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LASER SPECTROSCOPICAL METHODS FOR THE STUDY OF PRIMARY PROCESSES DURING THE PHOTODEGRADATION

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Abstract - Although flash and laser techniques have been widely applied to the spectroscopical investigation of small molecules, it appears that up to now, they have not been extensively used to study the primary photodegradation processes in polymeric materials. The study of polyvinylphenylketone shows that laser flash spectroscopy permits the identification of a particular kinetic decay of a quencher triplet state. Picosecond and nanosecond spectroscopy permits the study of the various phenomena involved in the photodegradation which occurs according to Norrish type II process : triplet and biradical generation, their decay and their absorption spectra.

INTRODUCTION

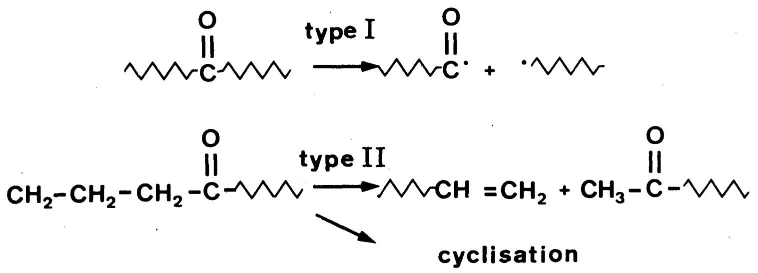
Compared with conventional models used in the photochemistry of small molecules, the specific physical and chemical properties of polymeric materials complicate appreciably the interpretation of data. On the other hand, time resolved spectroscopy constitutes a very convenient experimental method to study directly the behaviour of selectively excited chromophores in polymeric systems. Owing to this technique, which may give insight into the elementary steps of the photodegradation process, the problem of polymer stabilization can be thus approached in a more rigorous and fruitful way.

Being interested in the field of polymer photochemistry, we did apply the flash and laser techniques to the problem of polymer degradation and stabilization. We have investigated polyketone materials i.e. polyvinylphenylketone in which the chain scission occurs via a Norrish type II process; in such a system, fast techniques provide indeed some conclusive informations. The recent introduction of pulsed lasers as excitation source, presents the advantage of allowing observations in the time scale of a nanosecond and less. In these conditions we assume that no additional complication occurs when going from small molecules to polymers. The experiments we intend to describe hereby have been carried out in dilute solutions. Some of them should also be carried out on films in order to get a thorough knowledge of the polymer degradation process in rigid media. However, one would then have to pay special attention to many problems such as sample transparency or homogeneity of the excitation.

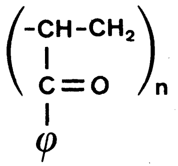
EXPERIMENTAL

Polyvinyl-Phenyl-Ketone (PVPK) and model compounds

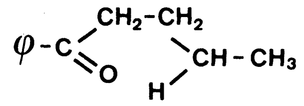
Polymers containing carbonyl groups absorb strongly in the near U.V., and irradiation by daylight may induce in general two processes :



As a consequence, there is always a change of the physical properties of the polymer due to chain scission. In order to avoid uncertainties due to the composition and the structure of polymers, G. Geuskens (1), I. Lukac (2), J.E. Guillet (3) and coworkers have studied a model in which the predicted photochemical degradation is a Norrish type II process. This system is given by PVPK :



One of the most appropriate model compound of this polymer is valerophenone :



The reactivity of both the triplet and singlet states leading to the type II photoelimination depends on the nature of the ketone. From Stern-Volmer plots the triplet lifetimes of valerophenone and PVPK have been estimated to be 7 (4) and 18 ns (3) respectively. Since the quantum yield of intersystem crossing is practically unity, the degradation process can therefore only be inhibited by very efficient triplet quenchers, such as naphthalene which has been extensively used. Fig. 1 shows the typical energy level diagram of the system.

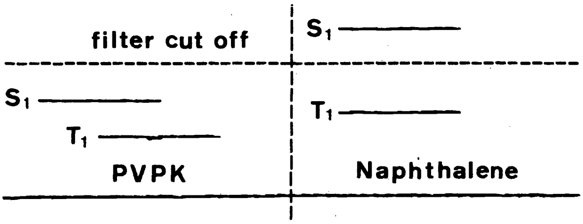


Fig. 1. Relative energy levels diagram for donor and quencher.

