Macromolecules 1980, *13*, 262-267

Photochemical Processes in Polymeric Systems. 2. Photochemistry of a Polycarbonate of Bisphenol A in Solution and in the Solid Phase[‡]

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Received July 31, 1979

ABSTRACT: Photochemical and photophysical processes occurring on excitation of a polycarbonate of bisphenol A have been investigated using quantum yield measurements on photoFries rearrangement and chain scission processes, laser kinetic flash spectroscopy, and emission quenching measurements. Quenching studies have been carried out with phenyl salicylate, *trans*-1,3-pentadiene, and oxygen. Two major quenching processes have been identified: self-quenching and singlet-singlet energy transfer to phenyl salicylate. Quenching rate data clearly indicate that facile migration of singlet energy occurs in the polymer.

In a previous communication,[1] we reported the quantum yield of the photoFries rearrangement in thin films of a polycarbonate, using a broad band source of optical excitation. The solid state data can be interpreted in terms of a concerted process involving a $_{\pi}2_s + _{\sigma}2_s$ rearrangement.[2] In this paper, we report quantum yields of rearrangement and chain scission in solution and in the solid state as well as rates of quenching by singlet and triplet quenchers. These data, along with transient absorption measurements and emission quenching studies reported herein, clearly indicate that the photorearrangement (and probably the chain scission as well) proceeds from the first ($n\pi^*$) singlet. This singlet undergoes a self-quenching process which accounts for the observed inefficiency of photochemistry in the solid state. Photorearrangement and chain scission, as well as fluorescence, are strongly quenched by the product of the photorearrangement, phenyl salicylate. This quenching process taking place between an excited singlet and a quencher, both bound to polymeric chain segments, indicates singlet energy migration in the polymer. Although triplet energy migration is well documented both along polymer chains and across chains,[3] examples of migration of singlet energy are less common.[4] The well-recognized tendency of singlet excited states to form excimers whose stabilization energy is appreciably higher than that of triplet excimers[5] might prevent facile migration of singlet energy in many polymeric systems. Singlet excimers can thus act as energy traps of appreciable depth while excimeric interactions in the triplet state are weak and arise only from second order (double) configuration interaction processes.[6] Consistent with this general observation, we see little excimeric stabilization in a polycarbonate of bisphenol A when monitoring its fluorescence as a function of concentration in a fluid solution or in the solid state. The objective of this study was to carry out a preliminary investigation of the photophysical and photochemical decay processes taking place in polycarbonate and model outdoor photodegradation of stabilized Lexan films from these rate data. Consideration of the overall mechanistic scheme including precise measurements of the intersystem crossing rate as well as the rates of inter- and intrachain migration of electronic energy will be deferred to later publications. The study of polycarbonate photochemistry in a hydrogen-donating solvent is also contemplated in order to test the caged radical pair theory of the photoFries rearrangement in this system.

Table I
Extinction Coefficients (L mol^{-1} cm^{-1} of the Compounds Used in this Study)

compd	wavelength, nm 355	340	320	253.7
phenyl salicylate		260	4140	6000
2,2′-dihydroxybenzophenone	8500		4100	
polycarbonate of bisphenol A				2.31 mL/(mgcm)

Experimental Section

A polycarbonate of bisphenol A (Lexan) obtained from General Electric was purified through repeated reprecipitations and characterized by UV-visible spectroscopy, IR spectroscopy, and high-pressure liquid chromatography. Quantum yields of phenyl salicylate formation and chain scission were determined at 253.7 and 313 nm, using a merry-go-round photochemical reactor.[7] A low-pressure mercury arc lamp was used as the source of 253.7-nm radiation while a medium-pressure Hg arc lamp (Hanovia, 450 W) equipped with a $K_2CrO_4/NaHCO_3$ solution filter[8] was used for 313-nm irradiations. Solution quantum yields were measured in spectroquality CH_2Cl_2, using solutions which were degassed by a freeze-pump-thaw procedure (three cycles) and then sealed off. Solid state quenching studies were carried out on thin films cast from CH_2Cl_2. The films were optically clear and had thicknesses ranging from 1-2.5 × 10^{-3} cm. Sections of this film were dissolved in CH_2Cl_2 and electronic spectra recorded to determine if the quencher is uniformly distributed through the sample. This was found to be the case, within error (<±5%). Phenyl salicylate formation was followed by monitoring the absorbance at 320 and 340 nm. The extinction coefficients used are given in Table I. Correction was made for the formation of 2,2′-dihydroxybenzophenone by monitoring the change of absorbance at 400 nm. The extent of these corrections indicated that the rate of benzophenone formation was appreciable even when competitive absorption by phenyl salicylate was negligible.

