After noting the

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Table II
Constants of Viscosity–Molecular Weight Relationships for PPVK and PMMA

		$K \times 10^5$	T(°C)	Solvent	Ref
PPVK	0.84	2.82	20	Benzene	Lukac *et al.* (1969)[10]
PMMA	0.76	6.27	30	Benzene	Fox *et al.* (1962)[11]

intensity of incident radiation, the films were placed in the temperature-controlled aluminum cell holder and allowed to come to thermal equilibrium. After 15 min the film was exposed to the ultraviolet radiation of 313-mμ wavelength for a time found to give an average of approximately 0.2 chain break/molecule. The intensity of the light transmitted by the film was noted and after irradiation the ultraviolet spectra of the films were measured. The amount of light actually absorbed was calculated using the incident intensity, the transmitted intensity, and corrected for reflection and scattering losses. The degradation was determined by two methods. The irradiated PS-PVK was dissolved in butyl acetate and injected on the gel permeation chromatograph. The molecular weight was determined from the calibration curve by the use of a computer program. For PMMA-MVK and PPVK the irradiated samples were weighed and then dissolved in exactly 7 ml of benzene in a dark stoppered bottle. The solution was stirred for 2 hr to dissolve the entire polymer film. The solution (5 ml) was then pipetted into a Desreux dilution viscometer immersed in a constant-temperature water bath at 30 ± 0.05°. Some red recorder ink was added to the water in the viscometer bath to screen the polymer solution from the radiation emitted by the fluorescent lights in the laboratory. The intrinsic viscosities of the polymers were determined by extrapolating ln η_{rel}/C and η_{spec}/C to zero concentration using five experimentally determined values for each.

It can easily be shown that the total number of main chain bonds broken, N, during degradation is given by

$$N = \frac{(\bar{M}_{n_0}/\bar{M}_n - 1)m}{\bar{M}_{n_0}} \quad (1)$$

where $\bar{M}_{n0}$ and $\bar{M}_n$ are the number-average molecular weights of the polymers before and after irradiation, respectively, and m is the mass of polymer irradiated. Substitution of

$$[\eta] = k\bar{M}_n\alpha \quad (2)$$

yields

$$N = \frac{\left[\left(\frac{[\eta]_0}{[\eta]}\right)^{1/\alpha} - 1\right]m}{\bar{M}_{n_0}} \quad (3)$$

where $[\eta]_0$ and $[\eta]$ are the intrinsic viscosities of the unirradiated and irradiated polymers, respectively. Therefore the quantum yield for chain scissioning (type II reaction) is given by

$$\Phi_{cs} = \frac{\left[\left(\frac{[\eta_0]}{[\eta]}\right)^{1/\alpha} - 1\right]m}{\bar{M}_{n_0} I} \quad (4)$$

where I is the radiation dose in einsteins.

The substitution of $[\eta]^{1/\alpha}$ for $\bar{M}_n$ in the above equation introduces an error if (a) the distribution and molecular weight is different from that of the samples used for determining the molecular weight–viscosity relationship and (b) the distribution of the sample changes on irradiation. However, it was shown by Amerik and Guillet[4] that for small changes in viscosity

$$\left(\frac{[\eta]_0}{[\eta]}\right)^{1/\alpha} \approx \frac{\bar{M}_{n_0}}{\bar{M}_n} \quad (5)$$

In fact we use the osmometrically determined number-average molecular weight in the denominator of eq 4 as this term is not a ratio of viscosities and no cancellation of error takes place. We have used the expression derived above with values of α given in Table II and obtained from the literature.[10,11]

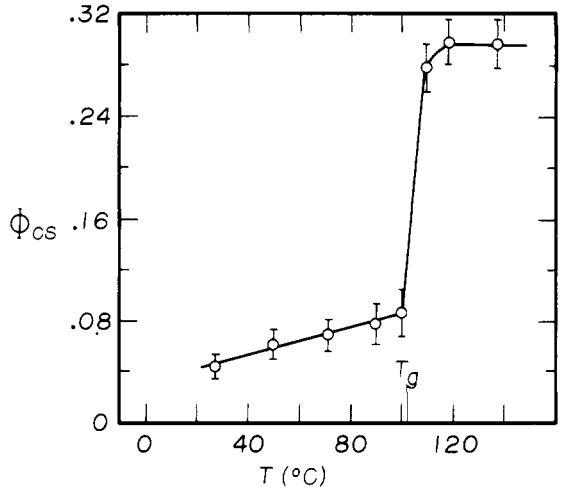

Figure 1. Quantum yield of Norrish type II reaction as a function of temperature for 0.5-mm PS-PVK films irradiated with monochromatic radiation of 313-mμ wavelength as measured by GPC. Error bars represent errors (±20%) in reproducibility of results.

