

SHORT COMMUNICATIONS

**Photochemical Transient Species of Poly(ethylene terephthalate)
Powders as Revealed by the Diffuse Reflectance
Laser Photolysis Method**

Keiji IMAGI, Noriaki IKEDA, Hiroshi MASUHARA,[†]
Masahiko NISHIGAKI,* and Masataka ISOGAWA*

*Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Matsugasaki, Kyoto 606, Japan*

** Central Research Laboratory, Kanegafuchi Chemical Industry Co., Ltd.,
Kobe, Hyogo 652, Japan*

(Received February 28, 1987)

KEY WORDS Laser Photolysis / Nanosecond / Polymer Powder / Diffuse
Reflectance Spectroscopy / Transient Absorption Spectra / Triplet State /
Poly(methyl methacrylate) / Polycarbonate / Poly(*p*-phenylene) / Polyacetal /

Photophysical and photochemical processes of polymers have been investigated by employing time-resolved spectroscopies. Particularly for the triplet state and neutral as well as ion radicals, the laser photolysis method which makes it possible to measure their UV absorption spectra is indispensable. Direct measurements of transient species in nanosecond and picosecond time domains provided detailed information on primary photoprocesses¹ and a high excitation intensity of laser pulse opened a new field of nonlinear photochemical behavior of polymers.² For non-transparent materials, this laser photolysis method cannot be used. However, a diffuse reflectance laser photolysis method was developed recently and has been applied to scattering powder samples such as organic microcrystals, CdS, organic molecules adsorbed on silica gel, zeolite etc.³ In the present work we applied this method to powder samples of representative polymers.

The details of our microcomputer-controlled ns diffuse reflectance laser photo-

lysis system will be published elsewhere.⁴ The excitation light source was a 308 nm excimer laser (Lumonix 430T-2, ~6 ns, ~35 mJ). Transient UV absorption spectra were displayed as % absorption according to Kessler *et al.*⁵ Commercial polymer pellets were ground into fine powders without further purification and poured into a quartz cuvette. The measurement was performed under aerated conditions at room temperature.

The transient spectrum of poly(ethylene terephthalate) (Kaneka Co. Ltd., abbreviated hereafter as PET) powders is shown in Figure 1 (A), where two broad and structureless bands are observed around 430 nm and 520 nm. Under the present time-resolution of our system (~300 ns), rise curves of these bands were identical with the response function. The 520 nm band decayed with a half-life of ~20 microsecond, while the 430 nm band has a longer value than the former. It is safely concluded that at least two transient species were produced by laser excitation. A similar absorption spectrum and dynamic

[†] To whom correspondence should be addressed.

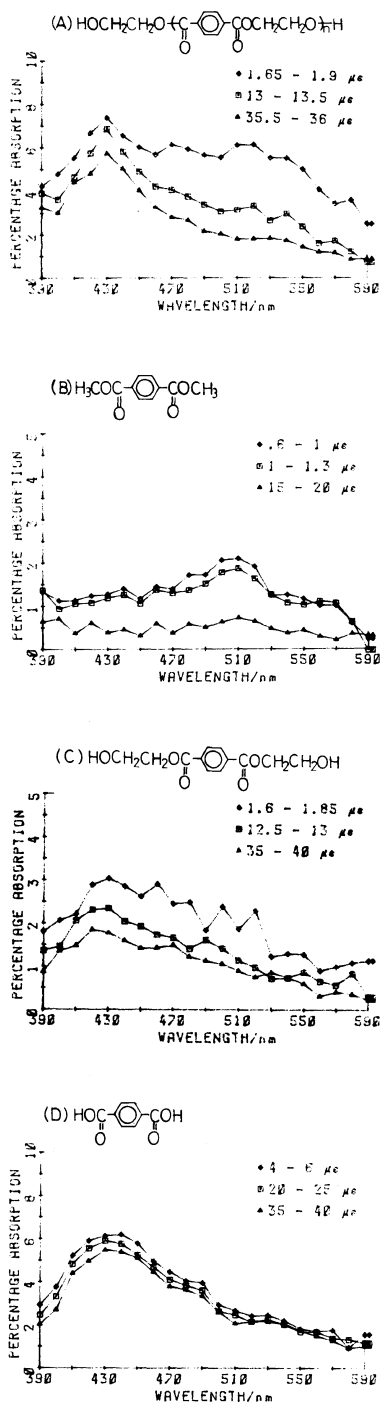


Figure 1. Transient Absorption Spectra of PET (A), dimethyl terephthalate (B), bis(2-hydroxyethylene) terephthalate (C), and terephthalic acid (D). The gated times are shown in the figure.

behavior were observed for the sample greatly purified by repeated re-precipitation from hexafluoro-isopropanol solution. This means that the present bands are characteristic of PET and cannot be ascribed to additives such as catalyst, plasticizer, stabilizer, etc.