Chain scission was monitored by gel permeation chromatography. Number average molecular weights were calculated from the molecular weight distribution obtained on a high-pressure liquid chromatograph, using standard polystyrene samples to calibrate the molecular weight scale.

Actinometry was performed by following the photorearrangement of *o*-nitrobenzaldehyde.[9] It is known that *o*-nitrobenzaldehyde is converted to *o*-nitrosobenzoic acid with a quantum yield of 0.50 ± 0.03 at wavelengths between 253 and 400 nm. This

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[‡] This paper represents one phase of the research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100, and was supported in part by the low cost solar array project, funded by the Department of Energy.

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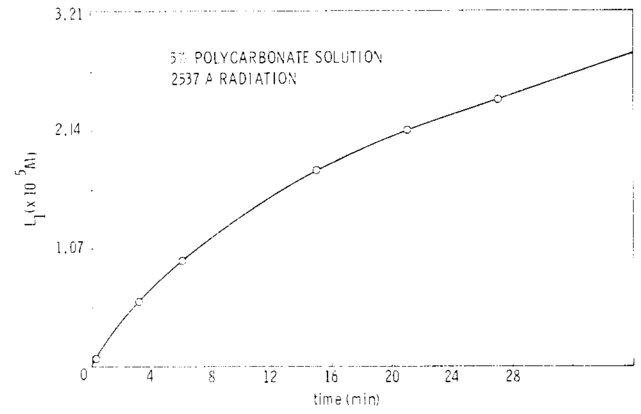

Figure 1. Formation of phenyl salicylate groups with time; degassed CH_2Cl_2 solution, λ_{ex} = 253.7 nm.

actinometer is not affected by the presence of oxygen. The quantum yield of formation of *o*-nitrosobenzoic acid has a negligible temperature coefficient and it can be incorporated in a polymer film.[9,10] Consumption of *o*-nitrobenzaldehyde was followed by monitoring the decrease of the absorption band at 1800 cm^{-1} due to the nitro group.

Nanosecond flash photolysis experiments were carried out in fluid solutions and in the solid state, using a molectron pulsed nitrogen laser with a pulse width of 10 ns as an excitation source. A xenon flashlamp serves as a probe beam. A complete description of this system has appeared elsewhere.[11]

Fluorescence measurements were carried out on a MPF-3A Perkin-Elmer spectrofluorometer. Emission spectra of fluid solutions, degassed and aerated, and of films were recorded at room temperature.

The quenchers used in this study were (1) *trans*-1,3-pentadiene, obtained from chemical samples distilled from $LiAlH_4$ just prior to use; (2) phenyl salicylate, obtained from Aldrich Chemicals and recrystallized twice; and (3) oxygen, obtained by exposing samples to air and by bubbling them with "high purity" oxygen (Matheson) for 5 min.

Results

A. Quantum yields of photoFries rearrangement rates of formation of phenyl salicylate groups were measured at 253.7 and 313 nm in fluid solutions of the polymer at concentrations of 0.1, 1, 3, and 5% w/v. Figure 1 shows a typical plot, obtained for 5% polymer concentration. It was found that the drop off in the rate was far in excess of what would be expected on the basis of competitive absorption by the phenyl salicylate groups. Hence, a simple kinetic treatment was devised to interpret the data:

Scheme I

$$L \xrightarrow{h\nu} L^{1*} \qquad (1)$$

$$L^{1*} \xrightarrow{k_2} L \text{ or } L^{3*} \text{ or } L^1 \qquad (2)$$

$$L^{1*} \xrightarrow{k_3} L_1 \qquad (3)$$

$$L^{1*} + L_1 \xrightarrow{k_q} L + L^{1*} \qquad (4)$$

In this scheme, L is the polycarbonate, L_1 is the phenyl salicylate group which is formed, while L^1 is the product of chain scission.