Results and Discussion

Photolysis of PS-PVK Films. Quantum yields for chain scission were measured for PS-PVK by determination of the number-average molecular weight by GPC.

Inokuti[12] derived the theoretical equation for the changes in various molecular weight averages with random cross-linking and scissioning. We have used these equations together with initial molecular weight distribution of PS-MVK to search, by a computer program for the scission to cross-linking ratio which would make the theoretically calculated molecular weights of the photolyzed sample agree with experimentally determined (GPC) values. The ratio obtained was 25:1 in favor of scissioning, therefore it was concluded that cross-linking was not important in the present investigation.

In control experiments unexposed films showed no change in viscosity or position in the GPC curve when stored for several weeks in the dark.

The quantum yields of chain scissioning obtained for this polymer at a series of temperatures are given in Figure 1 and Table III. The glass transition temperature of the polymer (determined by DSC) is also shown. In the determination of the molecular weight by GPC it was found that the assignment of the baseline to the GPC curve introduced an error of ±20% in the reproducibility of ϕ_{cs}, the quantum yield of chain scission shown by error bars in Figure 1. However, even with this uncertainty in the actual values of the quantum yields, a trend can be clearly seen. The quantum yield of chain scission of this polymer increases with increasing temperature in the glassy state. Above the glass transition temperature (102°), the quantum yield (0.30 ± 0.01) is the same as that obtained by Pitts *et al.*[13] for phenyl ketones (0.29) in solution at room temperature, implying that ϕ_{cs} in the glassy state depends on the mobility of the polymer

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Table III
Quantum Yield of Chain Scission as a Function of Temperature for PS-PVK Films

Expt No.	T (°C)	ϕ_{cs}	Av
A-93-27A	27.0	0.043	
A-93-27B		0.038	
A-93-27C		0.060	
A-97-27		0.032	
B-93-27A		0.049	0.044 ± 0.008
A-93-50	50.0	0.063	
B-93-50		0.060	0.062 ± 0.002
A-93-71	71.0	0.069	0.069
A-99-90	90.0	0.081	
A-93-90		0.075	
B-93-90		0.079	0.078 ± 0.003
A-99-100	100.0	0.068	
B-93-100		0.124	
B-93-100B		0.069	0.087 ± 0.024
A-101-110A	104.4	0.293	
A-101-110B		0.263	0.278 ± 0.015
A-101-120	118.5	0.297	0.297
A-101-130	137.5	0.295	0.295

Table IV
Quantum Yield for Chain Scission as a Function of Temperature for PMMA-MVK Films

Expt No.	T (°C)	ϕ_{cs}
A-166	26.5	0.019
A-167	40.7	0.030
A-168	61.1	0.047
A-170	70.2	0.055
A-174		0.056
A-169	80.9	0.126
A-175	98.7	0.188
A-172		0.189
A-173	110.5	0.212
A-171	120.9	0.212

chains. Since the ketone groups are directly pendant from the polymeric chains, only the type II reaction can give rise to chain scissioning, and one may equate the chain scissioning quantum yield to the type II quantum yield. It is well known[14] that the type II reaction usually involves a six-membered transition state. It seems likely that below the glass transition temperature the rate at which the polymer molecule attains this six-membered transition state controls the quantum yield. At higher temperatures, the probability of a hydrogen being in the correct conformation within the lifetime of the excited state increases due to the increased mobility of the polymer chain. Above the glass transition region, the mobility of the chain in the solid polymer with respect to the ability to achieve this particular conformation appears to be approximately the same as that in solution.

Poly(methyl methacrylate-methyl vinyl ketone) Copolymer (PMMA-MVK). Films of PMMA-MVK of approximately 0.5 mm thickness were irradiated at a series of temperatures. The changes in molecular weight were followed by viscosity measurements. For calculation of the chain scission quantum yield, eq 4 was used. The results are plotted in Figure 2 and Table IV. The quantum yield of chain scission again shows a temperature dependence in the glassy state with a discontinuity near T_g (102°). Above the glass transition temperature the quantum yield (0.21 ± 0.1) agrees with that obtained in solution by Amerik and Guillet (0.18 – 0.23). The β transition of PMMA occurs at about (−19°) and probably corresponds to the motion of the carbomethoxy group. The exact nature of this relaxation is not known, and in particular it is not clear to what extent the main chain motion is involved,[15] but it is clear that the temperature dependence of chain scission quantum yield in the glassy state is again due to changing molecular mobility. As stated before, the Norrish type II reaction usually involves the abstraction of a γ hydrogen *via* a six-membered transition state. The PMMA-MVK copolymer contains only 7.4 mol % ketone and therefore each ketone group is most likely to be surrounded by two MMA units which implies that no γ hydrogen is available adjacent to carbonyl groups.