Using classical flash photolysis, one is restricted to the observation of the naphthalene triplet, populated by energy transfer from the triplet of the carbonyl.

Flash photolysis experiments

The flash photolysis apparatus was a classical one, with a flash duration of 5 µs. Using a cut off filter (KNO_3/H_2O 2M), only the singlet state of PVPK was populated and the triplet-triplet absorption and triplet decay of the quencher were observed. At first solutions of PVPK in methylenechloride with variable concentrations of naphthalene were studied. The observed triplet absorption was very low, even at high concentration of naphthalene.

Under identical conditions, using valerophenone as the donor, a twenty fold increase of the absorption was observed. Such an important increase was also observed when copolymers of VPK and vinylnaphthalene were investigated (5) (synthesized according to the method described by I. Lukac).

These results indicate that diffusion of naphtalene into the macromolecule complicates the interpretation of the kinetics of the transients.

Investigating three polymers containing 1%, 5% and 11% of naphthalene units, it appears that the naphthalene triplet decays according to an exponential law :

$$D = D_0 e^{-k_T t}$$

D_0 and D the optical densities at the times t_0 and t ; k_T rate constant for triplet decay, is a function of the polymer concentration and the percentage of naphthalene units as illustrated by Fig.2. The rate constant k_T can be expressed by the following equation :

$$k_T = k_0 + k_1[\%N] + k_2[\text{copolymer}]$$

k_0 is the rate constant of the natural deactivation of naphthalene (smaller than the one of free naphthalene in methylenechloride). $k_1[\%N]$ corresponds to the intramolecular deactivation by an active site of the polymer chain and depends only on the naphthalene content. The last term represents the intermolecular deactivation by the same species and will thus depend on the concentration of VPK units.

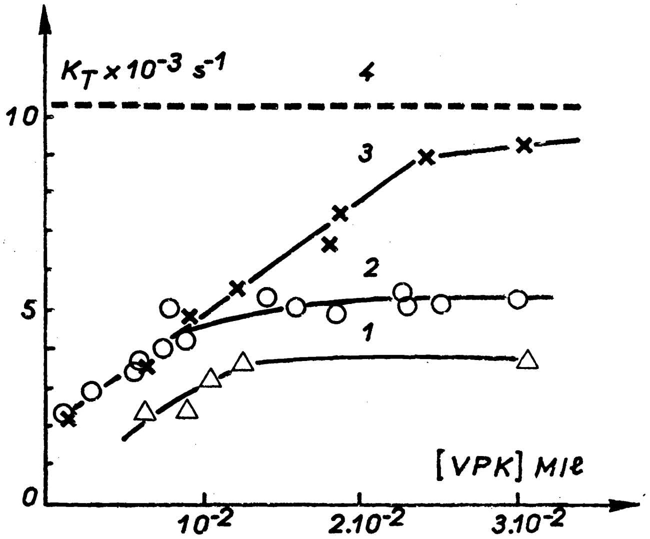


Fig. 2. Variation of k_T in function of the calculated concentration of the VPK units, for copolymers containing : (1) 1% - (2) 5% - (3) 11% of vinylnaphtalene.

Complementary experiments and results have been published recently by Schnabel et al (6) but no additional informations on the elementary processes can be obtained from classical flash photolysis. For this reason , we investigated the same system with a mode-locked ruby laser, in the picosecond and nanosecond time scale.

In contrast to the case of simple ketones, it clearly appears that the mechanism of quenching on polymers cannot be elucidaded by continuous irradiation experiments or by classical flash photolysis. The understanding of the elementary steps requires to shift the time scale of investigation towards much shorter time scale range.

Laser spectroscopy

Several kinds of fast spectroscopy experiments were performed to detect the transients mentioned above, and to determine the different processes of their evolution. A pulsed-laser photolysis apparatus gives the opportunity to operate in the 10 to 100 ns range and below. For measurements in the true nanosecond time scale, we need a picosecond spectroscopy technique.

a) Picosecond spectroscopy (Ref. 7)

- Lifetime measurements

The experimental set up is schematically depicted in Fig. 3. The U.V. beam obtained from the ruby laser after frequency conversion, is used as a pumping source to induce S_0-S_1 transition in the sample A, and serves simultaneous as probing beam and interrogating beam.