$$\frac{1}{d/dt}[\phi_{L_1}] = \frac{k_q}{k_3}[L_1] + \frac{k_2 + k_3}{k_3} \qquad (5)$$

and ϕ_{L_1} is the quantum yield of formation of L_1. Figure 2a shows a plot of $[1/(d/dt)][\phi_{L_1}]$ vs. $[L_1]_t$ for a 3% polymer solution. From the slope of this line, we can extract k_q, the bimolecular quenching rate constant, if k_3 can be determined independently. k_3 may be equated to $1/\tau_L{}^{1*} \times \phi_{L_1}{}^0$ when $\tau_L{}^{1*}$ is the lifetime of the excited state of L, and $\phi_{L_1}{}^0$ is the quantum yield of the L_1 formation extrapolated to zero conversion, obtained from the intercept in Figure 2a. Calculations of k_3 and k_q are given below. This kinetic treatment was extended to data on polymer solutions of concentrations ranging from 0.1–5% w/v. Data on the 0.1% solution is less precise, since competitive absorption by phenyl salicylate groups is appreciable at the higher level conversions used in this study. The plots tended to have a linear and a nonlinear portion, as shown in Figure 2b for the 5% solution where it is most pronounced. Slopes of the initial linear part varied somewhat with concentration, from 0.9 × 10^5 L mol^{-1} for the 0.1% solution to 1.35 × 10^5 L mol^{-1} for the 5% solution. Table II gives the initial quantum yields of phenyl salicylate group formation, obtained from the intercepts.

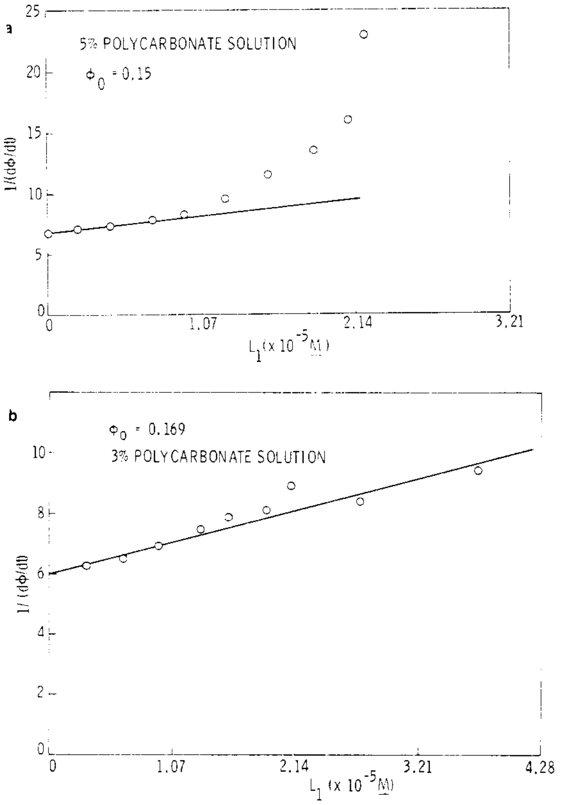

Figure 2. Plot of $[1/(d\phi/dt)]$ vs. $[L_1]$ when L_1 is phenyl salicylate.

Table II
Initial Quantum Yields of Phenyl Salicylate Group Formation

polym concn, % w/v	degassed 253.7 nm	degassed 313 nm	degassed + 0.2 M *trans*-1,3-pentadiene (313 nm)
0.1	0.200 ± 0.004		
1	0.177 ± 0.004	0.18 ± 0.01	0.18 ± 0.01
3	0.167 ± 0.003	0.16 ± 0.01	0.16 ± 0.01
5	0.150 ± 0.003		

A Stern–Volmer plot can be constructed out of these data by postulating a self-quenching process:

$$L^{1*} + L \xrightarrow{k_{sq}} L + L \qquad (6)$$

The slope of the Stern–Volmer plot, k_{sv}, is 1.0 ± 0.05 L mol^{-1}.[12] k_{sq} can be calculated from k_{sv}, if the lifetime of the excited state is known. This has been measured and is reported in Table III.

Quenching studies were carried out by adding controlled concentrations of phenyl salicylate to the solution of polycarbonate in CH_2Cl_2 and measuring initial quantum yield

Table III
Quenching Rate Constants and the Rate of Formation of Phenyl Salicylate Groups

type of measurement	k_q, × 10^{-11} L mol^{-1} s^{-1}	k_{sq}[a], × 10^{-7} L mol^{-1} s^{-1}	k_3, × 10^{-6} s^{-1}
lifetime measurement		1.1 ± 0.2	1.5 ± 0.1
ϕ_{L_1} measurements	1.5-2[b]	1.0 ± 0.2	
phenyl salicylate quenching studies	1.1 ± 0.2		
emission quenching	1.2 ± 0.2		

[a] Calculated assuming 1% w/v polymer ≡ 0.0394 mol L^{-1}. [b] Quenching rate varied somewhat with concentration.