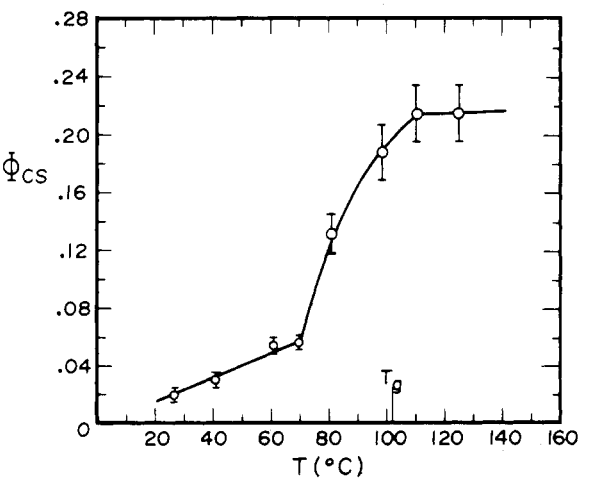

Figure 2. Quantum yield of Norrish type II reaction as a function of temperature for 0.5-mm MMA-MVK films irradiated with monochromatic radiation of 313-mμ wavelength as measured by viscometry. Error bars represent a 10% uncertainty in the accuracy of values due to errors introduced by the calibration of the light source.

The formation of a six-membered cyclic intermediate is favored over other cyclic conformations by entropy considerations. In solid polymers where certain conformations are more favored than others, entropy considerations might be less important. Amerik and Guillet[4] have shown effective main chain scissioning in PMMA-MVK, and postulated a seven-membered transition state.

Golemba and Guillet[3] have shown that the type II quantum yields for methyl alkyl ketones were approximately 0.2 regardless of the alkyl chain length. However, symmetrical alkyl ketones showed a decrease in the type II efficiency with increasing chain length, and extrapolation to long-chain lengths gave values which agreed with the experimentally observed quantum yield for poly(ethylene-carbon monoxide) (ϕ_{cs} = 0.02). The values of ϕ_{cs} for copolymers of methyl and phenyl ketones at temperatures above T_g are those obtained for the low molecular weight model ketones in solution at ambient temperatures.

Poly(phenyl vinyl ketone) (PPVK). Films of approximately 0.5 mm thickness were irradiated at several temperatures. The quantum yields of chain scissioning determined by viscometry are shown in Figure 3.

All the ketone-containing polymers discussed to this point, PE-CO, PS-PVK, and PMMA-MVK, have shown an increase in the quantum yield of chain scission with increasing temperature in the glassy state. However, as seen in Figure 3, in PPVK a slight negative temperature dependence was observed. It is possible that this difference

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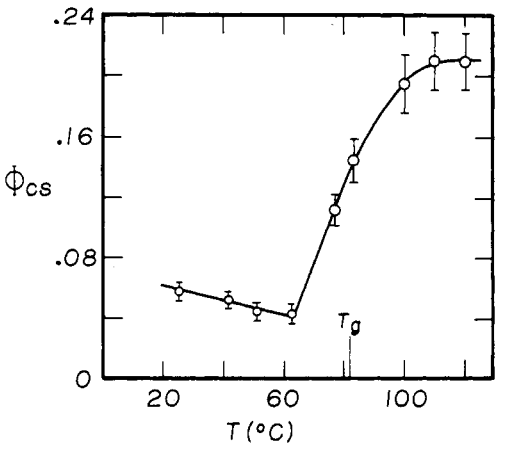

Figure 3. Quantum yield of Norrish type II reaction as a function of temperature for 0.5-mm PPVK films irradiated with monochromatic radiation of 313-mμ wavelength as measured by viscometry. Error bars represent a 10% uncertainty in the accuracy of values due to errors introduced by the calibration of the light source.