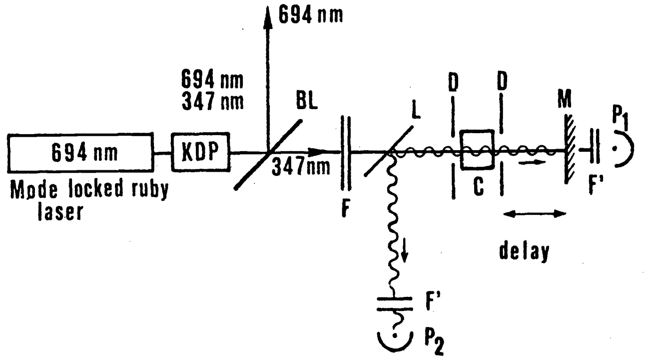


Fig. 3. Experimental set up for triplet lifetime measurement in the nanosecond range. BL : beam splitter ; F : 694 cut off filter ; L : slab ; D : diaphragms ; C : sample cell ; M : mirror : F' : filters ; P_1, P_2 : photocells.

This light, consisting in a train of 6 to 7 pulses, 10 ns separated, 300 ps half-duration at λ=347 nm, is first directed to the beam splitter BL to remove the red part not converted in the KDP crystal, then crosses over a sample and is received by the mirror M ; the weak part transmitted by this mirror is collected by the photocell P_1 ; the other part, after attenuation returns through the sample and reaches a slab which directs a part of this light to the photocell P_2. From the output ratio of these two cells, first with the cell containing only the solvent and then with the solution, it is possible to record the optical transmission. Thus, if the distance L separating the sample and the mirror M is varied, the transmission may be recorded as a function of the optical delay 2L/c (c : light velocity), that is to say as a function of time. Working in such way, we could get the change of transmission in the case of valerophenone after laser excitation. This curve is reported on the Fig. 4(a) in which one see, in a first step, the triplet population corresponding to a very fast decrease of the transmission and then, in a second step, the triplet state corresponding to an increase of the transmission.

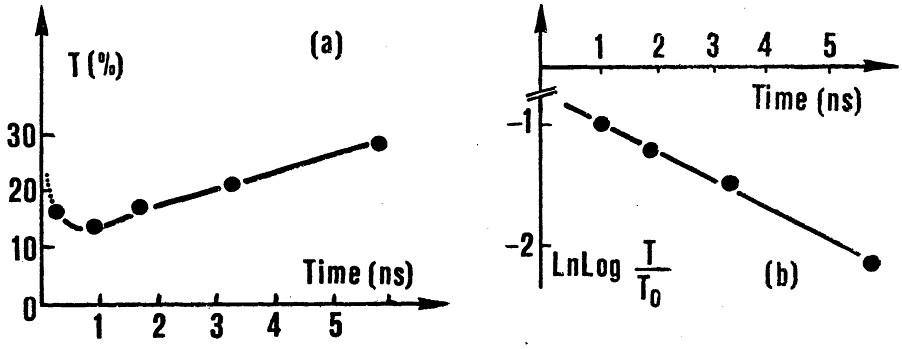


Fig. 4.(a) Transmission of a valerophenone solution in benzene versus the optical delay - (b) Plot of $\mathrm{LnLog}(T/T_0)$ versus time t (the slope of the straight line gives the value $1/\tau$).

The kinetic analysis of the transient state according to a first order decay leads to the values τ_T=4±0.2 ns (Fig. 4(b)) and $\sigma_{TT} \sim 7000\ M^{-1}cm^{-1}$.

Many other experiments have been performed upon polymeric material exhibiting the same photochemical behaviour ; in these cases, the kinetic analyses are more difficult due to the accumulation process which may take place when the triplet lifetime becomes longer than 5 ns. Nevertheless a mathematical analysis of a three level model gives the opportunity to use a trial and error computation which leads to the values of τ_T, k_{ST} and σ_{TT}.

For instance, in the case of solution of polyvinylphenylketone in aromatic solvents, we found τ_T=9±3 ns and $\sigma_{TT} \sim 5000\ M^{-1}cm^{-1}$. The intersystem crossing rate constant k_{ST} was to be solvent dependent when going from benzene to trichloromethylbenzene. The experimental values reported in Table I vary from 3.10^9 to $10^8 s^{-1}$ (8).