Transient absorption spectra of the microcrystalline powders of monomer model compounds are given in Figure 1 (B)—(D). It is surprisingly interesting that broad bands of PET were separately reproduced in these spectra. Apart from a small blue shift, the longer wavelength band was observed for dimethyl terephthalate which is a π -electronic unit of PET. Its decay was in the same order of tens of μ s. The other band at 430 nm was detected for bis(2-hydroxyethyl) terephthalate and terephthalic acid where no appreciable band was given at 520 nm. Their decay patterns were similar to those of the corresponding bands of PET. These results indicate that the OH group has an important role in forming transient species with the 430 nm band, but suppresses the 520 nm band. We consider that the former corresponds to the radical formed by an intermolecular interaction between carbonyl and OH groups, and that the latter is ascribed to the triplet state of the π -electronic unit. This assignment is supported by the fact that the decay rate of the 510 nm band decreased by degassing the monomer samples, while that of the 430 nm did not.

The same assignment is possible for PET, while a large difference between monomer and polymer systems is that both bands were observed in the latter. This is ascribed to the fact that some excited states produced near the end group go into the reaction and give the 430 nm band, while the other ones far from the OH group remain in the triplet state. Energy migration may be involved to a more or less extent, resulting in rather large absorption intensity of the 430 nm band in spite of the low OH concentration. The present explanation is a tentative one and a more detailed investigation is being done by both laser photolysis

measurements of powders and transparent solutions.

In conclusion, we succeeded for the first time in measuring directly transient UV absorption spectra of PET powders. Historically, photochemical processes of the present polymer have been studied from a practical viewpoint,⁶ where the photolytic scission of the chain $-O-CH_2-$ and a Norrish type II cleavage were mentioned as the primary processes of photodegradation. The latter process seems to be preferable at the present moment. However, more detailed studies are indispensable. Recently, this polymer film has received attention as material for laser ablation in electronic device technology.⁷ The diffuse reflectance laser photolysis method will be a fruitful tool for analysing these mechanism.

In order to show the high potential of this method in polymer science and engineering, we also performed similar experiments for poly(methyl methacrylate), polycarbonate, poly(*p*-phenylene), and polyacetal powders. Under the present S/N ratio, no transient absorption spectrum was detected in the present time range. These results are very interesting from the stand point of the photochemistry of polymer solids.

Acknowledgement. The present work was partly supported by the Grant-in-Aid for Scientific Research (No. 61470006) from the Ministry of Education, Science, and Culture of Japan to the H. M. and N. I.

REFERENCES

1. W. Schnabel, "Developments in Polymer Photochemistry," Vol. 3, N. S. Allen, Ed., Applied Science, London, 1982, p 237.
2. H. Masuhara, "Photophysical and Photochemical Tools in Polymer Science," M. Winnik, Ed., D. Reidel Publishing Co., Dordrecht, 1986, p 42.
3. R. W. Kessler and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 1*, **77**, 309 (1981); R. W. Kessler, D. Oelkrug, and F. Wilkinson, *Appl. Spectrosc.*, **36**, 673 (1982); G. Beck and J. K. Thomas, *Chem. Phys. Lett.*, **94**, 553 (1983); N. J. Turro, I. R. Gould, M. B. Zimmt, and C. C. Cheng, *Chem. Phys. Lett.*, **119**, 484 (1985).
4. N. Ikeda, K. Imagi, and H. Masuhara, to be published.
5. R. W. Kessler, G. Krabichler, S. Uhl, D. Oelkrug, W. P. Hagan, J. Hyslop, and F. Wilkinson, *Optica Acta*, **30**, 1099 (1983); G. J. Willsher, *J. Photochem.*, **28**, 229 (1985).
6. For example; B. Ranby and J. F. Rabek, "Photodegradation, Photo-oxidation and Photo-stabilization of Polymers," John-Wiley and Sons, London, 1975.
7. R. Srinivasan and V. Mayne-Banton, *Appl. Phys. Lett.*, **41**, 576 (1982).