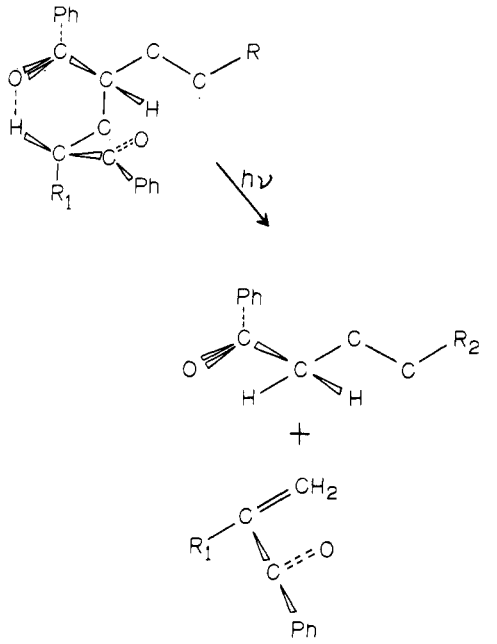

Figure 4. Proposed mechanism for the Norrish type II reaction for PPVK.

is due to special steric interactions in the polymer. For minimum steric interaction the bulkiest groups in the polymer, the benzoyl groups, will take up positions which will maximize the distance between them. This means that successive benzoyl groups are trans to one another and in such a conformation the hydrogens are ideally aligned for the six-membered transition state (see Figure 4) necessary for the type II reaction. As the temperature is raised, the mobility of polymeric groups might introduce variations from this ideal alignment reducing the type II quantum yield.[16]

There is independent evidence that order exists in solid PPVK as required by the model suggested above. In crystalline benzophenone containing small amounts of naphthalene, phosphorescence originating from the latter was detected at 77°K. Hochstrasser[17] related the intensity of this emission to the triplet-triplet energy transfer be-

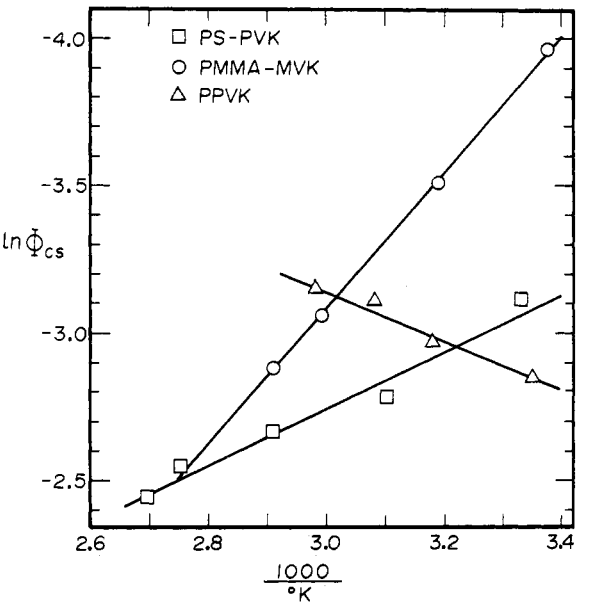

Figure 5. Plot of ln ϕ_{cs} *vs.* 1000/°K for the polymers studied to determine an activation energy for the Norrish type II reaction in solid glassy polymers.

tween molecules of the benzophenone lattice. Hunter *et al.*[18] have prepared benzophenone in a form of a glass in which the molecules are randomly oriented. The energy transfer efficiency in the glass was found to be orders of magnitude less efficient, and this was explained in terms of nonidentical electronic energies in the glass. Therefore, the effect of destroying the three-dimensional structure in the crystal was that within the lifetime of the excited state there was an increased probability that the excitation would remain on the initially excited molecule.

The slope of the logarithmic plot of relative phosphorescence intensity against quencher concentration at 77°K can be related to the average distance between an excited chromophore and a quencher. David *et al.*[19] have obtained interaction distances in PPVK and poly(vinylbenzophenone) which were much larger than could be assigned to the sum of the atomic radii of the excited chromophores and quencher species. This was believed to be due to intramolecular energy transfer in these polymers. In order to have effective intramolecular energy transfer, an interaction between neighboring chromophores is required. Such interaction has been shown to exist in ketone-containing systems even in instances where the carbonyl groups were not conjugated.[20,21]

If such a preferred orientation does exist below T_g, it would be expected to enhance the quantum yield due to favorable geometry for formation of the excited state, but this order might be reduced as the temperature is increased. A similar scheme was recently proposed by Harrah[22] with respect to excimer fluorescence from poly(2-vinylnaphthalene).

The natural logarithm of the quantum yield against inverse absolute temperature was plotted in Figure 5 for the three polymers studied here for temperatures below T_g. The apparent activation energies obtained from the slope

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of these lines are 1.9, 3.0, and −1.6 kcal per mol (±0.1) for PS-PVK, PMMA-MVK, and PPVK, respectively. Although the number of values of the quantum yield are too small for exact determination, the activation energies obtained are reasonable for the barriers to rotation about carbon–carbon bonds.