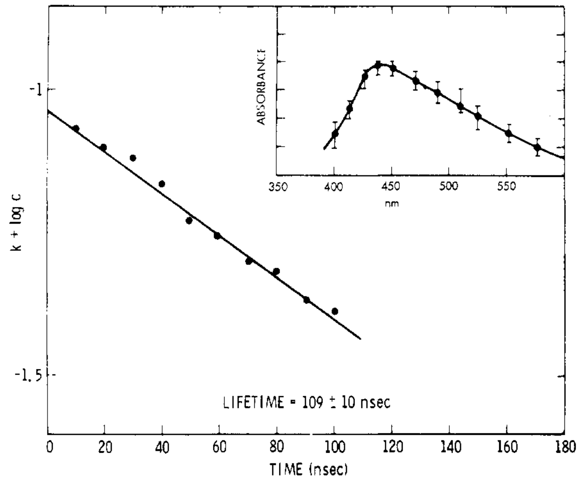

Figure 3. Laser flash photolysis studies of polycarbonate in CH_2Cl_2 solution; excited state absorption and lifetime measurement.

at very low conversions. A plot of ϕ_0/ϕ vs. [phenyl salicylate] shows some scatter and a pronounced upward curvature of the Stern–Volmer plot. Curvatures of the Stern–Volmer plots describing quenching in polymeric systems have been attributed to local concentration gradients arising from preferential interaction of the quencher molecules with the polymer chains in solution. At low concentrations of the quencher, the slope is approximately (1.2 ± 0.2) × 10^4 L mol^{-1} for a 3% polycarbonate solution.

B. Flash Spectroscopy. Laser flash kinetic spectroscopy yielded a transient absorption, the spectra and lifetime data of which are shown in Figure 3. A long-lived component was always present whose decay rate could not be precisely measured in our apparatus but whose spectrum matched the published spectrum of phenoxy radicals.[2] The short-lived transient was unquenched by oxygen or *trans*-1,3-pentadiene (1 M) while the long-lived transient was quenched by the diene. The short-lived transient undergoes self-quenching, and Figure 4 shows a plot of $1/\tau_L{}^0$ or $1/(k_2 + k_3)$ in Scheme I whose slope gives k_{sq}, the bimolecular self-quenching rate constant. These measurements were carried out at high polymer concentrations, so as to ensure that sufficient laser light was being absorbed by the sample. From these data, k_{sq} can be calculated to be (1.0 ± 0.2) × 10^7 L mol^{-1} s^{-1}. Now, using the lifetime data, we can calculate k_2 and k_q in Scheme I involving quenching by photochemically generated phenyl salicylate groups, k_q from quenching studies using added phenyl salicylate, and k_{sq} from initial values of ϕ_{L_1}. These rate constants are presented in Table III.

C. Chain Scission. The chain scission rate was measured at 0.1 and 3% polycarbonate concentrations. Results were less reproducible than those from the data on photorearrangement because chain scission has a much lower efficiency. Hence, longer irradiation periods are required to obtain appreciable chain scission detectable by high-pressure LC. Automatic viscosity measurements demonstrated by Guillet[13] might overcome this problem. Quenching by photoproducts (phenyl salicylate and 2,2′-dihydroxybenzophenone groups) became a major source of error in our system. We cannot easily correct this since we do not know the efficiency of chain scission of polymers containing phenyl salicylate groups. Chain scission is also strongly viscosity dependent, and hence, the relatively weak self-quenching phenomenon cannot be separated out of the much stronger viscosity dependence as measurements are carried out at higher concentrations. Our data on chain scission quantum yields are presented in Table IV.

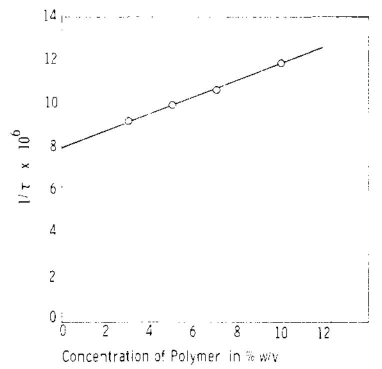

Figure 4. Laser flash photolysis studies: plot of reciprocal lifetime vs. concentration of polymer in CH_2Cl_2.