TABLE 1. Intersystem crossing constant and triplet lifetime of PVPK in various solvents.

Solvent	$k_{ST} \times 10^{-9}\ (s^{-1})$	$\tau_T \times 10^9$ (s)
Benzene	3	7±2
Chlorobenzene	3	7±2
o-Dichlorobenzene	1 - 3	8±3
s-Trichlorobenzene	0.5 - 1	8±3
Trichloromethylbenzene	0.1 - 0.5	9±3

The τ_T values are in good agreement within a factor of two with those previouly obtained by Wagner (4) from Stern-Volmer plots for valerophenone and PVPK in benzene. Likely triplet lifetimes are not influenced by the nature of the solvent. The quantum yield of triplet generation and consequently the six membered ring formation are highly dependent on the solvent viscosity.

- T-T spectrum.

This type of measurement involves an analysis beam produced by the laser emission of several fluorescent dyes choosen in order to investigate the spectral range from 347 to 450 nm.

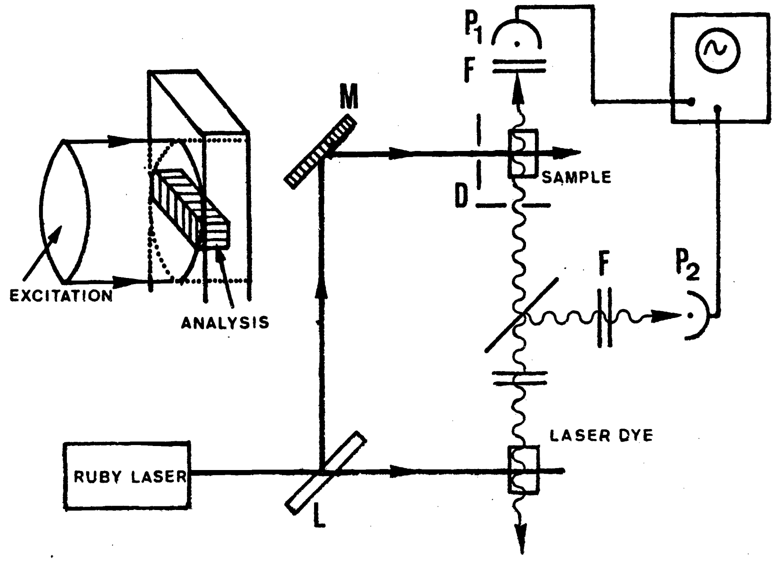


Fig. 5. Experimental arrangement for absorption picosecond spectroscopy. M : mirrors ; F : filters ; L : beam splitter ; D : diaphragms ; P_1, P_2 : photodiodes.

The scheme of the device is depicted in Fig. 5 and is analogous to a spectroscopic flash apparatus in which the problem of the risetime of the detection system would be eliminated. The experimental procedure involves the transmission measurements for each pulse of the train, first with the pumping train blocked before the sample(T_0) and then under excitation(T). The difference between the transmitted probe pulses in these cases, contains the information of the excited state relaxation, of the transient absorption and of the generation intermediary states from S_1. We can write :

$$\varepsilon_{TT}(\lambda) \alpha \text{ Log } T(\lambda)$$

The T-T spectrum is reported on figure 6.

b) Nanosecond spectroscopy (Ref. 9)

The photolysis apparatus is described in detail elsewhere and is made of a mode-locked ruby laser as the excitation source. The analysing system is disposed typically in a right angle arrangement to the pumping beam. The sample is contained in a fluorimetry cell. A set of diaphragms permits to select the homogeneous part of the excited solution.

The excited state absorption measurements were carried out with a high pressure Xenon arc (XBO 150W) associated with a detection system (M25 Huet monochromator, RCA XP 1005 photomultiplier, Tektronix 7904 oscilloscope). The photomultiplier was operated with only 6 stages and the risetime of the detection system was 2.3 ns when terminated in 50 Ω. To improve the signal to noise ratio, the current through the Xenon lamp was increased for a period of 500 µs, resulting in a 25 to 200 fold increase in light intensity depending on the wavelength (Fig. 7).

Transient absorption in the near U.V. wavelength range were observed and typical oscilloscope trace is shown in Fig. 8.