Conclusions

At room temperature and above, photochemical reactions may compete with very efficient radiationless processes. Below the glass transition temperature in PMMA-MVK, PS-PVK, and PPVK a temperature dependence exists for the Norrish type II reaction which can be attributed to the changes in the segment mobility of the polymeric molecule. In the case of PMMA-MVK and PS-MVK, higher type II quantum yields are obtained at higher temperatures in the glassy region. In the case of PPVK, the type II quantum yield decreases slightly with increasing temperature. The apparent activation energies obtained from the temperature dependences are 2–3 kcal/mol which are of the same order of magnitude as the energy barriers to rotation around C–C bonds.

In the glass transition region the type II quantum yield increases greatly in all the polymers studied due to the great increase in polymer segment mobility which occurs at this temperature. Above the glass transition region, the type II quantum yields in all polymers studied seem to be constant and, within experimental error, equal to the quantum yields obtained in solution for the same polymer and/or analogous low molecular weight model compounds.

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Crystal Structure of Poly(vinyl chloride) Single Crystals

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ABSTRACT: A refinement of the crystal structure of poly(vinyl chloride) is based on quantitative X-ray intensities obtained from oriented mats of single crystals. The orthorhombic crystal unit cell is very compact, with dimensions a = 10.24 Å, b = 5.24 Å, and c = 5.08 Å. The refined structure places the chains related by the screw axis in the center of the unit cell in such a manner that the C-Cl distance is 4.71 Å, compared with a van der Waals distance of 4.1 Å. This appears to preclude a direct C—H- -Cl hydrogen-bond type of interaction in poly(vinyl chloride).

The first crystal structure analysis of syndiotactic poly(vinyl chloride) was made by Natta and Corradini,[1] using samples of low crystallinity. Later, Natta, Bassi, and Corradini[2] prepared oriented fibers from a mixture of highly crystalline, low molecular weight material and poorly crystalline, high molecular weight material. They were able to deduce the structure and compare calculated X-ray intensities with visually estimated experimental intensities. It has since been possible to produce oriented single crystal mats of very high crystallinity.[3] From these we have obtained accurate quantitative X-ray intensities and have therefore felt it worthwhile to refine the structure.

Experimental Section

Low molecular weight poly(vinyl chloride) was made in butyraldehyde according to the method of Burleigh.[4] The material was fractionated by dissolving it in boiling cyclohexanone, cooling the solution, and separating the crystalline precipitate by ultracentrifugation. Dissolving this precipitate in boiling chlorobenzene and slow cooling of the solution produced single crystals, similar to those characterized by Smith and Wilkes[3] by electron microscopy and electron diffraction. Oriented mats of crystals approximately 0.5-mm thick were collected on fritted-glass filters, washed with acetone and vacuum dried for subsequent X-ray analysis.

Both nickel-filtered copper radiation and zirconium-filtered molybdenum radiation were used to obtain diffraction patterns on flat-plate films in a Statton-Warhus vacuum camera, with the beam parallel to the surface of the crystal mat. Quantitative X-ray intensities were measured from the films with a Joyce-Loebl recording microdensitometer. After the microdensitomer scans were corrected for background and amorphous scattering, the resulting peak heights were used as a measure of the relative intensities.

The 010 reflection, very critical to our subsequent Fourier analysis, was not well resolved in most of our X-ray films. In order to resolve the 010 and 200 reflections, the following special experimental conditions were used: 0.38-mm diameter pinholes set 15.0 cm apart; sample to film distance = 17.0 cm; Cu Kα radiation; vacuum.

Results and Discussion

Study of the X-ray patterns showed that the equatorial $hk0$ reflections were considerably sharper than the upper layer line $hk1$ reflections (Figure 1a). A small-angle meridional X-ray long spacing of 61.6 Å (second order = 30.8 Å, Figure 1b), consistent with the crystal thickness measured from electron micrographs,[3] suggests that only about 24 monomer units or 12 repeat units along the chain axis account for the crystal thickness. The sharp equatorial reflections indicate that order is considerable in the lateral directions. The orthorhombic unit cell, whose dimensions we determined to be a = 10.24 Å, b = 5.24 Å, and c = 5.08 Å, is more compact than that observed for less crystalline poly(vinyl chloride).[1,2] The lattice parameters most recently published by Natta[2] and coworkers are a = 10.4 Å, b = 5.3 Å, and c = 5.1 Å with a calculated density of 1.48 g/cm^3. Our calculated density is 1.53 g/cm^3.

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