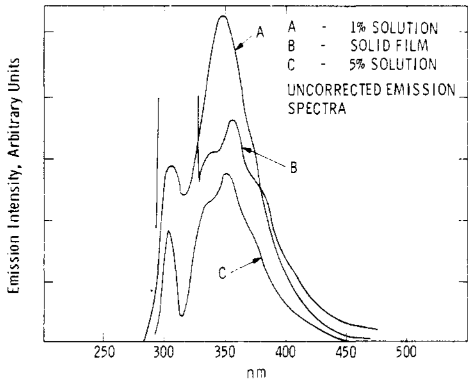

Figure 5. Emission spectra of polycarbonate as a function of concentration in CH_2Cl_2 and in the solid state.

Table IV
Quantum Yield of the Chain Scission, Obtained by Plotting $(\overline{M}_{n_0}/\overline{M}_{n_t})^{-1}$ vs. Time

irradiation time, min	0.1% soln, 253.7 nm	3% soln, 313 nm
8	0.025 ± 0.008	0.03 ± 0.01
10	0.03 ± 0.010	
12	0.034 ± 0.010	

Quenching by *trans*-1,3-pentadiene was attempted, but instead of quenching the rate appeared to accelerate on addition of diene, possibly due to chain transfer reactions. The quantum yields reported here are significantly lower than those reported by Humphrey.[2]

D. Fluorescence Quenching Studies. A polycarbonate of bisphenol A shows a weak emission, λ_{max} around 320 nm. Figure 5 shows the emission spectrum of the polycarbonate on excitation at 310 nm. This emission is unquenched by oxygen or *trans*-1,3-pentadiene but is quenched by phenyl salicylate. The quenching data can be fitted to a Stern–Volmer plot, with upward curvature,

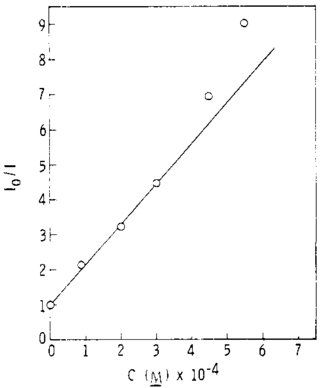

Figure 6. Plot of I_0/I_C vs. C when I is the fluorescence intensity and C is the concentration of phenyl salicylate.

the initial slope of which corresponds to a quenching rate of (1.2 ± 0.2) × 10^{11} L mol^{-1} s^{-1} (Figure 6). Emission spectra were also recorded as a function of polymer concentration in a CH_2Cl_2 solution and in the solid state (front surface of a 10-μm film). Broadening of the emission spectrum at the long wavelength edge indicated some excited state–ground state interaction, but no pronounced excimer formation could be detected. Measurement of the fluorescence quantum yield would require recording of the corrected spectra which is in progress.

E. Photolysis of Polymer Films. These irradiations were carried out at 253.7 nm by mounting the films on the outer surface of the "merry-go-round" reactor.[8] The quantum yield of phenyl salicylate formation was measured for very low conversions. A limiting quantum yield of 0.035 was obtained. Quenching studies were attempted by adding phenyl salicylate to the film, but at 253.7 nm greater than 90% of the light is absorbed in the first 10% of the thickness, causing large concentration gradients of photoproduct to develop and making necessary large corrections due to competitive absorption. These studies will be repeated at 302 nm and difference spectra (280–500 nm) will be electronically computed to obtain precise values of photoproduct formation rates at ultralow conversions. Figure 7 shows a typical plot of the increase in absorbance at 320 nm vs. time of irradiation for a film of pure polycarbonate.