An important point must be emphazised :

- The absorption signal does not grow continuously , which implies that an

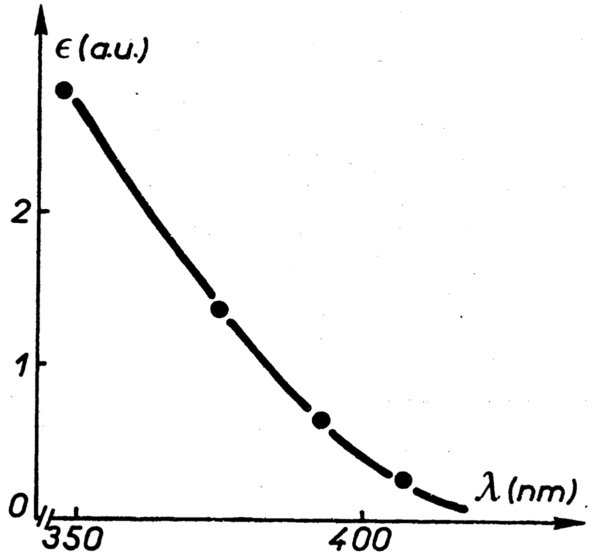


Fig. 6. T-T spectrum of the carbonyl group in PVPK obtained from picosecond spectroscopy.

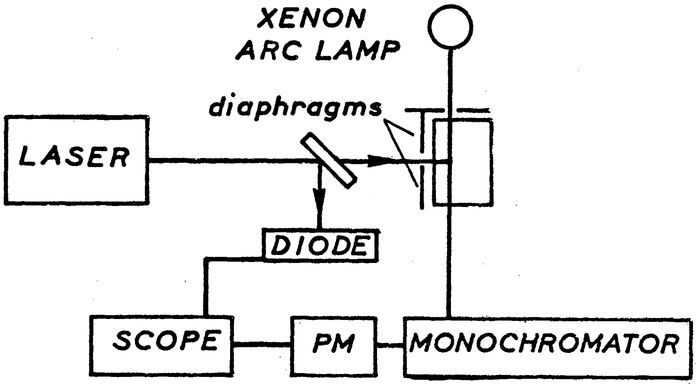


Fig. 7. Experimental set up for nanosecond spectroscopy.

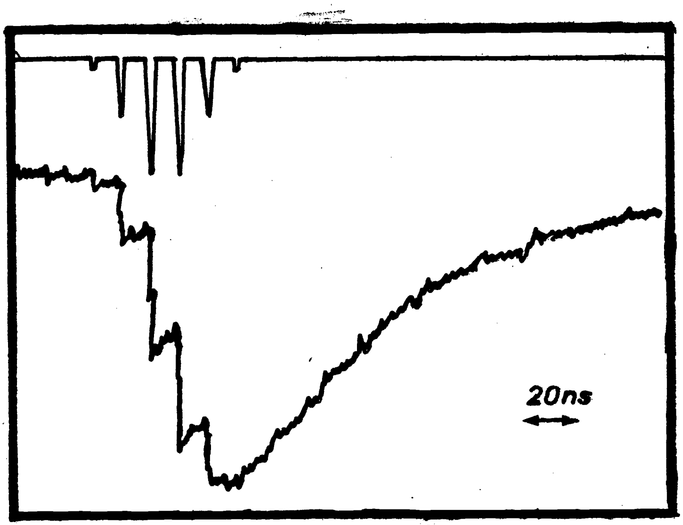


Fig. 8. Typical oscillogram of the transient formation and decay (lower curve), compared to the laser train of pulses (upper curve): λ = 420 nm.

important relaxation takes place between every excitation pulses. This behaviour is assumed to be due to the triplet relaxation, convoluting with a second absorption which grows during the pumping time.

After the train has passed through the sample , the relaxation of the transient is monitored and it decays according to a first order kinetic , with a rate constant equal to $k=1.6 \times 10^7\ s^{-1}$ in the case of PVPK. The same value is obtained in oxygen free solution, which means that this state cannot be identified as a triplet. We assume it to be the biradical postulated by many authors. The observed lifetime is in good agreement with that one deduced from chemical trapping experiments (4).

The Fig. 9 shows the individual contributions of the two species (triplet and biradical) to the transient absorption. This kind of treatment is based upon the assumption that the carbonyl triplet gives rise to the biradical which is directly responsible of the chain scission.