Discussion

Quenching studies described here provide an unambiguous identification of the reactive excited state as the first singlet. This conclusion is in agreement with CIDNP and triplet sensitization experiments carried out on photoFries rearrangement of phenyl acetate.[14] This state is probably nπ^* in character. The orbital symmetry of the lowest excited state cannot however be resolved unambiguously. From the ground state geometry of polycarbonate proposed by Williams and Flory[15] it would appear that the $\pi\pi^*$ state would be higher in energy than the nπ^* state. The quantum yield of fluorescence is quite low (<0.05), which makes the radiative lifetime of the first singlet quite long (>10^{-5} s). This low radiative probability is consistent with the nπ^* assignment. The lack of wavelength dependence of the quantum yield of photoFries rearrangement suggests that internal conversion is fast from upper excited singlets, and no evidence can be found for different reactivities for the nπ^* and $\pi\pi^*$ states proposed for the rearrangement of a polycarbonate of bisphenol A.[16] The lifetime appears to be long for an aromatic carbonyl singlet, but the rest of the data are consistent with this assignment. The singlet lifetime places an upper limit on the intersystem crossing rate which appears to be low compared to intersystem crossing rates of unconjugated ketones (10^7–10^8 s^{-1}). This low intersystem crossing rate could be due to extra stabilization of the second triplet relative to the first singlet, increasing the singlet-triplet energy gap. The question whether the photoFries rearrangement occurs via a concerted process or a radical pair process in this system is also not resolved easily. Givens et al.[17] recently proposed that the orthogonal geometry calculated by Williams and Flory[15] would tend to favor the biradical pathway. The maximum value of the rate of photoFries rearrangement is clearly ~10^7 s^{-1}, assuming that practically all the observed inefficiency is due to incage recombination. This rate is still quite low and definitely argues against a predissociative excited state proposed for phenyl acetate.[18] Self-quenching processes observed in this system are a common property of nπ^* aromatic carbonyl singlets, while only singlet-singlet energy transfer processes can attain biomolecular quenching rates observed on addition of phenyl salicylate to the system. Further evidence of energy transfer (i.e., quenching) in this system comes from the observation that 2,2′-dihydroxybenzophenone groups are formed at an appreciable rate even when competitive absorption by phenyl salicylate is negligible. It is possible to independently calculate the extent of energy transfer if one determines separately the quantum efficiency of the photorearrangement of phenyl salicylate containing polymer chains. Exothermic triplet-triplet energy transfer processes between small molecules are usually diffusion and encounter controlled and vary from 1 × 10^9 to 1 × 10^{10} L mol^{-1} s^{-1} in our system.

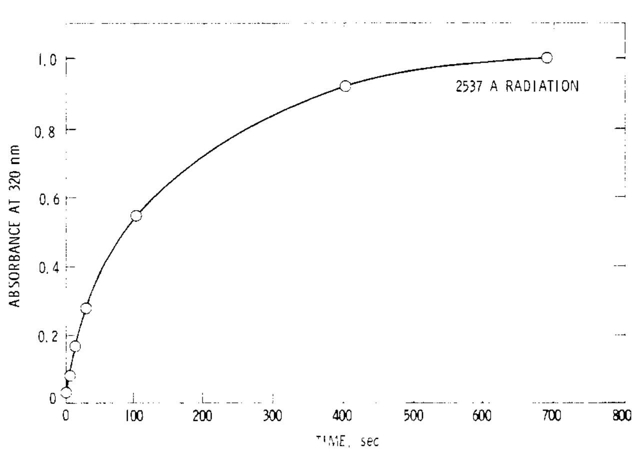

Figure 7. Absorbance (320 nm) of the polycarbonate film as a function of irradiation time irradiated in air at 20 °C: film thickness 15 μm, λ_{ex} = 253.7 nm.

The quenching studies carried out using added phenyl salicylate are characterized by nonlinear Stern–Volmer plots. This might be expected if quencher molecules aggregate near polymer chain segments to form areas of high concentration.[19] The efficiency of quenching observed for polymer chain segments containing phenyl salicylate groups (Table III) is also surprisingly high. The steady state concentration of the excited state did not exceed 10^{11} molecules/L. Pronounced quenching of these excited states was observed with salicylate group concentrations as low as 10^{-4} M, or approximately 1 salicylate per 20 polymer chains for the 5% polycarbonate solution. The high quenching efficiency observed for added phenyl salicylate is reminiscent of fluorescence quenching in poly(MVK) by biactyl reported by Somersall and Guillett.[20] The efficient quenching process was cited by them as evidence for singlet energy migration in poly(MVK) and poly(MIPK). Efficient quenching observed by both bound and added phenyl salicylate in the polycarbonate of bisphenol A may similarly be considered to be strong evidence of extensive singlet energy migration in this system. Both inter- and intrachain energy migration must be efficient since the quenching rate constant is nearly independent of polymer concentration in the concentration range 0.1–5%.

Evidence of interchain energy migration also comes from self-quenching rate measurements, since the rate of self-quenching increases with increasing polymer concentration in fluid solution. The quenching rate constant is nearly independent of polymer concentration all the way up to the solid state. Self-quenching usually requires quite specific geometric configuration of the chromaphore relative to a ground state molecule. The rate constant k_{sq} may then be written as follows:

$$k_{sq} = \alpha(f_i \sum \epsilon_i g_i G_i) \qquad (7)$$

where f_i = the frequency of hopping, G_i = ith geometric configuration, g_i = the number of ith geometric configurations in a unit volume, and ϵ_i = the efficiency of self-quenching at the ith geometric configuration. The invariance of k_{sq} with respect to polymer concentration may then be rationalized on the basis of the following assumption: (1) The energy migration is extremely facile. Hence, the migrating excitation can sample a large number of geometric configurations. (2) The change in the number of geometric configurations of any kind, g_i, is small as polymer concentration is increased from solution to solid state.

The large hopping frequency is not unusual for singlet states and is directly related to the "allowedness" of the transition.[21] As mentioned above, we find evidence of ground-state interaction from the broadening of the emission spectrum as the concentration of the polymer is increased, but there is no evidence of formation of a stable singlet excimer which would act as an energy trap, hindering energy migration. As for the second assumption that some quasicrystalline structure persists in fluid solution, the structure of the polycarbonate has been investigated in solution and in the solid state in some detail. From light scattering, sedimentation velocity, and viscosity measurements, Tsuji et al.[22] came to the conclusion that the polycarbonate chain retains a certain stiffness in dichloromethane, chloroform, and THF solutions in the same molecular weight range as was used in this study. They interpreted the data in terms of the wormlike chain model. This spiral configuration will allow occurrence of approximately parallel configurations of chromophores and ground states separated by less than 10 Å, so that intramolecular self-quenching and energy migration become possible in dilute solution. Crystal structures have been reported by Prietzchk[23] and Bonart[24] for the polycarbonate of bisphenol A, and in either case the structure may be analyzed in the form of layers of chains with chains rotated and displaced with respect to each other along the *C* axis. Williams and Flory[15] have proposed that the carbonate group is in a plane perpendicular to the plane of the two adjacent phenylene groups, while spectroscopic data indicate that there is substantial overlap between the carbonyl p and n orbitals and the molecular orbitals of the phenyl groups. It is also conceivable that the carbonate is in a plane parallel to the phenyl groups in the excited state. The magnitude of the stokes shift in the fluorescence spectrum is significant and indicates that the geometry of the excited state is appreciably different from that of the ground state.

Molecular motions in the solid state have been studied by Davenport et al.,[25] who find that the temperature dependence of the NMR second moment can only be interpreted by assuming that there is a torsional mode of oscillation (in the near time scale) involving the motion of the $-C_6H_4C(CH_3)_2C_6H_4-$ unit as a whole. A comprehensive mechanism of the quenching process in the solid state will have to take into account this process. The measurement of activation parameters of the quenching processes in the solid state may be useful from this point of view.

The decay modes of L^{1*} have not yet been characterized fully. The long-lived transient referred to above is quenched by *trans*-1,3-pentadiene. It has an absorption spectrum with a maximum at 450 nm. While the characteristics of this absorption match those of phenoxy radicals from the polycarbonate, part of this absorption could be due to the triplet. However, the quenching studies clearly show that the triplet state cannot be the reactive excited state, even if it is formed via intersystem crossing of L^{1*}. The intersystem crossing yield of L^{1*} needs to be determined, perhaps by controlled addition of a quencher containing a heavy atom such as bromocyclopropane or xenon and by monitoring increased triplet formation through triplet-triplet transient absorption studies. An intriguing possibility is that the first triplet is populated directly on the long wavelength excitation of the pure polymer film. This could account for the reported low quantum yields of the photoFries rearrangement upon broad band excitation with light from a high-pressure xenon lamp.[1]

The quenching processes analyzed here are of significance if one attempts to model outdoor photodegradation of polycarbonate. Self-quenching may be an important mechanism of radiationless deactivation of excited states in solid polymers and may thus contribute to stabilization of these polymers. This kind of stabilization is achieved without stabilizing agents and is thus the most desirable kind. Singlet quenching by phenyl salicylate also exerts a significant inhibitive effect on the photoreactivity of the system. While there is much speculation among polymer photochemists on the mechanism of stabilization by this common (and commercially used) UV stabilizer, there is a degree of consensus that screening or competitive absorption by phenyl salicylate makes an important contribution to the stabilization mechanism.

In the polycarbonate of bisphenol A, we find that quenching by phenyl salicylate is the dominant mode of stabilization. Indeed, 99% stabilization can be achieved corresponding to a broad band (295–400 nm) rearrangement quantum yield of less than 10^4 and a chain scission quantum yield of less than 10^{-5} by adding 10^{-2} M of phenyl salicylate to the system.