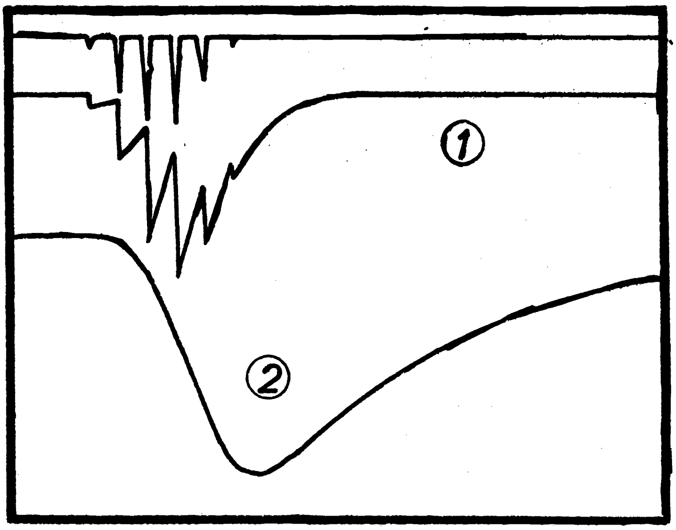


Fig. 9. Triplet state absorption (curve 1) and biradical (curve 2) plotted versus time, drawn from kinetic and spectrocopic results at λ = 420 nm.

When the analysing wavelength is changed, the biradical absorption is obtained (Fig. 10) and changes in the shape of the oscillograms due to the relative contribution of the absorbances of the two states is observed (we estimate that the ratio of the triplet and the biradical is about 2 at λ = 420 nm).

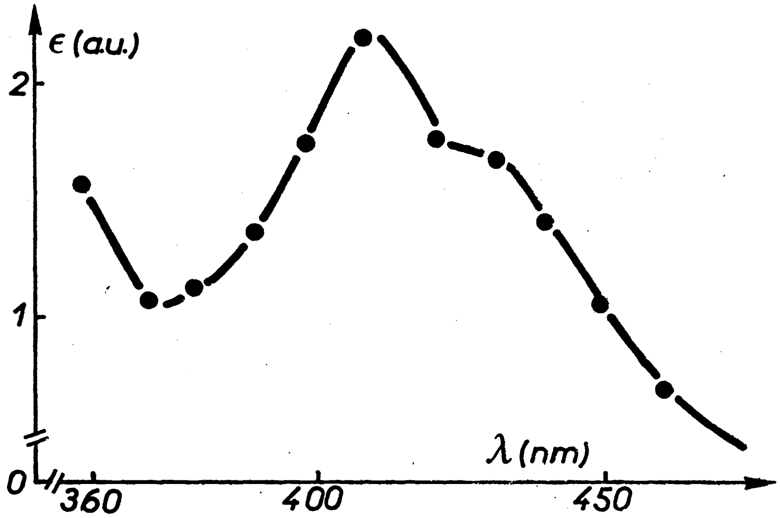


Fig. 10. Absorption spectrum of the biradical.

This spectrum is in good agreement with the one obtained by Schnabel et al. (10) which was attributed to the carbonyl triplet. A forthcoming paper will comment on this point (9).

CONCLUSION

Fast spectroscopy techniques are a very powerfull tool for elucidating elementary processes and, as shown here, have been successfully applied to solve a specific problem in the photodegradation of a polymer.

Flash spectroscopy reveals the complexity of diffusion controled reactions of the transients. In a polymeric solution, the kinetic treatment, which is valid for small molecules, can no longer be applied when the chromophores are bound to the polymer chain. The effect of concentration upon the kinetics of deactivation have already been pointed out by Schnabel et al. (6) for homo and copolymers of vinylphenylketone.

Since the observation of elementary steps requires fast techniques, it is obvious that only mode-locked laser spectroscopy permits investigation in the 1 ns time scale or less.

Using this technique the triplet lifetime of the carbonyl group was measured. It is found to be roughly independent of the solvent, in contrast to k_{ST} which is solvent dependent.

The spectrum of the biradical has been recorded and the growing of this transient from the triplet has been clearly established. These observations eliminate the ambiguity arising from the use of giant pulse laser spectroscopy whose time resolution is not sufficient to investigate this problem.

In the case of the Norrish type II photoscission, we have confirmed that the biradical yield is quite low. The problem of polymer stabilization might be fruitfully approached by investigating further the reactivity of this biradical.

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