There is a considerable discrepancy between solid state quantum yields reported here using 253.7-nm radiation (0.035 ± 0.01) and those reported earlier using broad band radiation from a high-pressure xenon lamp (0.003 ± 0.001). This discrepancy may be attributed to the broad band radiation being partly absorbed by end groups and also probably by ground state dimeric species, the presence of which is inferred from the fact that the polymer does not obey the Beer–Lambert law in its absorption tail (310–340 nm). This discrepancy might also be partly due to the increased screening efficiency of phenyl salicylate at longer wavelengths. These measurements show that rate data for the modeling of outdoor photodegradation should be obtained with a source which matches the solar spectrum in the region of interest, i.e., where the material absorbs radiation.

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Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 3. Hexad Sequence Assignments of Methylene Spectra of Polypropylene

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ABSTRACT: Theoretical ^{13}C NMR spectra for the methylene carbon of two polypropylene samples were obtained by assuming the chemical shifts calculated for C_9 of 2,4,6,8,10,12,14,16-octamethylheptadecane and deriving the resonance intensities for the various hexad stereochemical sequences from the observed methyl pentad sequence intensities. The satisfactory comparison of the stick spectra with the observed spectra provides hexad sequence assignments of the methylene resonances in polypropylene and confirms the smaller value of the γ-gauche parameter for this type of carbon with respect to the methyl carbon.

In the previous paper of this series,[1] here after referred to as paper 2, the ^{13}C NMR spectrum of (^{13}C enriched) C_7 of 2,4,6,8,10,12-hexamethyltridecane (HMTD) was reported and the six observed resonances assigned to different stereoisomers. It was also shown that the stereochemical shifts can be accounted for to a good approximation in terms of the so-called γ effect and of the five-state rotational isomeric model.[2,3]

The chemical shifts observed for C_7 of the *mmm* and *rrr* isomers of HMTD, 4(*R*), 6(*R*), 8(*S*), 10(*S*) or 4(*S*), 6(*S*), 8(*R*), 10(*R*) and 4(*R*), 6(*S*), 8(*S*), 10(*R*) or 4(*S*), 6(*R*), 8(*R*), 10(*S*) in the notation of Cahn et al.,[4] are different than those observed for the methylene carbons of isotactic and syndiotactic polypropylene, which span respectively the same tetrad stereochemical sequences. Clearly, at least hexad stereosequences are needed in order to account for the methylene carbon spectrum of polypropylene. This fact was already pointed out by Tonelli[5] and shows that both the methyl and methylene carbon chemical shifts are sensitive to the steric placement of methyl substituents up to a six-bond distance.

In order to account for such effects we calculated the chemical shifts for the methylene C_9 of the diastereomers of 2,4,6,8,10,12,14,16-octamethylheptadecane (OMHD), applying the method of paper 2. Theoretical stick spectra for the methylene carbon of two polypropylene samples of different tacticity were then obtained by taking the chemical shifts of C_9 of OMHD and by calculating the intensities of the various hexad sequences from the observed methyl pentad spectra, on the basis of a simplified two-state model of stereosequence propagation.[6] Hence comparison of the theoretical spectra with the actual spectra[15] allows us to assign (at least some of) the methylene resonances in terms of hexad sequences.

Table I
[1-^{13}C] Enriched and [3-^{13}C] Enriched Propene Polymerizations

polymer[a-c]	catalytic systems	yield, g
s[d]	VCl_4–$Al(CH_3)_2Cl$–anisole	0.6
a[e]	VCl_4–$Al(CH_3)_3$–$Zn(CH_3)_2$	0.2

[a] 15 mL of toluene was used as solvent. [b] Polymerization time 24 h. [c] Polymerization temperature −78 °C. [d] 0.7 g of [1-^{13}C] enriched propene (9%); VCl_4 and anisole 5×10^{-4} mol, $Al(CH_3)_2Cl$ 5×10^{-3} mol. [e] 0.3 g of [3-^{13}C] enriched propene (30%); VCl_4 2×10^{-5} mol, $Al(CH_3)_3$ 1.1×10^{-3} mol, $Zn(CH_3)_2$ 6×10^{-3} mol.

Experimental Section

Materials. All the solvents used were purified by treatment with $LiAlH_4$ and distillation, and the reactions were performed in an inert atmosphere (nitrogen or helium). VCl_4, $Al(CH_3)_3$, and

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